Molecular design of calixarenes. Part 3.[1] Complexation thermodynamics of light lanthanoid nitrates with a novel *p-tert*-butylcalix[4]arene Schiff base in acetonitrile: an enhanced Eu^{3+} selectivity by side-arm ligation

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A novel double-armed calix[4]arene derivative, 5,11,17,23-tetra-*tert*-butyl-25,27-bis{2-[*N*-(2-hydroxy-3-methoxybenzylidene)amino]ethoxy}-26,28-dihydroxycalix[4]arene (**3**), has been synthesized by the reaction of 1,3-alternately lower-rim-modified bis(2-aminoethoxy)-substituted calix[4]arene (**2**) with *o*-vanillin in 90% yield. Calorimetric titrations have been performed 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 **3**. Using the present and reported data, the complexation behavior of the structurally related cyanomethyl analogue (**1**), aminoethyl analogue **2**, and **3** is discussed comparatively from a thermodynamic point of view. Possessing donating vanillin side-arms and structural flexibility, **3** gave the highest K_S for Eu^{3+} among the light lanthanoid series. Having the same calix[4]arene skeleton in common, these hosts afforded distinctly different cation selectivity profiles. Thus, fairly low and invariant K_S values over the entire light lanthanoid series were obtained with the cyano analogue **1**, while the incorporation of amino side-arms in **2** greatly enhanced the K_S for La^{3+} and less extensively for Ce^{3+} but no change was observed thereafter, giving a sharply declining pattern from La^{3+} to Pr^{3+} followed by a sudden leveling-off. In contrast, the vanillino analogue **3** showed a global enhancement of K_S for all light lanthanoids, displaying a unique selectivity profile with a broad peak at Nd^{3+} and a sharp spike at Eu^{3+}. These results are accounted for in terms of the three-dimensional induced fit to lanthanoid ions by the lower-rim and side-arm donor atoms, which play a decisive role upon recognition of trivalent lanthanoid ions by the calix[4]arenes with flexible donating side-arms. Thermodynamically, the complexation is absolutely driven by the favorable enthalpy changes, but the cation selectivity is mainly determined by the less negative entropy changes.

Introduction

A wide variety of calixarene derivatives with donating or non-donating side-arms attached to the lower rim have been designed and synthesized in order to alter the original cation–molecule binding ability and selectivity.[2] Indeed, calixarene derivatives with additional binding sites at the lower rim give much enhanced binding ability and altered selectivity compared with the parent calixarenes.[3] However, little is known about the complexation thermodynamics of calixarenes with ionic or molecular guests,[4] probably due to the low solubility in aqueous or other polar solvents. We have recently demonstrated that 1,3-alternately lower-rim-modified bis(cyanomethoxy)- and bis(2-aminoethoxy)calix[4]arenes (**1** and **2**) display remarkably different cation binding abilities and selectivity profiles, giving much higher complex stability constants (K_S) for La^{3+} and Ce^{3+} upon complexation with **2**.[1b] An X-ray crystallographic study[1b] suggests that such a critical change in complexation behavior may be related to the original structures in the solid state, since the calixarene ring is distorted as a result of the repulsive interaction between the dipoles of 1,3-bis(cyanomethyl) groups. This seems reasonable as the cation binding by calix[4]arene depends not only on the ring size but also on the function of the substituents attached to the lower rim.[5] These results prompted us to further investigate the complexation thermodynamics of double-armed calix[4]arene derivatives with lanthanoid nitrates.

In the present study, we report the results of our study on the synthesis of novel *p-tert*-butylcalix[4]arene Schiff base **3**, shown in Chart 1, and the complexation thermodynamics of **3** with light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd), using titration calorimetry. The thermodynamic parameters for the complexation of light lanthanoid nitrates with double-armed calix[4]arene **3**, along with those for the relevant calix[4]arenes **1** and **2**,[1b] will serve our further understanding of this thermodynamically less investigated area of calixarene chemistry.[6] It is another point of interest to examine the thermodynamic consequence, as well as the scope and limitations, of the donating side-arm effect, using this relatively flexible calix[4]arene Schiff base.

