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Complexation thermodynamics of rare earth (III) with crown ethers. 3[1]. Calorimetric titration of light lanthanoid (III) nitrates with dibenzo-18-crown-6 in acetonitrile

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Abstract

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 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6) (**2**). Data analyses, assuming 1 : 1 stoichiometry were successfully applied to all the light lanthanoid–crown ether combinations employed. Using the present and reported data, the complexation behaviors of (**2**) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) (**1**) are compared from the thermodynamic point of view. The rigid structure of (**2**), as compared with (**1**), gave the higher K_s for Nd^{3+} and Sm^{3+} among the light lanthanoid nitrates. The complex stability sequence as a function of reciprocal ionic diameter of lanthanoid showed a monotonically declining pattern for (**1**) except for a jump at Ce^{3+}, and a characteristic peak profile at Nd^{3+} and Sm^{3+} for (**2**). Thermodynamically, the complexation of light lanthanoid nitrates with 18-crown-6 is mainly enthalpy-driven in acetonitrile, but the complexation with (**2**) is chiefly entropy-driven. © 1998 Elsevier Science B.V.

Keywords: Complexation; Crown ether; Rare earth (III); Stability

1. Introduction

Enormous effort has been devoted to thermodynamic studies of cation–crown ether complexation to elucidate the nature of the cation-binding in terms of the enthalpy and entropy changes [1–4]. However, most papers dealing with the complexation thermodynamics have concentrated mainly on alkali, alkali-earth, and some heavy metal salts. Less attention has been paid to the complexation thermodynamics of trivalent lanthanoids. We have recently shown that the induced three-dimensional cavity of carbon-pivot 16-crown-5 lariat(s) shows poor cation selectivity for the light lanthanoid series [5]. More recently, we have demonstrated that the nitrogen-pivot 16-crown-5 lariat possesses much higher cation-binding ability and selectivity compared with the carbon-pivot 16-crown-5 [1]. The high cation selectivity of an aza-16-crown-5 lariat is attributed to the entropic loss that is minimized only when a strict size match is realized between the ionic diameter of the lanthanoids and the relatively flexible three-dimensional cavity induced upon lariat ligation. It is interesting that Huang et al. and La Rosa et al. [6] studied the complexation of dibenzo-18-crown-6 with La^{3+}, using different methods and counterions, giving distinctly different stabi-

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[1] See Ref. [1] for previous paper.

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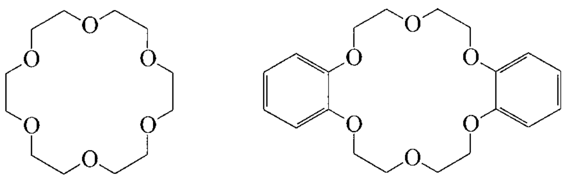
lity constants. These results prompted us to investigate the complexation behavior of the rigid dibenzo-18-crown-6 with light lanthanoid nitrates.

In the present study, 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 dibenzo-18-crown-6 ((**2**), Chart I). The thermodynamic parameters for the complexation of light lanthanoid nitrates with (**2**), together with those for 18-crown-6 (**1**) [6], will further our understanding of this thermodynamically less investigated area of crown ether chemistry [7,8]. Another point of interest is the reduced influence of the electron-withdrawing effect of the aromatic ring upon complexation of parent crown ether with light lanthanoid nitrates.



1 **2**

Chart I

2. Experimental

2.1. Materials

Commercially available (**2**) (Merck) was used without further purification. Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent (conductivity $<5\times10^{-7}$S cm^{-1}) for calorimetry. Light lanthanoid (III) nitrates (La–Gd) were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemical) in 50% aqueous nitric acid while heating for ca. 10 min. After evaporation, the solid residue was dehydrated with P_2O_5 in vacuo for several days to give a powdery product. Lanthanoid nitrate was dissolved in anhydrous acetonitrile and refluxed for 24 h over molecular sieves for further removal of water. The concentrations of lanthanoid nitrate solutions in acetonitrile 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 [9].

