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The complexation thermodynamics of light lanthanides by crown ethers

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Contents

Abstract

This article describes the complexation thermodynamics of light lanthanides by crown ethers, including symmetric crown ethers, less-symmetric crown ethers, unsaturated crown ether, lariat ether (*C*-pivot and *N*-pivot), and bis(crown ethers). Calorimetric and spectro-

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photometric titrations afforded the complex stability constants and thermodynamic parameters of the above ligand–lanthanide bindings, displaying high binding ability and cation selectivity towards different lanthanides. The high cation binding ability and cation selectivity by various crown ethers are discussed from the viewpoint of thermodynamics according to the crown ether's cavity size, electron density, softness, spatial arrangement, additional binding site, and other major factors governing cation–ligand complexation. The compensatory relationship between ΔH and $T\Delta S$ was found to be exhibited in the complexation of light lanthanides with crown ethers. The slope (α) and intercept ($T\Delta S_0$) of the regression line could be taken as measures of the conformational changes and the extent of desolvation caused upon complexation, respectively.

Keywords: Crown ether; Light lanthanide ions; Complexation; Thermodynamic parameter; Enthalpy–entropy compensation

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1. Introduction

Since Pedersen reported the synthesis of crown ethers and their binding ability towards alkali cations, macrocyclic chemistry has become a current field of interest [1]. This indicated that the chemistry moved into a new era. In the past three decades, a large number of synthetic coronands have been prepared and their binding ability towards a wide variety of cations have been thoroughly investigated [2–5]. Furthermore, the complexation thermodynamic studies were performed in order to elucidate the nature of the binding behavior in terms of the enthalpy and entropy changes [6]. Although some anions and neutral molecules were employed to investigate their complexation behavior and thermodynamics, the studies were limited. The works on the complexation thermodynamics with various crown ethers have concentrated mainly on metal cations, such as alkali, alkaline earth, and some heavy metal salts [7]. However, the complexation thermodynamic studies on complexation of light lanthanide ions were so far limited.

In this review, we deal with the complexation thermodynamics of light lanthanides with various crown ethers, as shown in Chart 1, reported mainly from our laboratory in the literature.

2. Method [8–15]

The thermodynamic data were obtained via calorimetric titrations except that of BisB15C5. The calorimetry is the only direct method for simultaneous determination of the Gibbs free energy and the enthalpy change in the crown ether complexation. Calorimetric titrations were performed under atmospheric pressure in a water bath thermostated at 25.0°C, by using an LKB 8721-2 precision calorimeter, or a TRONAC model 458 isoperibol titration calorimeter, connected to a personal computer for automated titration and data processing. The complex stability constants (log K_s) and the enthalpy change (ΔH) were determined for the 1:1 stoichiometric complex by using the non-linear least-squares method.

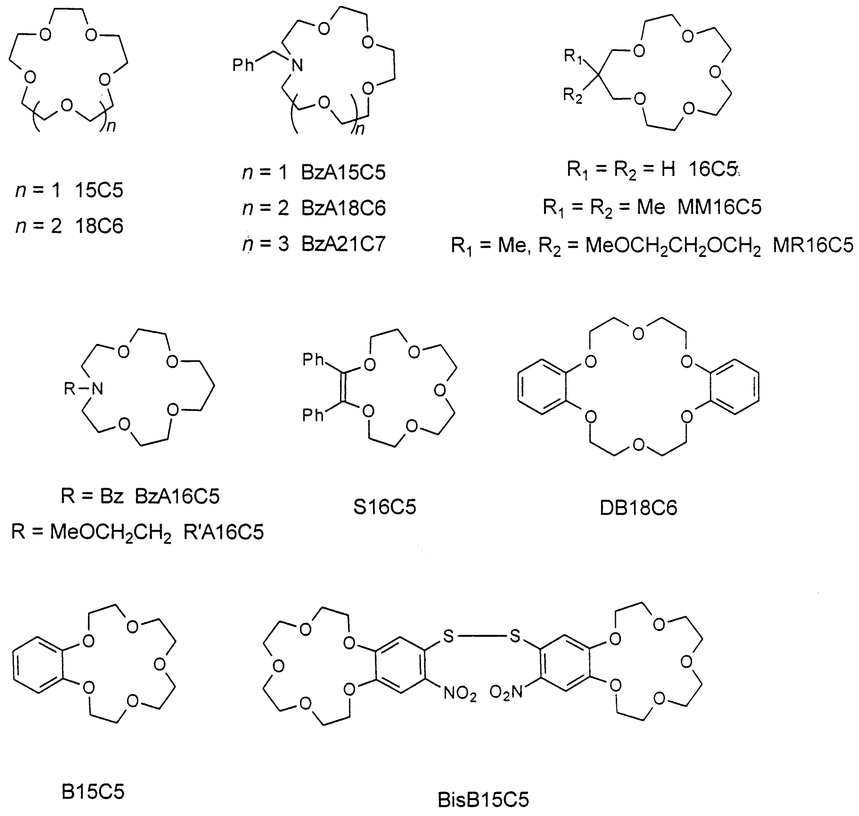

Chart 1

3. 15-Crown-5 series [16–20]

3.1. Complex stability constants and relative cation selectivity for 15C5 series

It has been demonstrated that, in general, size-matched combinations of crown ethers and cations afford the largest enthalpy changes arising from the strongest ion–dipole interaction, as exemplified by the representative combinations of Na^+ or Ag^+ with crown-5 and of K^+ or Tl^+ with crown-6 [21]. Possessing ionic diameters (1.88–2.06 Å) [22] comparable to those of Na^+ (2.04 Å) [22] and Ca^{2+} (2.00 Å) [22], trivalent lanthanide ions are expected, in principle, to be best accommodated in the size-fitted cavity of crown-5 (1.7–1.9 Å) estimated from CPK molecular models. This is true in part, since apparently size-matched 15-crown-5 gives high K_s values for the early light lanthanides (Table 1). However, the complex stability constants decreased monotonically with the reduction in the lanthanide radius. The best size-matched combination shows the highest stability constants ($\log K_s = 5.17$) for La^{3+}, as shown in Fig. 1.

Benzo-15-crown-5 gives a similar tendency in complex stability constants (Fig. 1), showing the highest K_s values for La^{3+}. However, except for La^{3+} (4.07) and Ce^{3+}

Table 1
Complex stability constant (log K_s) and thermodynamic parameters (in kcal mol^{-1}) for complexation of light lanthanide(III) nitrates with crown ethers in anhydrous acetonitrile ($T = 25.0$°C)

