Complexation Thermodynamics of p-tert-Butylcalix[4]arene Derivatives with Light Lanthanoid Nitrates in Acetonitrile

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Complexation Thermodynamics of *p-tert*-Butylcalix[4]arene Derivatives with Light Lanthanoid Nitrates in Acetonitrile

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Calorimetric titrations have been performed for the first time in anhydrous acetonitrile at 25°C to give the complex stability constant (K_S) and thermodynamic quantities for the complexation of light lanthanoid(III) nitrates (La-Gd) with 5,11,17,23-tetra-*tert*-butyl-26,28-bis(cyanomethoxy)-25,27-dihydroxycalix[4]arene (1) and 5,11,17,23-tetra-*tert*-butyl-26,28-bis(2-aminoethoxy)-25,27-dihydroxycalix[4]arene (2). X-ray crystallographic structures of 1 and 2 were also determined and compared. Possessing the cyanomethoxy and aminoethyl substituents, 1 and 2 displayed strikingly different cation binding abilities and selectivity profiles with much higher K_S values for La^{3+} and Ce^{3+}, which may be related to the original structures in the solid state. Thus, the binding profile for 2 showed a rapid decrease in K_S with decreasing ionic diameter from La^{3+} to Pr^{3+} and then became flat up to Gd^{3+}, while 1 gave a very flat profile which is superimposable with that for 2 between Pr^{3+}-Gd^{3+}. Thermodynamically, the complexation is driven absolutely by enthalpy which compensates the entropic loss arising from the structural freezing of the calix[4]arene derivatives upon simultaneous binding of lanthanoid ion by the phenolic oxygen and acetonitrile molecule in the cavity. The general validity and the meaning of the compensative enthalpy-entropy relationship observed are discussed.

INTRODUCTION

Calixarene derivatives are known to form complexes with a wide variety of ions and neutral molecules and have been applied successfully to biomimetic research and separation science and technology [1]. Hence, since the pioneering works of Gutsche [2], the inclusion complexation of cation and neutral molecule by calixarene and its derivatives has been of growing interest to theoretical and experimental chemists. The target of intensive studies is to elucidate the nature of the binding behavior [3]. However, only a limited number of thermodynamic studies have been undertaken so far for the complexation of ionic or molecular guests with calixarene due to its low solubility in aqueous or other polar solvents [4]. Danil de Namor *et al.*,

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reported the complexation thermodynamics of tetraethyl *p-tert*-butylcalix[4]arene-tetraacetate with alkali metal cations in various solvents, and suggested the possible binding of one acetonitrile molecule inside the ligand cavity, producing a synergistic effect which makes the hydrophilic cavity better preorganized to interact with cations [5]. In his recent report on the complexation of *p-tert*-butylcalix[4]arene derivatives with a series of neutral guests, Stibor *et al.*, have demonstrated that the stability of complex is controlled by the initial geometry of the uncomplexed ligand [6]. In this context, it is intriguing and useful to investigate the effect of co-inclusion of neutral molecule such as solvent and examine the scope and limitations of such synergetic binding of ionic and neutral guests, by employing 5,11,17,23-tetra-*tert*-butyl-26,28-bis(cyanomethoxy)-25,27-dihydroxycalix [4]arene (1) and 5,11,17,23-tetra-*tert*-butyl-26,28-bis(2-aminoethoxy)-25,27-dihydroxy-calix[4] arene (2) as calixarene hosts, light lanthanoid nitrates as guests, and acetonitrile as a solvent/co-guest.

In the present study, we wish to report our results of the first thermodynamic study on the complexation of light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with 1,3-lower-rim-disubstituted calix[4]arenes **1** and **2** using titration calorimetry. These thermodynamic parameters, associated with the X-ray crystallographic structure of **2**, will shed light on this thermodynamically less investigated area of calixarene chemistry [7] and also provide us with further insights into the synergetic binding phenomenon. The influence of the 1,3-lower-rim-disubstitution upon the complexation behavior of calix[4]arene with light lanthanoids is also discussed from the thermodynamic point of view. It is of our further interest to examine the general validity of the enthalpy-entropy compensation effect in the complexation of cations with calixarenes. We will compare the slope and intercept of the $\Delta H° \sim T\Delta S°$ plot, as measures of conformational change and desolvation
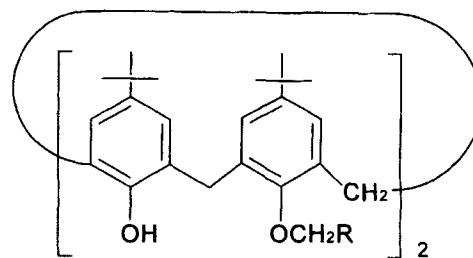
1 R = CN