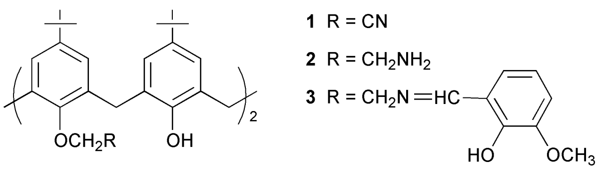

Chart 1

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Experimental

General

The melting points measured by an XT-4 apparatus are uncorrected. ^{1}H NMR spectra were recorded at 200 MHz in $CDCl_3$ solution, using tetramethylsilane as an internal reference. Infrared and ultraviolet spectra were recorded on Shimadzu Bio-Rad FTS 135 and Shimadzu UV-2401/PC instruments, respectively. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. Mass spectra were measured by using a VG ZAB-HS instrument.

Materials

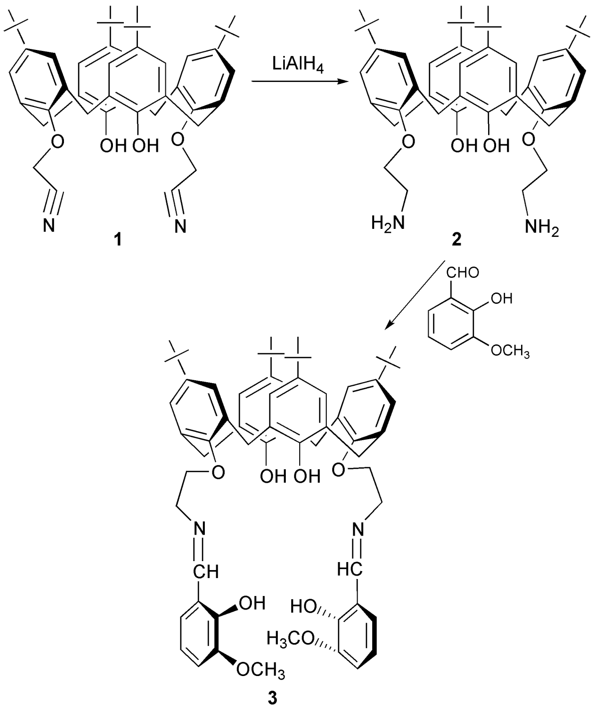
Starting materials were commercially available unless otherwise noted. 5,11,17,23-Tetra-*tert*-butyl-25,27-bis(2-cyanomethoxy)-26,28-dihydroxycalix[4]arene (**1**) was synthesized by the reaction of 5,11,17,23-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene with chloroacetonitrile in the presence of potassium carbonate and sodium iodide in anhydrous acetone, according to the procedure reported by Collins *et al.*[7] Calix[4]arene derivative **2** was obtained by reducing **1** with $LiAlH_4$ in anhydrous THF.[8] Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent ($<5 \times 10^{-7}$ S cm^{-1}) for calorimetry. Light lanthanoid(III) nitrates (Ln = La–Gd) were prepared by dissolving the corresponding oxides of 99.99% purity (Baotou Rare Earth Chemical Co.) in 50% aqueous nitric acid while heating for about 10 min. After evaporation, the solid residue was dried *in vacuo* over P_2O_5 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 lanthanoid nitrates in acetonitrile solutions were determined by the EDTA titration using xylenol orange as an indicator. The conductometric measurements showed that these light lanthanoid nitrates, as well as the ligand and its complexes, behave as nonelectrolytes in anhydrous acetonitrile ($<3 \times 10^{-5}$ S cm^{-1}).[9]