2.2. Apparatus and procedure

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 [10]. The principle of the measurement and the detailed experimental procedures have been described previously [11–13]. Typically, a crown ether solution (20-40 mM) in anhydrous acetonitrile was continuously introduced at a rate of 0.3321 cm^3 min^{-1} into a lanthanoid nitrate solution (1.0–2.0 mM, 50.0 ml) placed in the calorimeter. In order 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}), including agitation, heat flow between the vessel and its surrounding, and resistance heating by the thermistor used, and the temperature difference between titrant and titrate (Q_{TC}) in each run: $Q_{\mathrm{net}}=Q_{\mathrm{obs}}-Q_{\mathrm{D}}-Q_{\mathrm{HL}}-Q_{\mathrm{TC}}$. 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 the enthalpy change (ΔH^0) were calculated [13,14]. Reliability of the whole system and the calculation procedures were doubly checked as earlier [15] by test runs using the reported reaction systems:

(i) the enthalpy change ($\Delta H=-11.34$ kcal mol^{-1} at 25°C) upon titration of Tris with hydrochloric acid was consistent with that reported (-11.35 kcal mol^{-1}) [16]; and
(ii) log K_{s} and ΔH (1.97 ± 0.05, -6.22 kcal mol^{-1} at 25°C) for the complexation of 18-crown-6 with potassium chloride are in good agreement with the reported values (2.03 ± 0.10, -6.21 kcal mol^{-1}) [17].

3. Results and discussion

Assuming the 1 : 1 stoichiometry [18,19] for the complexation of $Ln(NO_3)_3$ (Ln=La, Ce, Pr, Nd, Sm, Eu, and Gd) with the dibenzo-18-crown-6 (CE) (Eq. (1)), the complex stability constant (K_{s}) and the enthalpy change (ΔH^0) were calculated by using the least-squares method to minimize the U value (Eq. (2)) [20,21]:

$$\mathrm{CE} + \mathrm{Ln} \overset{K_S}{\rightleftharpoons} \mathrm{CE\,Ln} \qquad (1)$$

$$U(K_s, \Delta H^0) = \sum_{t=1}^{m} (Q_t - \Delta H^0 \times N_t)^2 \qquad (2)$$

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. N_t is directly related to the complex stability constant K_s.

The stability constant K_s and the enthalpy change ΔH^0 for the complexation of lanthanoid nitrates with (**2**) 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 obtained was minimized satisfactorily to give the optimized set of K_s and ΔH^0 with standard deviations. No serious deviation was found in the fitting process, verifying the 1 : 1 stoichiometry of complexation as assumed above. The calculation of log K_s and ΔH^0 for the complexation (**2**) with lanthanoid nitrates in acetonitrile was illustrated in Figs. 1 and 2 for La^{3+} and Nd^{3+}, respectively. The complex stability constants and thermodynamic parameters obtained are listed in Table 1. For comparison, the thermodynamic quantities reported for the complexation with (**1**) in acetonitrile are also included in Table 1.

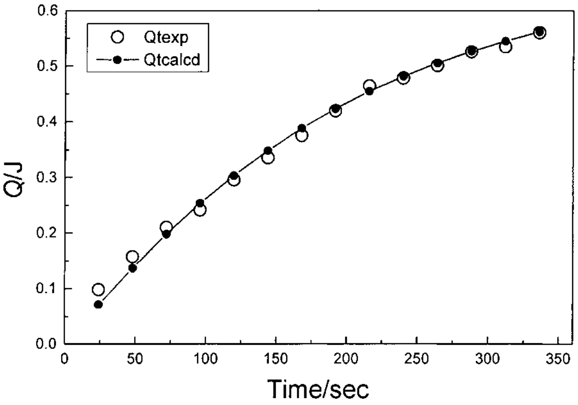


Fig. 1. Comparison of experimental and calculated data for the calorimetric titration of complexation of (**2**) with La^{3+}.

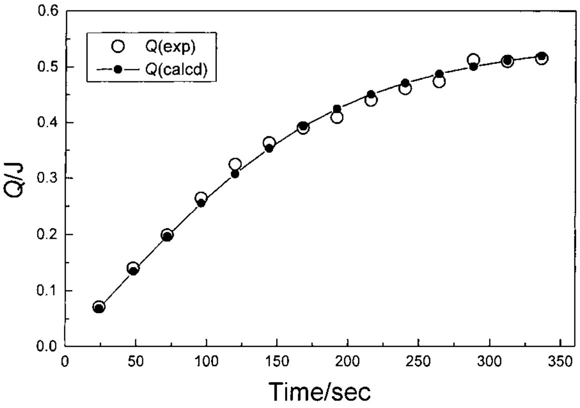


Fig. 2. Comparison of experimental and calculated data for the calorimetric titration of complexation of (**2**) with Nd^{3+}.