2 R = CH₂NH₂
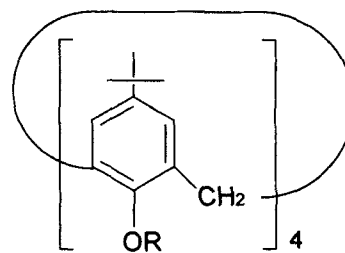
3 R = CH₂CO₂C₂H₅

CHART 1

respectively, with the relevant values obtained for the complexation of molecular guests. In this context, calixarene is a quite intriguing host which can accommodate cooperatively both organic molecules and inorganic cations at the different binding sites through the completely different types of interactions, *i.e.*, ion-dipole *versus* van der Waals. We will discuss the similarity and dissimilarity of both binding modes in the compensation behavior.

EXPERIMENTAL SECTION

General Procedure

IR spectra were recorded on a JASCO A-100 spectrometer. Mass spectra were obtained on a Hitachi RMV-6E instrument. ¹H NMR spectra were recorded on a JEOL GX-400 spectrometer. X-ray crystallographic data were collected on a Bruker SMART 1000 instrument. A TRONAC

model 458 isoperibol titration calorimeter was used to perform the calorimetric titrations.

Materials

1,3-Alternatively bis(cyanomethyl)-substituted calix[4]arene **1** was synthesized by the reaction of *p-tert*-butylcalix[4]arene with chloroacetonitrile in the presence of potassium carbonate and sodium iodide in dry acetone, according to the procedure reported previously by Collins *et al.* [8] Compound **2** was obtained by reducing **1** with $LiAlH_4$ in anhydrous THF [9]. Purification by recrystallization in methanol gave the pure white needle crystals. The IR and ^1H NMR spectra of **1** and **2** were in good agreement with those reported [8, 9].

Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent ($< 5 \times 10^{-7}$ S/cm) for calorimetry. Light lanthanoid(III) nitrates (La-Gd) were prepared by dissolving the corresponding oxide of 99.99% purity (Bostou Rare Earth Chemical Co.) in 50% aqueous nitric acid while heating for about 10 min. After evaporation, the solid residue was dehydrated with P_2O_5 *in vacuo* for several days to give a powdery product. The light lanthanoid nitrates obtained were 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 lanthanoid nitrites behave as nonelectrolytes in anhydrous acetonitrile [10].

Crystallographic Structural Determination

Crystals of **2** suitable for X-ray crystallography were grown by slow evaporation from a methanol solution of **2**. The structure was solved with the SHEXL-97 software. **2**: $C_{51}H_{72}N_2O_8$, $M = 735.07$ (excluding water and methanol molecules); trigon, $a = 12.5913(17)$ Å, $b = 12.5913(17)$ Å, $c = 28.733(6)$ Å, $V = 3945.0(11)$ Å^3, space group $P3_2$, $Z = 6$, $D_m = 2.124$ g $\cdot$ cm^{-3}.

The structure was solved by using direct method and refined employing full matrix least squares on F^2 (Siemens, SHELXTL, version 5.04). The final R indices [$I > 2\sigma(I)$] were $R_1 = 0.0637$ and $wR_2 = 0.1078$. Crystal details, including final atomic coordinates, bond lengths and angles, and anisotropic displacement parameters, are given in Supplementary Materials.