Crown ether	Lanthanide	log K	$-\Delta G$	ΔH	$T\Delta S$	Ref.
15C5	La^{3+}	5.17	7.05	−10.92	−3.87	[16]
	Ce^{3+}	4.62	6.30	−9.15	−2.85	
	Pr^{3+}	4.45	6.07	−6.77	−0.70	
	Nd^{3+}	3.93	5.36	−8.09	−2.73	
	Sm^{3+}	2.81	3.83	−10.93	−7.10	
	Eu^{3+}	2.26	3.08	−7.96	−4.88	
	Gd^{3+}	2.03	2.77	−8.05	−5.28	
B15C5	La^{3+}	4.07	5.55	3.02	8.57	[17]
	Ce^{3+}	3.41	4.65	3.33	7.98	
	Pr^{3+}	2.41	3.29	4.93	8.22	
	Nd^{3+}	2.48	3.38	4.47	7.85	
	Sm^{3+}	2.48	3.38	4.32	7.70	
	Eu^{3+}	2.49	3.40	3.62	7.02	
	Gd^{3+}	2.49	3.40	2.92	6.32	
S15C5	La^{3+}	2.22	3.03	−22.28	−19.25	[18]
	Ce^{3+}	2.21	3.01	−19.59	−16.58	
	Pr^{3+}	3.04	4.15	−8.73	−4.58	
	Nd^{3+}	2.35	3.21	−16.91	−13.70	
	Sm^{3+}	2.13	2.91	−21.64	−18.73	
	Eu^{3+}	2.10	2.87	−7.58	−4.71	
BisB15C5	La^{3+}	2.68	3.65	−9.64	−6.02	[19]
	Ce^{3+}	2.87	3.92	3.04	6.98	
	Pr^{3+}	3.15	4.29	6.90	11.19	
	Nd^{3+}	3.52	4.80	8.78	13.46	
	Sm^{3+}	2.98	4.07	1.85	5.91	
	Eu^{3+}	3.65	4.98	3.53	8.48	
	Gd^{3+}	2.51	3.43	13.97	17.41	
BzA15C5	La^{3+}	4.55	6.21	−12.36	−6.15	[20]
	Ce^{3+}	3.95	5.39	−9.47	−4.07	
	Pr^{3+}	4.22	5.76	−11.09	−5.33	
	Nd^{3+}	3.99	5.44	−11.16	−5.72	
	Sm^{3+}	3.85	5.25	−11.87	−6.62	
	Eu^{3+}	3.31	4.51	−13.99	−9.47	
	Gd^{3+}	3.24	4.42	−15.54	−11.12	
16C5	La^{3+}	2.54	3.46	−14.51	−11.05	[16]
	Ce^{3+}	2.49	3.40	−8.47	−5.07	
	Pr^{3+}	2.76	3.76	−8.55	−4.79	
	Nd^{3+}	3.81	5.20	−3.72	1.48	
	Sm^{3+}	4.14	5.65	−5.75	−0.10	
	Gd^{3+}	3.66	4.99	−5.46	−0.47	
MM16C5	La^{3+}	2.23	3.04	−6.21	−3.17	[23]
	Ce^{3+}	2.60	3.55	−2.85	0.70	
	Pr^{3+}	2.28	3.11	−3.90	−0.79	
	Nd^{3+}	2.68	3.66	−3.07	0.59	
	Sm^{3+}	3.72	5.07	−1.76	3.31	
	Eu^{3+}	3.46	4.72	−1.25	3.47	
	Gd^{3+}	3.62	4.94	−0.82	4.12	
MR16C5	La^{3+}	3.76	5.13	−6.99	−1.86	[16]

Table 1 (Continued)

Crown ether	Lanthanide	$\log K$	$-\Delta G$	ΔH	$T\Delta S$	Ref.
	Ce^{3+}	3.18	4.34	−5.05	−0.71	
	Pr^{3+}	3.07	4.19	−5.57	−1.38	
	Nd^{3+}	3.04	4.15	−2.49	1.66	
	Sm^{3+}	3.01	4.11	−7.54	−3.43	
	Gd^{3+}	3.10	4.23	−7.63	−3.40	
BzA16C5	La^{3+}	2.52	3.44	−10.48	−7.04	[23]
	Ce^{3+}	2.43	3.31	−9.82	−6.51	
	Pr^{3+}	3.27	4.46	−4.70	−0.24	
	Nd^{3+}	2.48	3.38	−14.40	−11.02	
	Sm^{3+}	2.46	3.36	−14.48	−11.12	
	Eu^{3+}	2.36	3.22	−14.51	−11.29	
	Gd^{3+}	2.37	3.23	−14.59	−11.36	
R′A16C5	La^{3+}	2.82	3.85	−8.20	−4.35	[24]
	Ce^{3+}	3.01	4.11	−5.14	−1.03	
	Pr^{3+}	3.47	4.73	−2.98	1.75	
	Nd^{3+}	4.41	6.02	−1.59	4.43	
	Sm^{3+}	3.50	4.77	−4.70	0.07	
	Eu^{3+}	2.71	3.70	−8.33	−4.63	
	Gd^{3+}	2.82	3.85	−10.24	−6.39	
18C6	La^{3+}	4.40	6.00	−8.65	−2.65	[26]
	Ce^{3+}	4.50	6.14	−10.28	−4.14	
	Pr^{3+}	3.70	5.05	−10.52	−5.47	
	Nd^{3+}	3.50	4.78	−8.65	−3.87	
	Eu^{3+}	2.70	3.68	−3.06	0.62	
	La^{3+}[a]	3.29	4.49	2.81	7.30	[27]
	Ce^{3+}[a]	3.57	4.87	2.54	7.41	
	Pr^{3+}[a]	2.63	3.59	4.46	8.05	
	Nd^{3+}[a]	2.44	3.33	4.77	8.10	
	Sm^{3+}[a]	2.03	2.77	3.67	6.44	
	Eu^{3+}[a]	1.84	2.51	3.06	5.57	
	Gd^{3+}[a]	1.32	1.80	3.73	5.53	
DB18C6	La^{3+}	3.32	4.53	3.84	8.37	[28]
	Ce^{3+}	2.34	3.20	2.42	5.62	
	Pr^{3+}	2.54	3.47	6.56	10.03	
	Nd^{3+}	3.82	5.21	2.76	7.97	
	Sm^{3+}	3.84	5.23	−0.72	4.51	
	Eu^{3+}	3.14	4.29	0.60	4.89	
	Gd^{3+}	2.91	3.97	0.98	4.95	
	La^{3+}[b]	5.54	7.56	6.35	13.91	[29]
	Ce^{3+}[b]	4.61	6.29	6.39	12.68	
	Pr^{3+}[b]	3.34	4.56	6.69	11.24	
	Nd^{3+}[b]	2.96	4.04	8.76	12.80	
	Sm^{3+}[b]	2.23	3.04	8.58	11.62	
	Eu^{3+}[b]	2.10	2.87	8.97	11.83	
	Gd^{3+}[b]	2.57	3.51	6.80	10.30	
BzA18C6	La^{3+}	3.77	5.14	−21.92	−16.78	[30]
	Ce^{3+}	3.46	4.72	−19.53	−14.81	
	Pr^{3+}	3.62	4.94	−13.91	−8.97	
	Nd^{3+}	4.05	5.53	−13.73	−8.21	
	Sm^{3+}	4.33	5.91	−11.38	−5.47	

Table 1 (Continued)

Crown ether	Lanthanide	log K	$-\Delta G$	ΔH	$T\Delta S$	Ref.
	Eu^{3+}	4.35	5.93	−10.53	−4.60	
	Gd^{3+}	4.59	6.26	−9.92	−3.66	
BzA21C7	La^{3+}	3.01	4.12	−5.89	−1.78	[31]
	Ce^{3+}	2.66	3.63	−4.02	−0.39	
	Pr^{3+}	2.72	3.71	−5.47	−1.76	
	Nd^{3+}	2.28	3.11	−11.76	−8.65	
	Sm^{3+}	2.67	3.65	−9.10	−5.50	
	Eu^{3+}	2.59	3.49	−11.04	−7.54	
	Gd^{3+}	2.35	3.19	−16.12	−13.04	

[a] In methanol.

[b] $Ln(ClO_4)_3$.

(3.41), the K_s values for the other five light lanthanides are very close to each other. Furthermore, it shows less binding ability than its parent 15C5 for most light lanthanide ions. The reasonable explanation is that the introduction of the benzo moiety makes the ring show relative rigidity, and, on the other hand, the electron-withdrawing effect decreases the electron density of the donor atoms.

Diphenyl substituted unsaturated crown-5(stibenzo-crown-5, S15C5) shows a different profile of stability constants, giving a peak at Pr^{3+} (Fig. 1). Because the double-bond in the ring and the substitution of two phenyl moieties increase the molecular rigidity of the crown ring, this results in the unfavorable orientation of donor atoms. All these factors, including the electron-withdrawing effect, contribute to destabilizing the S15C5 lanthanide ion complex.

The complex stability constants of BisB15C5 are larger than those of B15C5 for the light lanthanide ions except La^{3+} and Ce^{3+}, which is attributed to the stronger electron-withdrawing effect and the cooperative binding of two crown-5 rings.