4. Complex stability and cation selectivity

In order to visualize the cation-binding properties of crown ethers (**1**–**2**), the changing profile of the complex stability constant (K_s) is plotted as a function of reciprocal ionic diameter of the lanthanoid in Fig. 3.

As can be seen from Fig. 3, the profile of K_s for (**1**) shows a characteristic peak at Ce^{3+} and gradually declines with increasing atomic number or decreasing ionic radius from Ce^{3+} to Eu^{3+}, probably owing to their fitted cavity size (2.6–3.2 Å) and proper donated orientations. Although the lanthanoid diameter is much smaller (2.12–1.88 Å), it is noteworthy that the ion-pair form of lanthanoid(III) nitrates, behaving as nonelectrolyte in anhydrous acetonitrile, must be much larger than the naked trivalent lanthanoids. This result indicates that (**1**) 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 lanthanoid ion selectivities of (**2**), since this rigid framework crown ether gives higher K_s values for the latter half of the light lanthanoids than Ce^{3+} and Pr^{3+}. One possible explanation for this obvious deviation from the size-fit concept for (**2**) complexation with Ce^{3+} (2.06 Å) through Gd^{3+} (1.88 Å) [22] is attributed to the increasing surface charge density due to the lanthanoid contraction and the subsequent tighter solvation for heavier lanthanoids. This seems reasonable, since the extensive thermodynamic studies on cation-crown ether complexation have shown that the cation-binding ability of the crown ether

Table 1
Complex stability constant (log K_s) and thermodynamic parameters (in kJ mol^{-1}) for 1 : 1 complexation of light lanthanoid (III) nitrates with (**1**) and (**2**) in anhydrous acetonitrile at 25.0°C[a]

Crown ether	Lanthanoid	log K_s	ΔG^0	ΔH^0	$T\Delta S^0$	Ref.
(**1**)	La^{3+}	4.40	−25.10	−36.19	−11.09	[6c]
	Ce^{3+}	4.50	−25.69	−43.01	−17.32	[6c]
	Pr^{3+}	3.70	−21.13	−44.02	−22.89	[6c]
	Nd^{3+}	3.50	−20.00	−36.19	−16.19	[6c]
	Eu^{3+}	2.70	−15.40	−12.80	2.59	[6c]
(**2**)	La^{3+}	3.32±0.02	−18.95	16.07±0.38	35.02	This work
	Ce^{3+}	2.34±0.06	−13.39	10.13±0.17	23.51	This work
	Pr^{3+}	2.54±0.07	−14.52	27.45±0.42	41.97	This work
	Nd^{3+}	3.82±0.05	−21.80	11.55±0.38	33.35	This work
	Sm^{3+}	3.84±0.09	−21.88	−3.01±0.38	18.87	This work
	Eu^{3+}	3.14±0.08	−17.95	2.51±0.33	20.46	This work
	Gd^{3+}	2.91±0.02	−16.61	4.10±0.25	20.71	This work

[a] Values are the averages of more than three independent measurements in this work.

containing benzo groups is lower than that for the parent crown ether, and have demonstrated that the reduced 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 (**2**), shown in Fig. 3, do not show a regular trend and are totally different from those of the reference compound (**1**). There are hitherto limited data for the complexation of lanthanoids 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 lanthanoid ion-pair form. Possessing structural rigid skeleton as compared with parent (**1**), (**2**) gave the highest K_s for Sm^{3+} and Nd^{3+} and the lowest for Ce^{3+} and Pr^{3+} among the light lanthanoid ions, eventually showing the highest cation selectivity for Sm^{3+} and Nd^{3+}. Therefore, the highly selective complexation for (**2**) with Sm^{3+} and Nd^{3+} is attributed to the increased molecular rigidity of crown ether, which leads to small conformational change upon the complexation.