Thermodynamic Determination

Calorimetric titrations were performed at atmospheric pressure in a temperature-controlled water bath maintained at 25.0°C with a personal computer connected to the calorimeter for automated titration and data processing. The detailed experimental procedure were reported elsewhere [11, 12]. Typically, a solution of calix[4]arene derivative (10–15 mM) in anhydrous acetonitrile was introduced continuously at a rate of 0.3321 cm^3/min into a lanthanoid nitrate solution (1.0–2.0 mM, 50 mL) placed in the calorimeter. A titration curve was obtained by plotting the temperature change (measured by E/mV) against the amount of the calixarene solution added, from which the complex stability constant (K_S) and the enthalpy change (ΔH°) were simultaneously determined. Reliability of the whole system and the calculation procedures were doubly checked as previously [13, 14] by comparing the obtained thermodynamic parameters with the reported values [15], and satisfactory results were obtained.

RESULTS AND DISCUSSION

Assuming the 1:1 stoichiometry [16, 17] for the complexation of $Ln(NO_3)_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with the calix[4]arene derivatives (Calix in Eq. (1)), the complex stability

constant (K_S) and the enthalpy change ($\Delta H°$) were calculated by using the least-squares method to minimize the U value in Eq. (2) [18, 19]:

$$\text{Calix} + \text{Ln} \overset{K}{\rightleftharpoons} \text{Calix} \cdot \text{Ln} \qquad (1)$$

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

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 stability constant K_S.

The stability constant K_S and the enthalpy change $\Delta H°$ for the complexation of each lanthanoid nitrate with 1 and 2 were calculated by computer simulation by continuously changing K_S, *i.e.*, N_t, to minimize the U value. For each lanthanoid-calix[4]arene 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 $\Delta H°$ 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 for 1 and 2, together with those for tetraethyl *p-tert*-butylcalix[4]arenetetraacetate (3), are listed in Table I.

Cation Binding Ability and Selectivity

It is noted that the cyanomethyl- and aminoethyl-substituted calix[4]arenes 1 and 2, differing structually only at the rather peripheral position, afford distinctly different binding constants and relative cation selectivities upon complexation with light lanthanoids(III). It has been believed that the lower rim substituents of

TABLE I Complex stability constants (log K_S) and thermodynamic parameters (in kcal/mol) for complexation of 1 and 2 with light lanthanoid(III) nitrates in anhydrous acetonitrile and of 3 with alkali metal ions in acetonitrile and in methanol at 298.15 K

Ligand	Solvent	Cation	log K_S	$-\Delta G°$	$-\Delta H°$	$T\Delta S°$	Ref.
1	CH_3CN	La^{3+}	2.64 ± 0.03	3.60 ± 0.04	3.76 ± 0.08	−0.16 ± 0.04	a
		Ce^{3+}	2.55 ± 0.03	3.48 ± 0.04	4.16 ± 0.07	−0.68 ± 0.07	a
		Pr^{3+}	2.53 ± 0.01	3.45 ± 0.01	2.38 ± 0.06	1.07 ± 0.05	a
		Nd^{3+}	2.53 ± 0.01	3.45 ± 0.02	4.58 ± 0.07	−1.14 ± 0.05	a
		Sm^{3+}	2.52 ± 0.01	3.44 ± 0.01	2.53 ± 0.09	0.90 ± 0.08	a
		Eu^{3+}	2.58 ± 0.01	3.52 ± 0.01	5.04 ± 0.04	−1.52 ± 0.05	a
		Gd^{3+}	2.55 ± 0.01	3.48 ± 0.01	2.53 ± 0.02	0.96 ± 0.02	a
2	CH_3CN	La^{3+}	3.92 ± 0.09	5.34 ± 0.12	13.61 ± 0.30	−8.26 ± 0.20	a
		Ce^{3+}	3.12 ± 0.08	4.25 ± 0.08	14.50 ± 0.05	−10.25 ± 0.08	a
		Pr^{3+}	2.55 ± 0.01	3.49 ± 0.01	16.67 ± 0.15	−13.19 ± 0.16	a
		Nd^{3+}	2.56 ± 0.04	3.49 ± 0.01	7.23 ± 0.17	−3.74 ± 0.14	a
		Sm^{3+}	2.56 ± 0.02	3.50 ± 0.03	6.51 ± 0.13	−3.01 ± 0.10	a
		Eu^{3+}	2.44 ± 0.01	3.33 ± 0.01	16.14 ± 0.17	−12.81 ± 0.16	a
		Gd^{3+}	2.46 ± 0.03	3.36 ± 0.03	18.57 ± 0.07	−15.22 ± 0.04	a
3	CH_3CN	Li^+		8.73	11.66	−2.93	b
		Na^+		7.91	14.71	−6.80	b
		K^+		6.14	10.48	−4.34	b
		Rb^+		2.59	4.46	−1.87	b
		Cs^+		3.82	2.74	1.08	b
	CH_3OH	Li^+		3.55	−1.21	4.76	b
		Na^+		6.82	10.90	−4.08	b
		K^+		3.27	3.40	−0.13	b

a This work; average of more than three independent measurements.
b Ref. [5].