However, the stability constants (K_s) for BzA15C5 is, in general, similar to that of 15C5, as shown in Fig. 1. But the K_s values for lanthanides with BzA15C5 are less than those for 15C5 by 0.6 orders of magnitude, while the K_s for Sm through Gd are higher than those for 15C5 by 1–1.2 orders of magnitude. This is attributed to the nitrogen donor atoms in the ring and the lariat ligation effect.

3.2. Thermodynamic parameters for 15C5 series

Fig. 2 shows the changing profile of thermodynamic parameters for the crown ether–lanthanide combination. It can be recognized more easily from Fig. 2 that, the complex formation itself is undoubtedly enthalpy-driven in acetonitrile for 15C5, S15C5 and BzA15C5. However, the large enthalpic gain ($-\Delta H$) does not immediately mean high complex stability, but is often canceled by the larger 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. It is interesting to note that the enthalpy and entropy for S15C5 are much

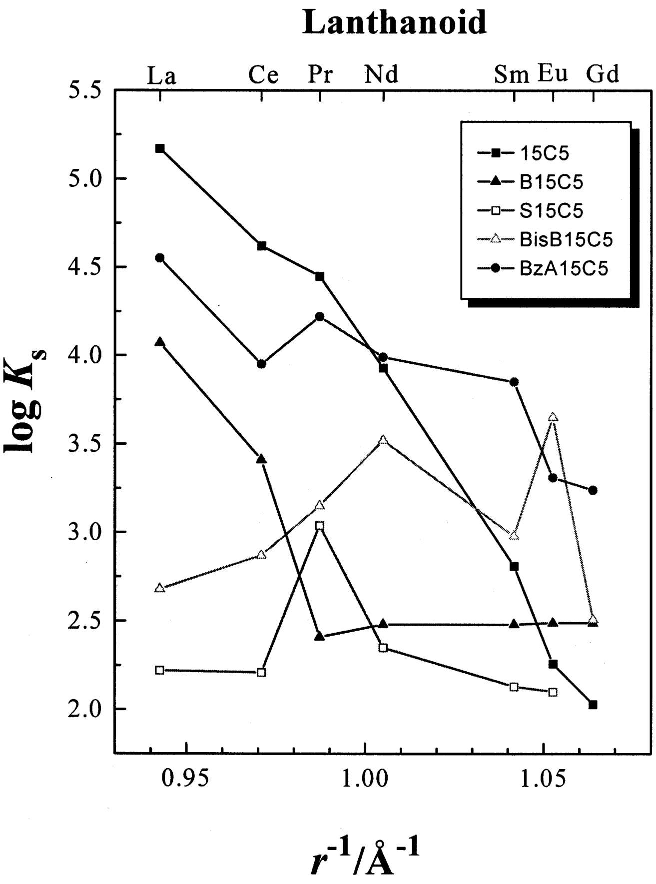

Fig. 1. Complex stability constants (K_s) at 25.0°C as a function of reciprocal ionic radius (r^{-1}) for the complexation of light lanthanides with 15C5 (■), B15C5 (▲), S15C5 (□), BisB15C5 (△), and BzA15C5 (●) in acetonitrile.

higher than those of the other two compounds, i.e. 15C5 and BzA15C5. As to B15C5, the complexation is entropy-driven, accompanying with considerable positive enthalpy change. BisB15C5 shows the same case except La^{3+}. The favorable entropy change is attributed to the desolvation upon complexation.

4. 16-Crown-5 series [16,23,24]

4.1. Complex stability constants and relative cation selectivity for 16C5 series

The profile of K_s observed for 16C5 is evidently different from that of 15C5, as shown in Fig. 3. The less-symmetrical 16C5 gives higher K_s values not for the first half but for the latter half of the light lanthanide ions. Probably, the size-fit concept is more rigorous in the complexation of lanthanides, and operates best only when

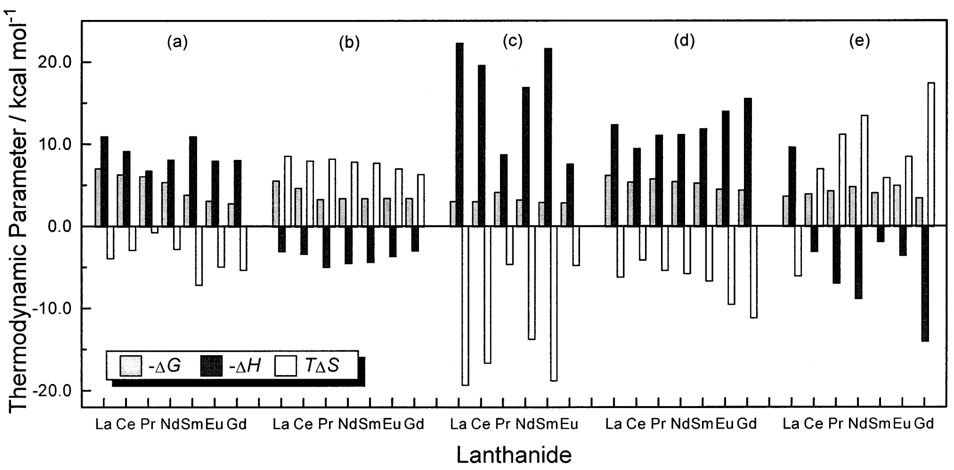

Fig. 2. Thermodynamic parameters for the complexation of light lanthanides with (a) 15C5, (b) B15C5, (c) S15C5, (d) BzA15C5, and (e) BisB15C5 in acetonitrile at 25.0°C.

very strict size-matching is realized between the ligand cavity and the cation diameter, as was the case with 16C5 (1.8–1.9 Å), and Na^{3+} (1.97 Å) through Gd^{3+} (1.88 Å).

Consequently, the introduction of non-donating methyl group(s) to 16-crown-5 at the 15-position is known to lower the binding constant significantly without any serious accompanying changes in the relative cation selectivity. As shown in Fig. 3, analogous tendencies are seen with MM16C5 and 16C5 in the complex stability constant (K_s) for all light lanthanides examined. Except for the generally lower K_s for MM16C5, the profile of K_s for MM16C5 gives a sudden jump at Sm^{3+} and maintains 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 [25].

However, this is not the case for MR16C5, which possesses donating atoms in a lariat arm. In contrast to the reference compound 16C5 and MM16C5, the lariat ether MR16C5 shows a very flat K_s profile. This could be explained from a thermodynamic viewpoint (vide infra).

On the other hand, aza-16-crown-5 BzA16C5 and R′A16C5 give different profiles of K_s values. The introduction of an extra methylene group to BzA15C5, affording less-symmetrical BzA16C5, leads to the cation-binding constants and relative cation selectivities totally different from those for the reference BzA15C5, as shown in Fig. 3. The ring enlargement drastically lowers the complex stability (K_s) for all lanthanides by 1–2 orders of magnitude, but its effect upon K_s is not uniform in the light lanthanide series. The decrease in K_s caused by the ring enlargement declines in general with increasing atomic number from La^{3+} to Gd^{3+}, flattening the K_s profile of BzA16C5 except for Pr^{3+}. Interestingly, the K_s for Pr^{3+} does not adhere to this general tendency and decreases only by less than 1 order of magnitude from 4.22 for BzA15C5 to 3.27 for BzA16C5, showing a highest selectivity of up to 8 for