Synthesis

5,11,17,23-Tetra-*tert*-butyl-25,27-bis{2-[*N*-(2-hydroxy-3-methoxybenzylidene)amino]ethoxy}-26,28-dihydroxycalix[4]arene (**3**) was prepared by the reaction of *o*-vanillin (328.6 mg, 2.16 mmol) with 1,3-alternately substituted 25,27-bis(2-aminoethoxy)-26,28-calix[4]arene **2** (800 mg, 1.08 mmol) in absolute ethanol (50 mL) with stirring for an hour on a steam bath. After cooling, the precipitate obtained was filtered and recrystallized from ethanol to give bright yellow crystals of **3** (975 mg, 0.972 mmol) in 90% yield (Scheme 1). Mp 202–203 °C; FAB-MS *m*/*z* 1003.3 (M^+); UV–Vis λ_{max} (CH_3CN)/nm (ε/M^{-1} cm^{-1}) 329 (4420), 261 (27340); FT-IR ν (KBr)/cm^{-1} 3413.4, 2962.2, 2906.2, 2869.5, 1630.7, 1484.0, 1465.1, 1363.6, 1255.4, 1198.7, 1124.7, 1085.2, 1045.3, 974.1, 872.4, 778.6, 736.5; ^{1}H NMR ($CDCl_3$, TMS) δ 9.90 (s, 2 H, OH), 8.55 (s, 2 H, CH), 6.98 (s, 4 H, ArH), 6.91–6.78 (m, 6 H, ArH), 6.75 (s, 2 H, ArOH), 6.70 (s, 4 H, ArH), 4.27 (t, 4 H, $J = 5.2$ Hz, OCH_2), 4.22 (d, 4 H, $J = 12$ Hz, $ArCH_2Ar$), 4.10 (t, 4H, $J = 5.2$ Hz, NCH_2), 3.80 (s, 6 H, OCH_3), 3.29 (d, 4 H, $J = 12$ Hz, $ArCH_2Ar$), 1.27 (s, 18, $C(CH_3)_3$), 0.88 (s, 18, $C(CH_3)_3$). Anal. Calcd. for $C_{64}H_{78}N_2O_8$: C, 76.62, H, 7.84, N, 2.79. Found: C, 76.53, H, 7.63, N, 2.87%.

Thermodynamics

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. Detailed experimental procedures are reported elsewhere.[10,11] Typically, a solution of double-armed calix[4]arene **3** (14.62 mM) in anhydrous acetonitrile was continuously introduced at a rate of 0.3321 mL min^{-1} into a lanthanoid nitrate solution (1.0–2.0 mM, 50 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 non-chemical contributions (Q_{HL}) arising from agitation, heat flow between the vessel and its surroundings, 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 E/mV) against the amount of the added solution of **3**, from which the complex stability constant (K_S) and enthalpy change ($\Delta H°$) were simultaneously determined. Reliability of the whole system and the calculation procedures were doubly checked as previously[12,13] by comparing the obtained thermodynamic parameters with the reported values,[14] and satisfactory results were obtained.



Scheme 1

Results and discussion

Assuming 1 : 1 stoichiometry[15,16] for the complexation of $Ln(NO_3)$ (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) to the double-armed calix[4]arene [Calix in eqn. (1)], the complex stability

$$\text{Calix} + \text{Ln} \xrightleftharpoons{K_S} \text{Calix}\cdot\text{Ln} \qquad (1)$$

constant (K_S) and the enthalpy change ($\Delta H°$) were calculated by using the least-squares method to minimize the U value in eqn. (2),[17,18] where Q_t refers to the net heat of complexation

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

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 stability constant K_S.

The stability constant K_S and the enthalpy change $\Delta H°$ for the complexation of lanthanoid nitrate with **3** were calculated by computer simulation by continuously changing K_S, *i.e.* N_t, to minimize the U value. For each lanthanoid–host combination, the measurement was repeated more than three times and the U value obtained was minimized satisfactorily to give the

Table 1 Complex stability constant [log(K_S/dm^3 mol^{-1})] and thermodynamic parameters (in kcal mol^{-1}) for complexation of light lanthanoid(III) nitrates with calix[4]arene derivatives (**1**–**3**) in anhydrous acetonitrile at 25 °C