the p-tert-butylcalix[4]arenes, due to equality of the fragments directly attached to the lower rim, have similar effect on the electronic nature of cavities [6]. Therefore, the binding properties of lower rim 1, 3-disubstituted p-tert-butylcalix[4] arene studied may be controlled mainly by ligand geometry. In order to visualize the complexation behavior of 1 and 2 with lanthanoid(III) nitrates, the changing profile of the complex stability constants (K_S) is plotted as a function of reciprocal ionic radius of lanthanoid in Figure 1.

Although the two calix[4]arenes share the same structural features at least around the cavity, the binding profiles exhibit significant deviations in particular for La^{3+} and Ce^{3+}. Thus, the K_S values obtained with 2 for the first two members of the lanthanoid family are much higher than those obtained with 1, but rapidly

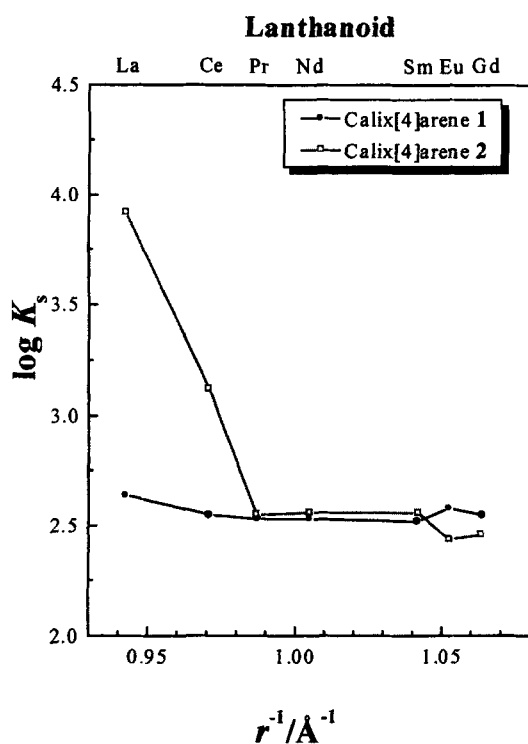**Lanthanoid**

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 (solid circle) and 2 (hollow square) in acetonitrile at 298.15 K.

decrease with increasing atomic number, or decreasing ionic radius, from La^{3+} to Pr^{3+}, eventually showing that 2 has fairly high relative cation selectivities. This contrasting result would not be anticipated from the apparently minor difference in the peripheral substituents. It may be deduced that the lower-rim disubstitution plays a crucial role in determining the spatial arrangement and orientation of the calix[4] arene's donor atoms. Probably, the involvement of the amino substituent in the formation of the circular array of intramolecular hydrogen bond network induces a more favorable conformation for the "size-matched" host-guest complexation, whereas the weaker binding by 1 may be attributed to the distortion of calixarene structure arising from the repulsive interaction between the dipoles of 1,3-bis(cyanomethyl) groups. We may conclude therefore that the spatial arrangement and orientation of the donor atoms of calix[4]arenes, for which the intramolecular hydrogen bond plays a key role, alter not only the binding ability for trivalent lanthanoid ions but also the relative cation selectivities significantly.