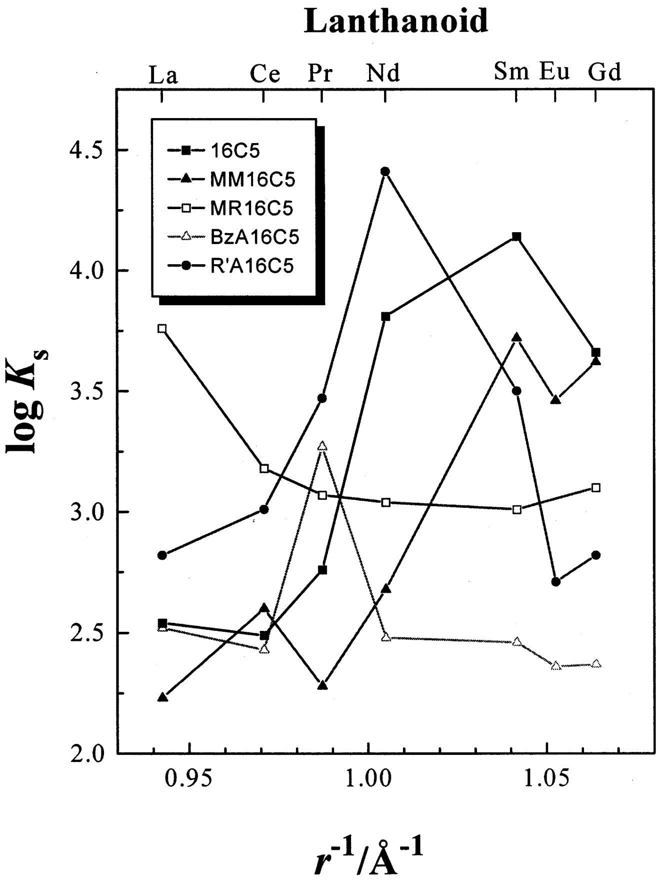

Fig. 3. Complex stability constants (K_s) at 25.0°C as a function of reciprocal ionic radius (r^{-1}) for the complexation of light lanthanides with 16C5 (■), MM16C5 (▲), MR16C5 (□), BzA16C5 (△), and R′A16C5 (●) in acetonitrile.

Pr^{3+} over any other lanthanides. This specific cation selectivity for Pr^{3+} may be attributed to the appropriate ring size and donor orientation of BzA15C5 for Pr^{3+}.

Possessing a relatively flexible molecular structure as compared with the carbon-pivot 16-crown-5 lariat (MM16C5), the nitrogen-pivot 16-crown-5 lariat (R′A16C5) gave the highest K_s for Nd^{3+} and the lowest for La^{3+} and Eu^{3+} among the light lanthanide ions, eventually showing the highest cation selectivity for Nd^{3+}. It is noted that the relative cation selectivity for Nd^{3+} over the neighboring Pr^{3+} and Sm^{3+} amounted to 8 and 9, respectively, which are exceptionally high for the lanthanide series possessing quite similar chemical and physical properties. This is reasonably accounted for in terms of the steric requirement upon sidearm ligation; only the best fitting lanthanide ion accommodated in the cavity of 16-crown-5 fully enjoys further ligation by the donating sidearm with relatively large structural flexibility, making the operation of exact size-matching easy. Therefore, the in creased conformational freedom of the lariat ether is essential for the highly selective complexation of the size-matched trivalent lanthanide ions.

4.2. Thermodynamic parameters for the 16C5 series

It can be seen that all the complexation of trivalent lanthanide ions with 16C5 series are exothermic, and most are enthalpy-driven, while several are entropy-governed, as shown in Fig. 4. The positive $T\Delta S$ or smaller entropic losses for the complexation of *C*-pivot 16-crown-5 (MM16C5) with lanthanide ions indicate that the two methyl groups at C-15 lock the 16-crown-5 framework in a conformation favorable for complexation. However, the axial methyl groups at C-15 of MM16C5, as examined by the CPK model, do not lead to serious steric hindrance for the cation accommodated in the cavity of the crown ether, afford an analogous tendency to the parent 16C5 in the binding and thermodynamic profiles. Furthermore, the decreased enthalpic gain for MM16C5 (0.65–8.3 kcal mol^{-1}) caused by methylation is compensated to some extent, by the increased entropic gain (3.21–7.88 kcal mol^{-1}).

The complexation of lanthanides with MR16C5 is characterized by relatively small and mutually similar enthalpy and entropy changes throughout the light lanthanide series, as shown in Fig. 4. The small $T\Delta S$ values would be somewhat unexpected in view of the possible substantial structural changes upon lariat ligation to the lanthanide 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 three-dimensional cavity differs in size and adjustability from the inherent 16-crown-5 type, such that complexation in the induced three-dimensional cavity of the lariat ether is not advantageous from the viewpoint of the strict size-matching required for highly selective complexation of lanthanide ions.

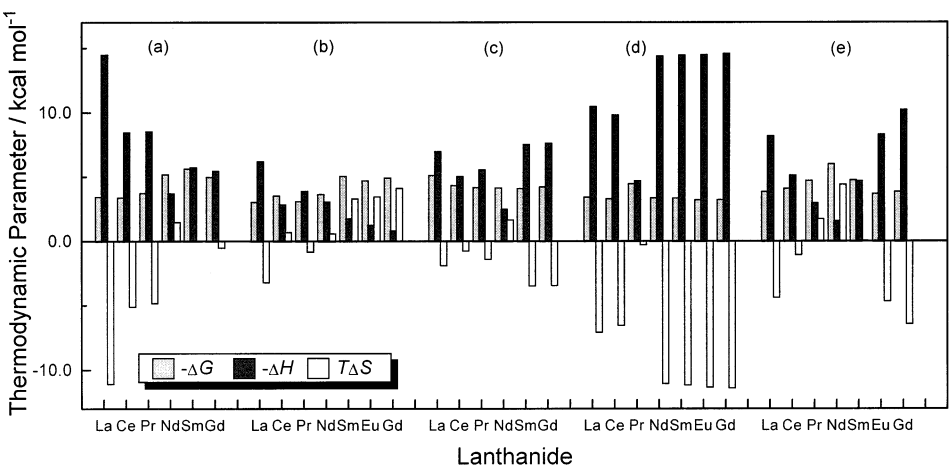

Fig. 4. Thermodynamic parameters for the complexation of light lanthanides with (a) 16C5, (b) MM16C5, (c) MR16C5, (d) BzA16C5, and (e) R′A16C5 in acetonitrile at 25.0°C.

As can be more easily observed from Fig. 4, all the ΔH values for the complex formation of crown ethers BzA16C5 with trivalent lanthanide 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 ($-\Delta H$) for BzA16C5 and BzA15C5 may indicate stronger ion–dipole interactions between the lanthanide cation and the donor nitrogen in aza-crown-5, 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 lanthanides with BzA16C5. Compared with BzA15C5, an extra methylene group in BzA16C5 inevitably enhances the entropic loss ($T\Delta S$) for La, Ce, and Nd–Gd by 0.24–5.3 kcal mol^{-1}, leading to low complex stabilities, but specifically diminishes the loss for Pr^{3+} by 5.09 kcal mol^{-1}, 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 the entropy change for all crown ethers examined.

The ΔH values of the complex formation with R′A16C5 are all negative with negative or slightly positive entropic changes. This means that these complexations are chiefly enthalpy-driven in acetonitrile. However, the cation–ligand combinations accompanying smaller entropic losses lead to higher complex stabilities. Thermodynamically, the entropic loss arising from the structural freezing upon lariat ligation to lanthanide ion accommodated in the cavity is often compensated by the gain from the accompanying extensive desolvation, giving rise to a positive $T\Delta S$ value, as high as 4.43 kcal·mol^{-1}, for the complexation of lariat ether R′A16C5 with Nd^{3+}. Thus, it is concluded that the complexation itself is mainly enthalpy-driven in acetonitrile but the cation selectivity is governed by the entropy change for all ligands.