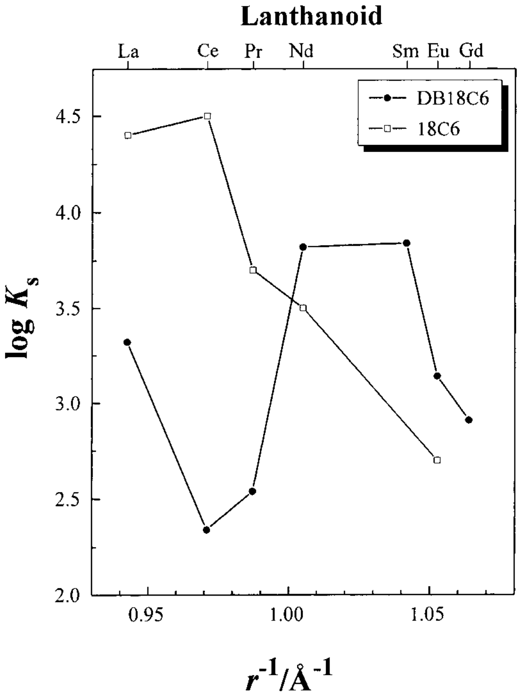


Fig. 3. Complex stability constant (K_s) as a function of reciprocal ionic radius (r^{-1}/Å^{-1}) for the complexation of light lanthanoids with (□) (**1**) and (●) (**2**) in acetonitrile at 25°C.

5. Thermodynamic parameters

In order to discuss the changing profile of K_s and the relative cation selectivity from the thermodynamic point of view, thermodynamic quantities for complexation with (**1**) and (**2**) are plotted against the

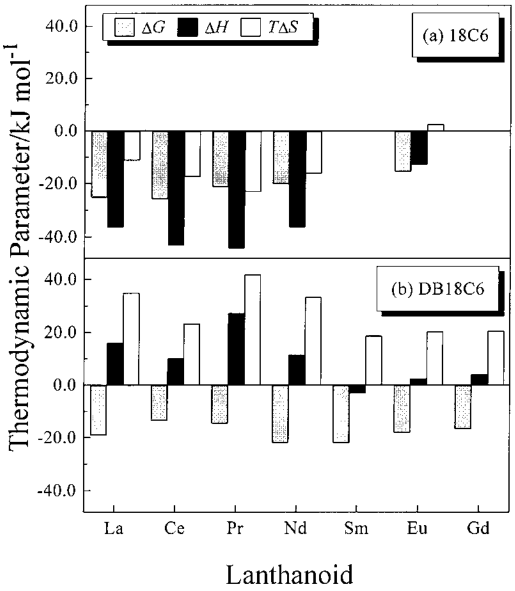


Fig. 4. Thermodynamic parameters for the complexation of light lanthanoids (La–Gd) with (a) (**1**) and (b) (**2**) in acetonitrile at 25°C.

lanthanoids in Fig. 4. As can be recognized more easily from Fig. 4, the ΔH^0 values of the complex formation for (**1**) 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^0 values observed for (**2**) are positive with the larger positive entropic changes, except for Sm^{3+} which accompanies slightly negative enthalpy changes. These results indicate that the complexation of (**2**) with the light lanthanoid ions are mainly entropy-driven in acetonitrile. As can be seen from Figs. 3 and 4, the cation selectivity and the thermodynamic profiles observed for two crown ethers are distinctly different. One possible explanation for the different thermodynamic parameters obtained for (**1**) and (**2**) throughout the light lanthanoid series would be found in the presence of the benzo groups at (**1**), 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 making the operation of size-fitting difficult. On the other hand, the results obtained indicate that the desolvation becomes more extensive upon complexation of (**2**) 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 (**2**) complexation with most lanthanoids are contributed to the complex stabilities as a consequence of compensation effects. As can be seen from Figs. 3 and 4, although the complex stability decreases for (**2**) complexation with La^{3+} and Ce^{3+} as compared with the parent (**1**), the relative cation selectivities are enhanced for (**2**) complexation with Nd^{3+} and Sm^{3+}. Thus, (**2**) is shown to possess the most advantageous structure for highly selective complexation of lanthanoids.

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