The contribution of the aminoethyl substituents to the spatial arrangement of the donor atoms in 2 can be assessed from the X-ray crystallographic structure shown in Figure 2. The amino groups are clearly hydrogen-bonded to the phenolic oxygens and fix the calixarene structure, forming a pseudo-cavity of ca. 2.9 Å in diameter, which is surrounded by four oxygen and two nitrogen atoms. This original cavity size in the solid state does not appear to be suitable for immediate binding of lanthanoid ions, but may be induced-fitted to the appropriate size upon complexation of smaller cations like lanthanoids. Alternatively, the initial binding of lanthanoid ion may occur at the exactly size-matched calixarene cavity, since the gap between O1 and O2 is exactly fitted to the size of La^{3+} (2.06 Å, coordiantion number = 6) [20] and Ce^{3+} (2.02 Å), which is followed by the additional ligation by the nitrogen atoms. Thus, crystalline 2 possesses a unique conjugated
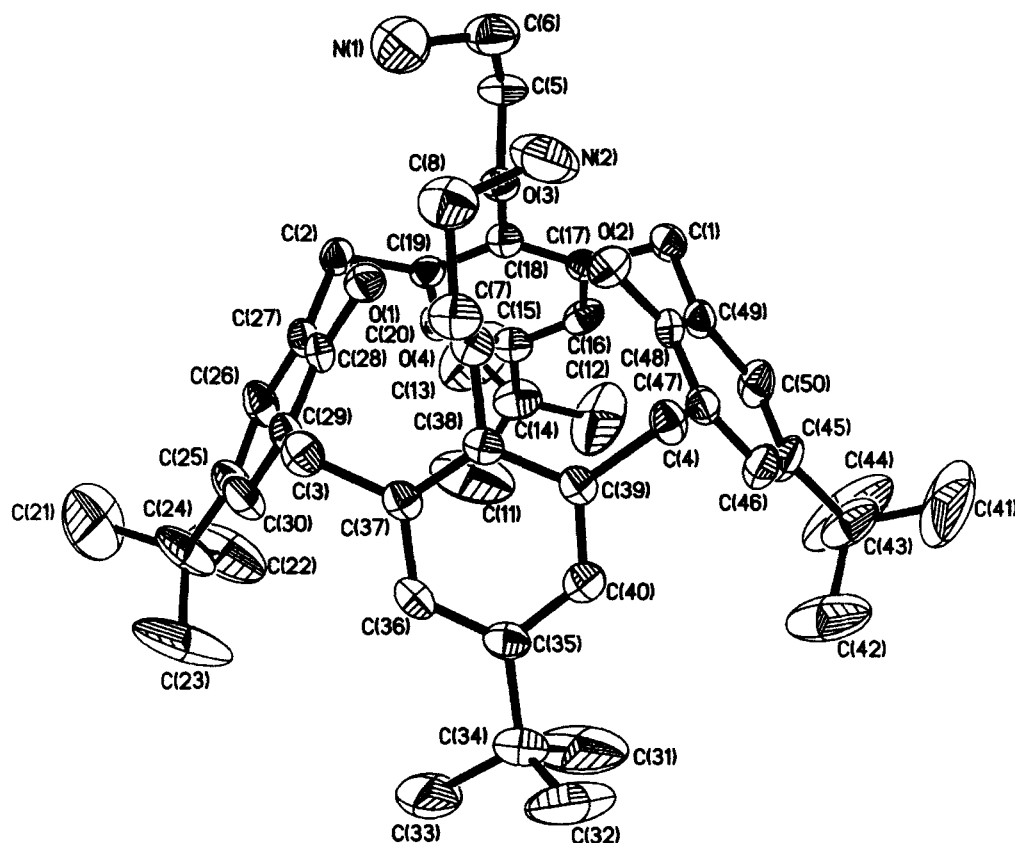
FIGURE 2   ORTEP drawing of the molecular structure of 2 in crystal.

dual-cavity structure with the original hydrophobic calixarene cavity and the additional hydrophilic ion-binding cavity, which are directly connected and therefore expected to affect each other upon complexation. In contrast, the two cyanomethyl groups in 1, simply spreading out due to the repulsive dipole–dipole interaction, do not positively contribute to the complexation with lanthanoids but rather deform the original symmetrical cone structure. These structural features of 1 and 2 around the cavity can rationalize at least in part the significant differences in the binding constants especially for the size-matched lanthanoids.

Thermodynamic Parameters

The thermodynamic quantities determined for the complexation of lanthanoids with 1 and 2 are

graphically presented in Figure 3. The comparison of the two sets of data (Figs. 3a and 3b) reveals a dramatic difference in the thermodynamic behavior of 1 and 2. Thus, aminoethylcalixarene 2 gives highly negative enthalpy changes (ΔH°) and entropy changes (ΔS°) for all lanthanoids examined, while cyanomethylcalixarene 1 gives only moderately negative ΔH° and almost negligible ΔS°. Yet, the complex stabilities ($-\Delta G^\circ$) are comparable to each other for most lanthanoids examined, except for La^{3+} and Ce^{3+} as mentioned above.