It is interesting to compare the thermodynamic parameters for the nitrogen-pivot 16-crown-5 lariat (R′A16C5) with those for the carbon-pivot 16-crown-5 (MR16C5), since these two lariats, possessing *C*- and *N*-pivot, suffer substantially different structural changes upon lariat ligation. As can be seen from Figs. 3 and 4, the cation selectivity sequences and the thermodynamic profiles observed for two lariat ethers are distinctly different. One possible explanation for the relatively small and mutually resembling parameters obtained for MR16C5 throughout the light lanthanide series would be found in the presence of the methyl group at C-15 that may contribute to the lock of the 16-crown-5 lariat framework in a conformation favorable for complexation of some cation but makes the operation of strict size fitting difficult. In contrast to the reference lariat ether MR16C5, *N*-pivot 16-crown-5 R′A16C5, possessing the relatively large structural flexibility, can strictly adjust the induced three-dimensional cavity to the size of the most favorable lanthanide ion, i.e. Nd^{3+}. In this case, the desolvation becomes more extensive upon complexation with Pr^{3+}–Sm^{3+} to give the positive entropy changes ($T\Delta S$), which lead to higher cation-binding ability. Thus the *N*-pivot 16-crown-5 R′A16C5 is shown to possess the most advantageous structure from the viewpoint of the strict size-matching required for highly selective complexation of lanthanides. Thermodynamically, this drastic change in the cation selectivity sequence is at-tributed to the positive entropy change that is maximized only when a very strict size-fit relationship is attained between the induced three-dimensional cavity of the *N*-pivot lariat ether and the ionic diameter of the lanthanides. In this context, the tailoring of lariat ether's three-dimensional cavity by the introduction of a donating side arm to a less-symmetric aza-crown ether is a convenient and powerful tool to enhance the cation-binding ability and relative cation selectivity for lanthanide ions.

5. 18-Crown-6 series [26–30]

5.1. Complex stability constants and relative cation selectivity for 18C6 series

As can be seen from Fig. 5, the profile of K_s for 18C6 in acetonitrile shows a characteristic peak at Ce^{3+} and gradually declines with increasing atomic number

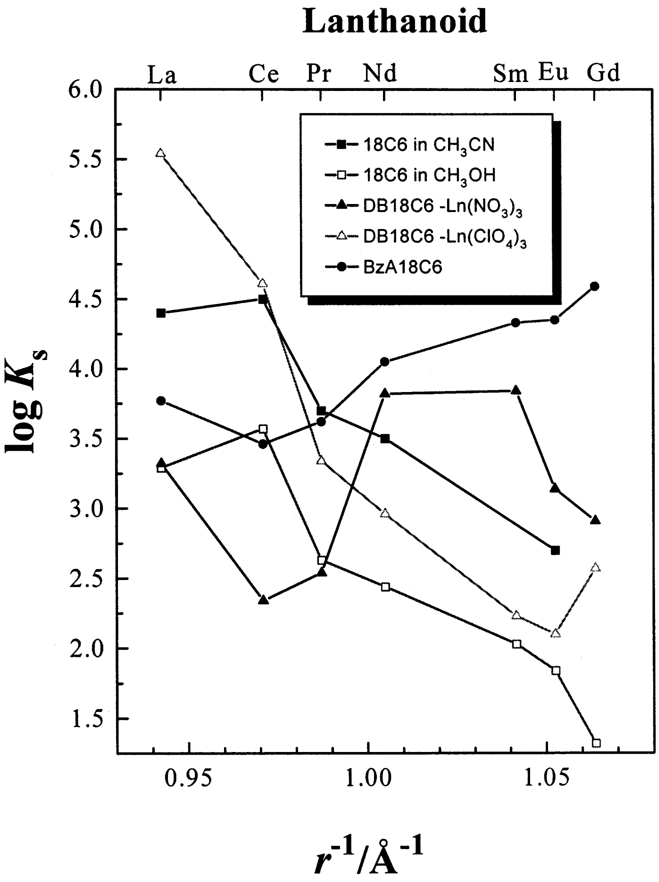

Fig. 5. Complex stability constants (K_s) at 25.0°C as a function of reciprocal ionic radius (r^{-1}) for the complexation of light lanthanide nitrates with 18C6 in acetonitrile (■) and in methanol (□), respectively, of DB18C6 with light lanthanide nitrates (▲) and light lanthanide perchlorates (△) in acetonitrile, respectively, and of light lanthanide nitrates with BzA16C5 (●) in acetonitrile.

or decreasing ionic radius from Ce^{3+} to Gd^{3+}, probably owing to their fitted cavity size (2.6–3.2 Å) and proper donated orientations. Although the lanthanide diameter is much smaller (2.12–1.88 Å), it is noted that the ion-pair form of lanthanide(III) nitrates, behaving as non-electrolyte in anhydrous acetonitrile, must be much larger than the naked trivalent lanthanides. This result indicates that 18C6 possesses the stronger binding ability for Ce^{3+}. On the other hand, the size-fit concept has been shown to be unsuccessful in explaining the trivalent lanthanide ion selectivities of DB18C6, since this rigid framework crown ether gives higher K_s values for the latter half of the light lanthanides than Ce^{3+} and Pr^{3+}. One possible explanation for this obvious deviation from the size-fit concept for DB18C6 complexation with Ce^{3+} (2.06 Å) through Gd^{3+} (1.88 Å) is attributed to the increasing surface charge density due to the lanthanide contraction and the subsequent tighter solvation for heavier lanthanides. This seems reasonable, since the extensive thermodynamic studies on cation-crown ether complexation have shown that the cation-binding ability of the crown ether containing benzo groups is lower than that for the parent crown ether, and have demonstrated that the diminished complex stability is due to the decreased electron density of donor oxygens produced by the electron-withdrawing aromatic ring. Therefore, it is very interesting and significant that the cation-binding constants and relative cation selectivities observed for DB18C6, shown in Fig. 5, do not show a regular trend and are totally different from those of the reference compound 18C6. There are hitherto limited data for the complexation of lanthanides with crown ethers to elucidate the nature of the binding behavior. The irregular trend of the complexation ability may be attributable to the conformational change of the 18-crown-6 ring upon the complexation resulting from the attachment of two benzo groups and the lanthanide ion-pair form. Possessing a structurally rigid skeleton as compared with the parent 18C6, DB18C6 gave the highest K_s for Sm^{3+} and Nd^{3+} and the lowest for Ce^{3+} and Pr^{3+} among the light lanthanide ions, and eventually showing the highest cation selectivity for Sm^{3+} and Nd^{3+}. Therefore, the highly selective complexation for DB18C6 with Sm^{3+} and Nd^{3+} is attributed to the increased molecular rigidity of the crown ether, which leads to a small conformational change upon complexation.

However, the profile of complex stability constants of light lanthanide(III) perchlorates in acetonitrile is different from that of nitrates (Fig. 5). The K_s values decline from La^{3+} through Eu^{3+}. The reasonable explanation is that lanthanide(III) perchlorates behave as electrolytes, and exist as ions in acetonitrile solution, which leads to the different sequence of K_s from that of nitrates.

It is interesting to note that the tendency of K_s values for BzA18C6 with lanthanides is unique in this 18-crown-6 series (Fig. 5). The complex stability increases with the decrease in the radius of lanthanide ions. This is attributed to the efficient participation on the nitrogen donor atom in the complex formation and the lariat ligation effect of the benzyl moiety.

5.2. Thermodynamic parameters for 18C6 series

As reported by Izatt et al. [27], the complex formation of light lanthanide ions with 18C6 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^{-1}) and somewhat smaller positive enthalpy changes ($\Delta H = 2.5$–4.8 kcal mol^{-1}), as shown in Fig. 6. As a consequence of compensation between these positive $T\Delta S$ and ΔH values, the complex stability (K_s) in methanol decreases in general with increasing atomic number. Amman and Bünzli [26] demonstrated that the use of acetonitrile as solvent enhances the K_s values for all lanthanides by one order of magnitude, while the profile of the complex stability sequence is kept unchanged throughout the light lanthanide series, see Fig. 5. 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 of K_s in methanol and acetonitrile, the thermodynamic parameters behave in a completely opposite manner in these two solvents; the complexation of lanthanides with 18C6, though entropy-driven in methanol, is absolutely enthalpy-driven in acetonitrile.