Ligand	Cation	log K_S	$-\Delta G°$	$-\Delta H°$	$T\Delta S°$	Ref.
1	La^{3+}	2.64 ± 0.03	3.60 ± 0.04	3.67 ± 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	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	La^{3+}	3.22 ± 0.05	4.39 ± 0.07	14.78 ± 0.07	−10.39 ± 0.04	[b]
	Ce^{3+}	3.55 ± 0.06	4.85 ± 0.08	13.20 ± 0.06	−8.35 ± 0.08	[b]
	Pr^{3+}	3.70 ± 0.04	5.05 ± 0.05	11.70 ± 0.07	−6.65 ± 0.10	[b]
	Nd^{3+}	3.78 ± 0.05	5.15 ± 0.07	13.10 ± 0.03	−7.95 ± 0.10	[b]
	Sm^{3+}	3.57 ± 0.05	4.87 ± 0.07	14.23 ± 0.03	−9.36 ± 0.04	[b]
	Eu^{3+}	3.94 ± 0.07	5.37 ± 0.09	10.33 ± 0.06	−4.96 ± 0.11	[b]
	Gd^{3+}	3.46 ± 0.05	4.72 ± 0.07	14.18 ± 0.03	−9.46 ± 0.07	[b]

[a] Ref. 1*b*. [b] This work, average of more than three independent measurements.

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, along with those for the complexation with calix[4]arene derivatives **1** and **2** under comparable conditions.

Cation binding ability and selectivity

It is well documented that the complex stability constants and the relative cation–molecule selectivity for the complexation reaction with calixarenes are influenced by several factors, including the relative size of cavity and guest, surface charge density, structural rigidity of host and guest, spatial arrangement of the donor atoms, molecular symmetry, and the function of the substituted groups attached to calixarene. As shown in Table 1, the introduction of vanillino side-arms into the aminoethyl analogue **2** completely altered the binding constant as well as the relative cation selectivity for the trivalent lanthanoids. In order to visualize the cation-binding properties of calix[4]arene derivatives **1**–**3**, the changing profile of K_S is plotted as a function of reciprocal ionic diameter of lanthanoid in Fig. 1.

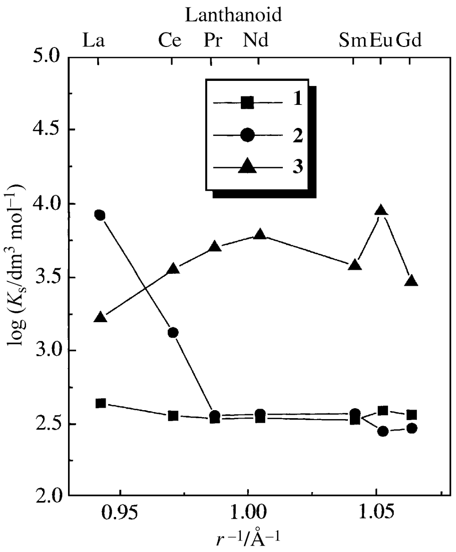


Fig. 1 Logarithm of the complex stability constant (K_S) as a function of reciprocal ionic radius (r^{-1}/Å^{-1}) for the complexation of light lanthanoids with calix[4]arene derivatives **1**–**3** in acetonitrile at 25 °C.

As can be seen from Fig. 1, bis(cyanomethyl)calix[4]arene **1** gives a very flat K_S profile and lower cation-binding abilities than **2** (for La^{3+} and Ce^{3+}) and **3** (for all lanthanoids examined). This poor cation selectivity and binding ability may be attributed to the distortion of calixarene structure arising from the repulsive interaction between the dipoles of 1,3-bis(cyanomethyl) groups. In contrast, bis(2-aminoethoxy)calix[4]arene **2** gives much higher K_S only for La^{3+} and Ce^{3+} but comparable K_S for Pr^{3+}–Gd^{3+}, displaying a rapid decrease up to Pr^{3+} and the subsequent level-off in the K_S profile. Probably, the involvement of the amino substituent in the formation of the circular array of intramolecular hydrogen bond network induces most favorable conformation for the strictly "size-matched" host–guest complexation. Therefore, it is 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, leading to the alteration of the cation binding ability and selectivity for lanthanoids.