It should be noted that all of the complexation reactions examined are exclusively exothermic ($\Delta H^\circ < 0$), indicating that the complexation of light lanthanoids with the calixarenes is unequivocally an enthalpy-driven process in acetonitrile. The larger enthalpic gains ($-\Delta H^\circ$) for 2 than for 1 may be rationalized by stronger
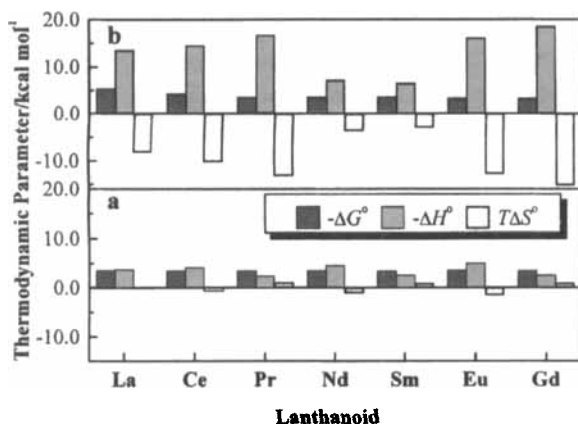
FIGURE 3 Thermodynamic parameters for the complexation of light lanthanoids (La-Gd) with 1 (a) and 2 (b) in acetonitrile at 298.15 K.

ion-dipole and/or coordination interactions between lanthanoid ion and donor oxygen, and probably nitrogen, atoms in 2. As shown in Figure 2 and discussed above, the solid-state structure of 2 clearly indicates the presence of a spherical cavity. The unique ligand structure of 2 not only furnishes additional ligation by two amino nitrogens but also promotes selective binding of the light lanthanoids fitted to the pseudo-cavity, probably with some conformational changes induced upon complexation, which rationalizes the much higher enthalpic gains arising from the stronger interactions as well as the higher relative cation selectivities for the size-matched cations, although attempts to obtain single crystals of lanthanoid complexes of 2 for X-ray crystallographic analysis were unsuccessful. Such a large enthalpic gain $(-\Delta H^{\circ})$, due to the stronger interactions, does not immediately mean high complex stability since it is often cancelled out by the equally large entropic loss $(T\Delta S^{\circ})$ arising from structural freezing upon complexation. This is exactly the case with the complexation of Pr^{3+}-Gd^{3+} with 2 in acetonitrile, where the relatively weak solvation by acetonitrile does not appear to play the major role and the accommodation of lanthanoid in the pseudo-cavity of 2 leads to strong ion-dipole/coordination interactions but simultaneously reduces the freedom of the complex

formed. In contrast, the less-symmetrical donor arrangement [8] in cyanomethylcalixarene 1, lacking such a pre-organized spherical pseudo-cavity, would easily lead to the weaker ion-dipole interactions and therefore the smaller enthalpic gain. In other words, the original structure of 1 is not best fitted for the accommodation of lanthnoids.

Enthalpy-entropy Compensation

In our recent papers and reviews [4,21–23], we have demonstrated that the thermodynamic parameters for the complexation of various organic guests with cyclophanes and calixarenes, as well as crown ethers, cryptands, cyclodextrins and other related cation/molecule-binding hosts, exhibit unambiguous enthalpy-entropy compensation effect. Thus, the $\Delta H^{\circ}-T\Delta S^{\circ}$ compensation plot for each host category afforded distinctly different slope (α) and intercept $(T\Delta S_0)$, which can be taken as quantitative measures of the conformational changes and the degree of desolvation induced by complex formation [4,21–23; some of the previous results are listed in Table II. Upon complexation of molecular and ionic guests, cyclophane/calixarene hosts gave a rather scattered $\Delta H^{\circ}-T\Delta S^{\circ}$ plot with $\alpha=0.78$ and $T\Delta S_0=3.4$ [22b], indicating relatively large conformational changes and moderate desolvation upon complexation.