These opposing results may be attributed to the nature of the lanthanide salt and solvent used. In methanol, both the dissociated trivalent lanthanide ion and the free ligand are heavily solvated through ion–dipole and hydrogen-bonding interaction, respectively. Hence, the complexation demands fairly extensive desolvation of both cation and ligand, affording the highly positive entropy change upon complexation, as observed (Table 1). On the other hand, lanthanide nitrates do not dissociate in acetonitrile as indicated by conductometric measurements, and therefore solvation to the salts is not as heavy as in methanol. Moreover, no strong solvation to free ligand is expected to occur in acetonitrile in the absence of the hydrogen-bonding interaction with the solvent. Under such circumstances, the complexation of lanthanide nitrates with crown ethers, which is essentially a molecular association process, is driven mainly through the ion–dipole interaction without accompanying

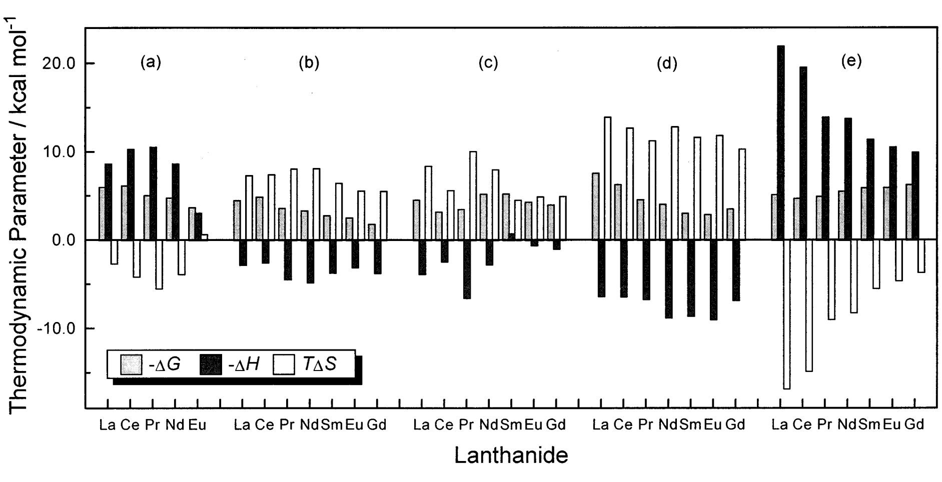

Fig. 6. Thermodynamic parameters for the complexation of light lanthanide nitrates with 18C6 in (a) acetonitrile and (b) methanol, respectively, of DB18C6 with (c) light lanthanide nitrates and (d) light lanthanide perchlorates in acetonitrile, respectively, and of light lanthanide nitrates with BzA16C5 (e) in acetonitrile at 25.0°C.

extensive desolvation, giving highly negative ΔH and more or less negative $T\Delta S$ values.

As can be recognized more easily from Fig. 6, the ΔH values of the complex formation for 18C6 are all negative with negative entropic changes, except for the complexation with Eu^{3+} accompanying slightly positive entropic changes. This means that these reactions are chiefly enthalpy-driven in acetonitrile. On the other hand, the ΔH values observed for DB18C6 with light lanthanide nitrates are positive with the larger positive entropic changes, except for Sm^{3+} accompanying slightly negative enthalpy changes. As is the case with light lanthanide perchlorates in acetonitrile. However, the thermodynamic parameters (ΔH and $T\Delta S$) are all larger than those of nitrates. These results indicate that the complexation of DB18C6 with the light lanthanide ions are mainly entropy-driven in acetonitrile. As can be seen from Figs. 5 and 6, the cation selectivity and the thermodynamic profiles observed for two crown ethers are distinctly different. One possible explanation for the different thermodynamic parameters throughout the light lanthanide series would be found in the presence of the benzo groups that may be attributable to the rigidity of the 18-crown-6 framework in a conformation which is favorable for complexation of some cation, giving favorable entropy changes, but makes the operation of size-fitting difficult. On the other hand, the results obtained indicate that the desolvation becomes more extensive upon complexation of DB18C6 with La^{3+}–Gd^{3+}, which also lead to the higher positive entropy changes ($T\Delta S$). The larger positive entropic changes and somewhat small positive enthalpic changes for DB18C6 complexation with most lanthanides are contributed to the complex stabilities as a consequence of compensation effects. As can be seen from Figs. 5 and 6, although the complex stability decreases for DB18C6 complexation with La^{3+} and Ce^{3+} as compared with the parent 18C6, the relative cation selectivities are enhanced for DB18C6 complexation with Nd^{3+} and Sm^{3+}. Thus DB18C6 is shown to possess the most advantageous structure for highly selective complexation of lanthanides.

The ΔH values of BzA18C6 complexation with light lanthanides are all negative, accompanying slightly smaller entropy loss. It is evident that complexation is driven by the enthalpy term, however, the complex stability is entropy governed.

6. Benzyl-aza-3*m*-crown-*m* ($m = 5$, 6, and 7) series [20,30,31]

6.1. Complex stability constants and relative cation selectivity for BzA3mCm series

As shown in Table 1, aza-3*m*-crown-*m* ($m = 5$, 6,and 7) lariat ethers 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 lanthanide nitrates. In order to visualize the cation-binding properties of these serial aza-crown ethers, the changing profile of the complex stability constant ($\log K_S$) is plotted in Fig. 7 as a function of the reciprocal ionic radius of lanthanide.

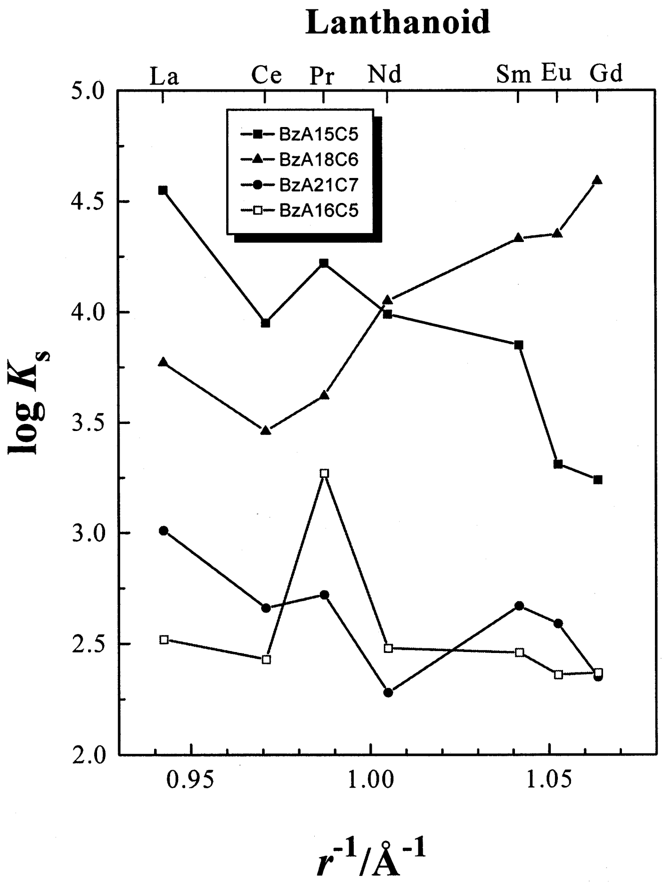

Fig. 7. Complex stability constants (K_s) at 25.0°C as a function of reciprocal ionic radius (r^{-1}) for the complexation of light lanthanides with BzA15C5 (■), BzA18C6 (▲), BzA21C7 (●), and BzA16C5 (□)in acetonitrile.

As can be seen from Fig. 7, the profile of K_s for BzA15C5, possessing a small local peak at Pr^{3+}, shows a global decreasing tendency with increasing atomic number, or decreasing ionic radius, from La^{3+} to Gd^{3+}. This gradually decreasing trend of K_s may be ascribed to the relatively rigid structure of BzA15C5 and the size-fit relationship between the cation and the cavity. Since BzA15C5 has a cavity size of 2.20 Å, which matches the cation diameter of La^{3+} (2.06 Å), it is reasonable for BzA15C5 to show the highest stability constant for La^{3+} and the lowest for Gd^{3+} (1.88 Å).