Interestingly, the cation binding ability and selectivity of double-armed calix[4]arene **3** are totally different from those of the structurally related reference compounds **1** and **2**. Possessing multiple donor atoms in the relatively flexible side-arms, calix[4]arene Schiff base **3** affords much higher K_S values over the whole range of lanthanoids employed than the corresponding values obtained with **1** or **2** (except for La). As can be seen from Fig. 1, the K_S profile is unique, exhibiting a broad hill top at Nd with a keen peak at Eu. It is noted that the Schiff base side-arms in **3** not only globally enhance the K_S values for all trivalent light lanthanoids but also completely alter the selectivity profile. The global enhancement of K_S and the relatively flat K_S profile obtained with **3** are reasonably accounted for in terms of the encapsulating ligation of flexible side-arm donors to the lanthanoid(III) accommodated in the pseudo cavity. The specific selectivity for Eu^{3+} would arise from the exact match of the spatial arrangement of the lower-rim and side-arm donors to the size of Eu^{3+}, which is supported by the Corey–Pauling–Koltun (CPK) model examinations.

Thermodynamic parameters

In order to elucidate the thermodynamic origin of the unique K_S profile for **3**, the thermodynamic quantities for the

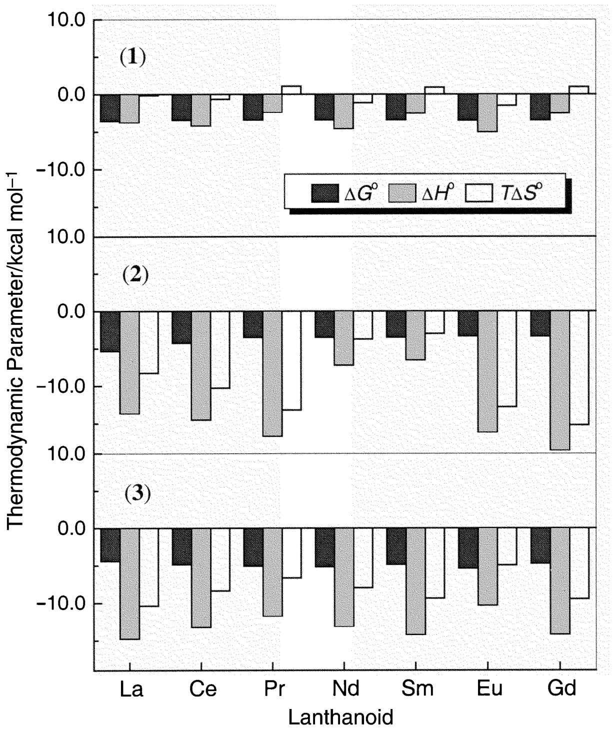


Fig. 2 Thermodynamic parameters for the complexation of light lanthanoids (La–Gd) with **1**–**3**.

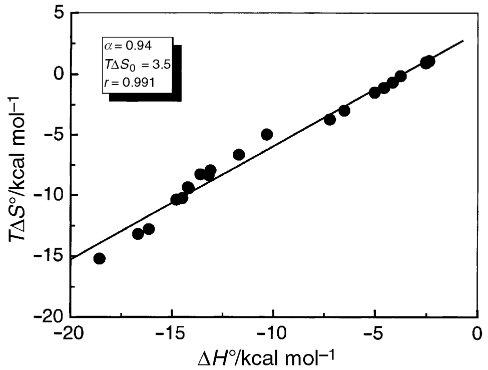


Fig. 3 Enthalpy–entropy compensation plot for the complexation of light lanthanoids (La–Gd) with calix[4]arene derivatives **1**–**3** in acetonitrile; the regression line gives the slope ($\alpha = 0.94$) and the intercept ($T\Delta S_0 = 3.5$) (see the text and ref. 4 for the detailed treatment and meanings of these values).

complexation of calix[4]arene derivatives **1**–**3** are plotted for the lanthanoids in Fig. 2, which reveal dramatic differences in the thermodynamic behavior of cyanomethyl-, aminoethyl-, and Schiff base calix[4]arenes **1**–**3**.