TABLE II Slope (α) and intercept $(T\Delta S_0)$ of the $\Delta H^{\circ}-T\Delta S^{\circ}$ plots for 1:1 host-guest complexation in homogeneous solution

Host	Guest	α	$T\Delta S_0$	Ref.
glyme/podand	cation	0.89	2.0	a
crown ether	cation	0.77	2.9	a
Cryptand	cation	0.42	4.0	a
Cyclodextrin	molecule	0.93	3.3	a
Modified cyclodextrin	molecule	1.02	4.3	b
Calixarene	cation	0.97	3.4	c

[a] Ref. [4].
[b] Ref. [22].
[c] This work.

We do recognize the lack of sufficient thermodynamic data on calixarene complexation, yet it is intriguing to examine the validity of the compensation effect in the present case. Using the 14 sets of thermodynamic parameters listed in Table I for calixarenes 1 and 2, we obtain an excellent linear relationship (correlation coefficient $r = 0.99$) between $\Delta H°$ and $T\Delta S°$ to give a large slope ($\alpha = 0.97$) and moderate intercept ($T\Delta S_0 = 3.4$), as shown in Figure 4. Interestingly, most of the thermodynamic data reported previously for the complexation of alkali metal ions with tetraethyl *p-tert*-butylcalix[4]arenetetraacetate 3[5] and also for the complexation of trimethylphenylanilinium ion with Shinkai's water-soluble calixarene-*p*-sulfonates [24] nicely fall on the same plot with small deviations. Although the available data size is limited, it appears that the compensatory enthalpy-entropy relationship is well validated for the complexation thermodynamics of calixarene derivatives. The slope and intercept obtained
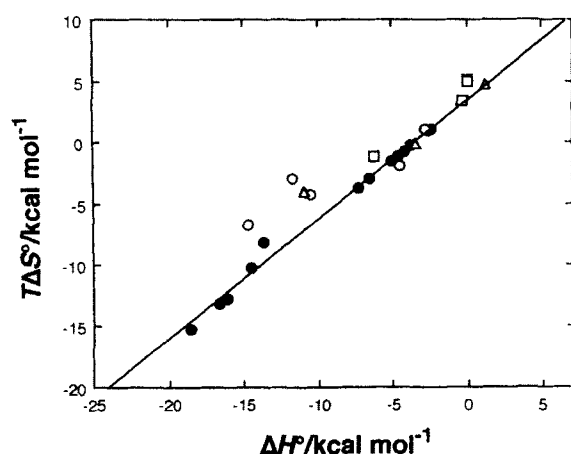
for calixarenes 1 and 2 are included in Table II, along with those for the cation binding by acyclic, cyclic, and bicyclic polyethers and the molecular binding by cyclodextrins. The large slope for calixarenes ($\alpha = 0.97$), which is comparable to those for native and modified cyclodextrins ($\alpha = 0.90$ and 1.02, respectively), may indicate extensive conformational changes of the flexible sidechains introduced to 1-3 and the calixarene skeletone upon complexation with metal ions. So it can be inferred that, possessing flexible methylene linkers connecting rigid aromatic moieties, these calixarene hosts can easily alter their conformation upon complexation.

In order to obtain more comprehensive and reliable data of the slope and intercept of the compensation plot, endeavors to measure and compile the thermodynamic quantities for the complexation of various guests with calixarenes are currently in progress.

FIGURE 4 Enthalpy-entropy compensation plot for the complexation of lanthanoids with cyanomethyl- and aminoethyl-*p-tert*-butylcalix[4]arene derivatives 1 and 2 in acetonitrile (solid circle), of alkali metal ions with tetraethyl *p-tert*-butylcalix[4]arenetetraacetate 3 in acetonitrile (open circle) and in methanol (open triangle), and of trimethylphenylanilinium ion with calix[4]- calix[6]- and calix[8]arene-*p*-sulfonates (hollow square) in water, with a regression line drawn for the complexation of lanthanoids with 1 and 2 (slope $\alpha = 0.97$ and intercept $T\Delta S_0 = 3.4$).

Acknowledgments

Supporting Information

Atomic coordinates, anisotropic displacement parameters, and bond lengths and angles of crystal of 2 (6 pages). Crystal data can be available from author upon request.

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