In contrast, BzA18C6 gives almost the opposite binding profile for the light lanthanide series. Thus, the K_S value first drops at Ce^{3+} and then steadily increases up to Gd^{3+}. This trend cannot be simply accounted for in terms of the size-fit concept, and therefore the wrapping complexation of the lanthanides (diameter ca. 2.0 Å) with the larger-sized BzA18C6 (cavity ca. 2.6–3.2 Å) is considered to be responsible for the contrasting trend. Similar cation binding behavior has been observed for the complexation of the lanthanides with dibenzo-18-crown-6. The increasing surface charge density of lanthanide ions due to the lanthanide contraction from La^{3+} to Gd^{3+} and the larger ligand flexibility jointly facilitate the operation of wrapping complexation of these formally size-mismatched cations with the aza-18-crown-6.

Somewhat unexpectedly, the aza-21-crown-7, possessing a still larger cavity (> 3.5 Å), gave substantially low K_S values throughout the light lanthanide series, which are smaller than those obtained with BzA15C5 or BzA18C6 by more than one order of magnitude, and a relatively flat cation binding profile, which is analogous in shape to that observed for BzA15C5. Probably, the cation diameters of the lanthanides (1.88–2.06 Å), obviously unsuited to the large cavity of BzA21C7, are still too small to be accommodated in the presumed three-dimensional cavity of BzA21C7, which would be formed upon wrapping complexation. Even so, the size-fit concept still appears to play some role in the (wrapping) complexation by BzA21C7, showing a weak but appreciable preference for the lighter lanthanides, although its control becomes fairly loose. It is inferred that only a limited number of donor atoms on BzA21C7 are directly involved in the complex formation, which eventually leads to the cation selectivity profile similar in shape to that for BzA15C5 and also to the much-lower K_S values.

6.2. Thermodynamic parameters for the BzA3mCm series

It should be noted that all complex formation of light lanthanides with BzA3*m*C*m* are favored predominantly by the large enthalpic gain, which is however canceled by the similarly large entropic losses to a varying extent depending on the combination of the ligand and lanthanide, as shown in Fig. 8. Thus, the complexation of aza-crown ethers with trivalent lanthanide ions is exclusively driven by the

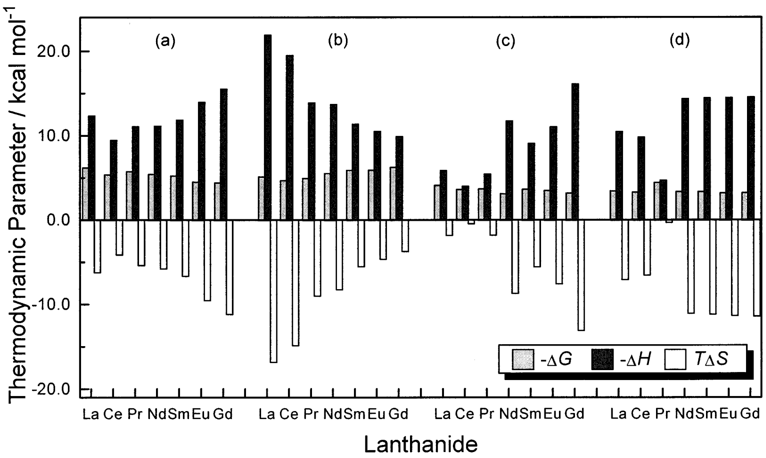

Fig. 8. Thermodynamic parameters for the complexation of light lanthanides with (a) BzA15C5; (b) BzA18C6; (c) BzA21C7; and (d) BzA16C5 in acetonitrile at 25.0°C.

enthalpy term. However, the profile of the $-\Delta G$ value as a function of the lanthanide series is completely different, or even inverted, from that of the $-\Delta H$ value, and the high enthalpic gains are canceled out by the yet larger entropic losses for all cation–ligand combinations examined. It may be concluded therefore that, in the complexation of light lanthanides with aza-crown 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 BzA15C5 and BzA21C7 as is the case with K_S, a closer examination reveals that, in the first half of the lanthanide series up to Pr^{3+}, the much smaller enthalpic gains for BzA21C7 than those for BzA15C5 are responsible for the low complex stabilities, while for the latter half (from Nd^{3+} to Gd^{3+}) the fairly large enthalpic gains are extensively canceled out by the similarly large entropic losses to give the fairly smaller complex stabilities for BzA21C7 than those for BzA15C5. The gradually increasing trend in enthalpic gains from 9.47 to 15.54 kcal mol^{-1} for BzA15C5 and from 4.02 to 16.12 kcal mol^{-1} for BzA21C7 may be attributed to the increasing surface charge of the lanthanides, which enhances the ion–dipole interactions between the ligand donors and the lanthanide 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 ΔH and ΔG values for BzA21C7 may be ascribed to the partial weaker ligation of the donor atoms upon wrapping complexation by BzA21C7. On the other hand, the large ring size of BzA21C7 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 ΔH and ΔG values.

BzA18C6 shows a totally different thermodynamic profile. The enthalpic gain ($-\Delta H$) is gradually diminishes with increasing atomic number from La^{3+} to Gd^{3+}. The entropic loss ($T\Delta S$) also shows a similar trend, but the decline is rather mild, giving the higher complex stability for heavier lanthanides, as shown in Fig. 8. One possible explanation for the thermodynamic parameters obtained for BzA18C6 through the light lanthanide series is the steric hindrance caused by the *N*-benzyl substituent, which particularly interferes the tight wrapping complexation of small lanthanide ions with BzA18C6. It may be concluded therefore that the enthalpic gain arises mostly from the ligation of donors to trivalent lanthanide 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 role in addition to the size-fit concept in the complexation of aza-crown ethers with a non-donating bulky side chain.

7. Relative cation selectivity

In summary, with respect to the complexation of light lanthanides, 16-crown-5 series show good relative cation selectivity, such as 16C5 for Sm^{3+} and Nd^{3+}, S16C5 and BzA16C5 for Pr^{3+}, MR16C5 for Sm^{3+}, R′A16C5 for Nd^{3+}. Meanwhile, 18C6 shows high relative cation selectivity for Ce^{3+} and La^{3+}, and DB18C6 for Nd^{3+} and Sm^{3+}. The high cation selectivity indicates the compensation effect of enthalpy and entropy changes in the complex formation.

8. Enthalpy–entropy compensation

The enthalpy–entropy compensation relationship was revealed in the complexation thermodynamics of a wide variety of both guests and hosts [32,33]. The slope (α) and intercept ($T\Delta S_0$) of the regression line of the $T\Delta S$–ΔH plot can be taken as a measure of the conformational changes and the extent of desolvation upon complexation. Using the compiled thermodynamic quantities listed in Table 1 (number of data sets (n) = 117), the entropy change ($T\Delta S$) was plotted against the enthalpy change (ΔH) to give an excellent regression line (correlation coefficient $r = 0.994$) of a large slope ($\alpha = 1.00$) and intercept ($T\Delta S_0 = 4.2$ kcal mol^{-1}), as shown in Fig. 9. Even if the data for BisB15C5 were not included in the plot, the results were almost identical. The unexpectedly large extrathermodynamic parameters are not in agreement with those obtained before. The slopes and intercepts are listed in Table 2, along with those obtained for the representative cation binders, such as glyme/podand, crown ether, cryptand, and bis(crown ether)s.

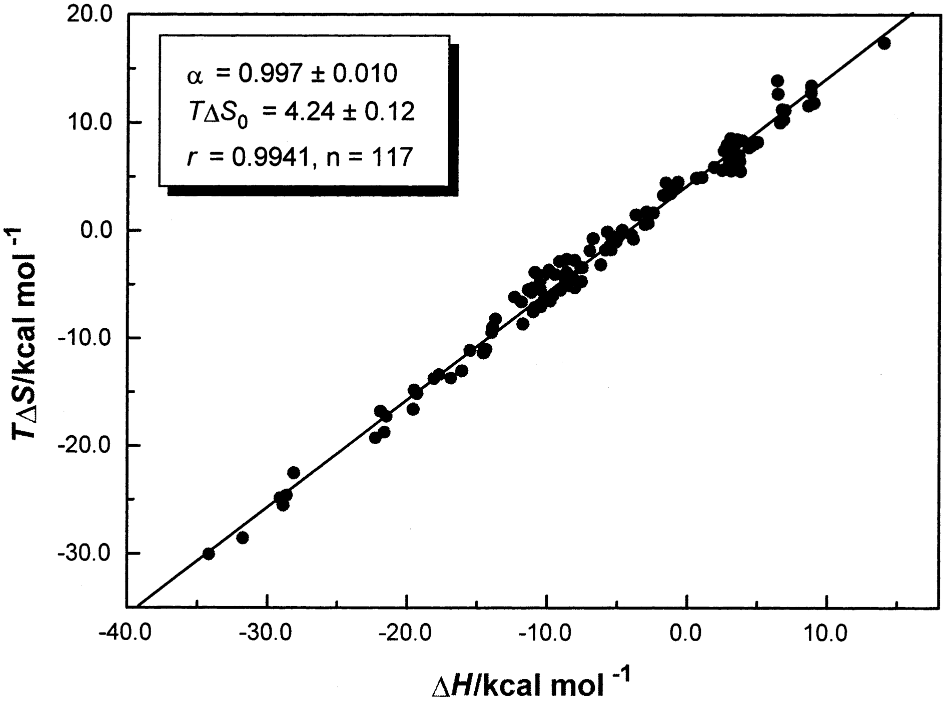

Fig. 9. Enthalpy–entropy compensation plot for complexation of light lanthanides with crown ethers (Chart 1); see Table 1 for the original data.

Table 2
Slope (α) and intercept ($T\Delta S_0$) of the ΔH–$T\Delta S$ plots for 1:1 host–guest complexation in homogeneous solution

Host	Guest	α	$T\Delta S_0$	Ref.
Glyme/podand	Cation	0.86	2.3	[13]
Crown ether	Cation	0.76	2.4	[13]
Cryptand	Cation	0.51	4.0	[13]
Bis(crown ether)	Cation	1.03	4.6	[13]
Crown ether	Lanthanide	1.00	4.2	This work

The extrathermodynamic parameters obtained in this text are incidentally very similar to those for bis(crown ether)s irrespective of the molecular structure, and much larger than those for crown ether. This seems reasonable, the slopes and intercepts obtained before were derived from the thermodynamic data for the complexation of cation binders with univalent alkali cations. However, the trivalent light lanthanide ions, possessing high electropositivity and small cation radius, should be heavily solvated in solution. Upon complexation, there must occur very extensive desolvation, accompanying the induced substantial conformational changes.

Acknowledgements

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References

[1] C.J. Pedersen, Angew. Chem. Int. Ed. Engl. 28 (1988) 1021.
[2] J.J. Christensen, D.J. Eatough, R.M. Izatt, Chem. Rev. 74 (1974) 351.
[3] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 91 (1991) 1721.
[4] R.M. Izatt, J.S. Bradshaw, K. Pawlak, R.L. Bruening, B.J. Tarbet, Chem. Rev. 92 (1992) 1261.
[5] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Chem. Rev. 95 (1995) 2529.
[6] R.M. Izatt, J.H. Rytting, D.P. Nelson, B.J. Haymore, J.J. Christensen, Science 164 (1968) 443.
[7] Y. Inoue, T. Hakushi, Y. Liu, in: Y. Inoue, G.W. Gokel (Eds.), Cation Binding by Macrocycles, Marcel Dekker, New York, 1990 (Chapter 1).
[8] L.D. Hansen, E.R. Lewis, J. Chem. Thermodyn. 3 (1971) 35.
[9] J.J. Christensen, J. Ruckman, D.J. Eatough, R.M. Izatt, Thermochim. Acta 3 (1972) 203.
[10] D.J. Eatough, J.J. Christensen, R.M. Izatt, Thermochim. Acta 3 (1972) 219.
[11] D.J. Eatough, R.M. Izatt, J.J. Christensen, Thermochim. Acta 3 (1972) 233.
[12] Y. Inoue, T. Hakushi, Y. Liu, L.–H. Tong, J. Hu, G.-D. Zhao, S. Huang, B.-Z. Tian, J. Phys. Chem. 92 (1988) 2371.
[13] Y. Liu, L.-H. Tong, S. Huang, B.-Z. Tian, Y. Inoue, T. Hakushi, J. Phys. Chem. 94 (1990) 2666.
[14] Y. Liu, Y.-K. Wang, Z.-Q. Guo, S.-Y. Yang, D.-S. Jin, Acta Chim. Sin. 44 (1986) 22.
[15] F. de Jong, D.N. Reinhoudt, Stability and Reactivity of Crown Ether Complexes, Academic Press, New York, 1981.

[16] Y. Liu, T.-B. Lu, M.-Y. Tan, T. Hakushi, Y. Inoue, J. Phys. Chem. 97 (1993) 4548.
[17] D.-Q. Huang, B.-G. Jiang, J.-Z. Yin, H.-K. Yan, Acta Chim. Sin. 48 (1990) 452.
[18] Y. Liu, T.-B. Lu, M.-Y. Tan, Y. Inoue, T. Hakushi, Acta Phys. Chim. Sin. 10 (1994) 336.
[19] Y. Liu, A.-D. Qi, Y.-T. Chen, Y.-M. Zhang, Acta Chim. Sin. 55 (1997) 1091.
[20] Y. Liu, T.-B. Lu, M.-Y. Tan, Y. Inoue, T. Hakushi, Acta Chim. Sin. 51 (1993) 874.
[21] Y. Inoue, F. Amano, N. Okada, H. Inada, M. Ouchi, A. Tai, T. Hakushi, Y. Liu, L.-H. Tong, J. Chem. Soc. Perkin Trans. 2 (1990) 1239.
[22] R.D. Shannon, Acta Crystallogr. Sect. A 32 (1976) 751.
[23] Y. Liu, X.-P. Bai, Y. Inoue, M. Ouchi, J. Phys. Chem. B 102 (1998) 4871.
[24] Y. Liu, B.-H. Han, Y.-M. Li, R.-T. Chen, M. Ouchi, Y. Inoue, J. Phys. Chem. 100 (1996) 17361.
[25] Y. Inoue, K. Wada, Y. Liu, M. Ouchi, A. Tai, T. Hakushi, J. Org. Chem. 54 (1989) 5268.
[26] B. Ammann, J.C.G. Bünzli, Experientai Suppl. 37 (1979) 49.
[27] R.M. Izatt, J.D. Lamb, J.J. Christensen, B.L. Haymore, J. Am. Chem. Soc. 99 (1977) 8344.
[28] Y. Liu, B.-H. Han, Z.-H. Zhang, J.-H. Guo, Y.-T. Chen, Thermochim. Acta 317 (1998) 1.
[29] X.-R. Huang, B.-G. Jiang, J.-Z. Yin, H.-K. Yan, Acta Chim. Sin. 49 (1991) 359.
[30] Y. Liu, T.-B. Lu, M.-Y. Tan, Y. Inoue, T. Hakushi, J. Chin. Rare Earths 12 (1994) 111.
[31] Y. Liu, S.-P. Dong, H. Zheng, Y. Inoue, M. Ouchi, Supramol. Chem. 11 (2000), in press.
[32] Y. Inoue, T. Wada, in: G.W. Gokel (Ed.), Advances in Supramolecular Chemistry, vol. 4, JAI Press, Greenwhich, CT, 1997, pp. 55–96.
[33] Y. Liu, B.-H. Han, B. Li, Y.-M. Zhang, P. Zhao, Y.-T. Chen, T. Wada, Y. Inoue, J. Org. Chem. 63 (1998) 1444.