As readily recognized from Fig. 2, all of the ΔH° values for the lanthanoid complexation are highly negative particularly for **2** and **3** but only slightly negative for **1**, while the entropy change ($T\Delta S^\circ$) is moderately negative for **2** and **3** but very small for **1**, thus affording an excellent enthalpy–entropy compensation plot shown in Fig. 3. These results indicate that the complexation of light lanthanoids with calix[4]arene derivatives **1**–**3** are absolutely enthalpy-driven in acetonitrile, but the large enthalpic gains ($-\Delta H^\circ$) do not immediately lead to high complex stabilities and are inevitably cancelled by the larger entropic loss ($T\Delta S^\circ$) arising from the structural freezing upon complexation. The analysis of the compensation plot reveals that this entropic drawback amounts to 94% of the enthalpic gain as calculated from the slope of Fig. 3.[4] The larger enthalpic gains for **2** and **3** than for **1** mean stronger ion–dipole interactions upon complexation of a size-matched lanthanoid ion, which are most probably attributable to the additional ligation of the side-arm donors, *i.e.* the amino nitrogens in **2** and the imino nitrogens and vanillin oxygens in **3**. In contrast, the less-symmetrical donor arrangement[7] in **1**, lacking a pre-organized spherical pseudo-cavity, and possible electrostatic repulsion with the side-arm cyano groups upon complexation would easily lead to weaker ion–dipole interactions and therefore the smaller enthalpic gain.

In this context, it is interesting to point out that the strongest binding of Eu^{3+} by **3** is attained not by the largest enthalpic gain but by the smallest entropic loss. This is compatible with the proposed encapsulating complexation of Eu^{3+} in the spherical pseudo-cavity of **3** as a result of the strict size-fit, since such a tight binding inevitably causes extensive desolvation from the lanthanoid ion and the involved donor atoms, accompanying a significant increase of entropy and a moderate loss of solvation energy as observed indeed for the Eu^{3+}–**3** combination (the smallest absolute values of ΔH° and $T\Delta S^\circ$).

In conclusion, we have demonstrated that the flexible donating side-arms introduced to calix[4]arene can fine-adjust the size and shape of the induced pseudo cavity upon complexation with light lanthanoid nitrates, which not only globally augments the cation binding ability but also specifically enhances the cation selectivity for the exactly size-matched cation. Such a fine tuning and pin-point control of the cation binding ability and selectivity for a specific lanthanoid ion is quite beneficial for the inherently difficult mutual separation of the lanthanoid family. Endeavors to elucidate the detailed mechanism and to alter the specific cation selectivity by changing donating side-arms are currently in progress.

Acknowledgements

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References

1 (*a*) Part 1. Y. Liu, B.-T. Zhao, L.-X. Chen and X.-W. He, *Microchem. J.*, 2000, **65**, 75; (*b*) Part 2. Y. Liu, S. Li, X.-P. Bai, T. Wada and Y. Inoue, *Supramol. Chem.*, in the press.

2 (*a*) C. D. Gutsche, *Calixarenes*, ed. J. F. Stoddard, The Royal Society of Chemistry, Cambridge, 1989, vol. 1; (*b*) J. Vicens and V. Böhmer, *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, 1991; (*c*) C. D. Gutsche, *Calixarenes Revisited*, The Royal Society of Chemistry, Cambridge, 1998.

3 (*a*) S. Shinkai, *Tetrahedron*, 1993, **49**, 8933; (*b*) S. Shinkai and M. Takeshifa, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 1088; (*c*) V. Böhmer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 713; (*d*) S. Shinkai and A. Ikeda, *Chem. Rev.*, 1997, **97**, 1713.

4 Y. Inoue and T. Wada, *Advances in Supramolecular Chemistry*, ed. G. W. Gokel, JAI Press, Greenwich, CT, 1997, vol. 4, pp. 55–96.

5 A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767.

6 A. F. Danil de Namor, R. M. Cleverley and M. L. Zapata Ormachea, *Chem. Rev.*, 1998, **98**, 2495.

7 E. M. Collins, M. A. Mckervey, E. Madigan, M. B. Moran, M. Owens, G. Ferguson and S. J. Harris, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3137.

8 W.-C. Zhang and Z.-T. Huang, *Synthesis*, 1997, 1073.

9 A. Seminara and A. Musumeci, *Inorg. Chim. Acta*, 1980, **39**, 9.

10 Y. Liu and J. Hu, *Acta Phys. Chem. Sin.*, 1987, **3**, 11; Y. Liu and J. Hu, *Chem. Abstr.*, 1987, **106**, 202750n.

11 I. Wadsö, *Sci. Tools*, 1966, **13**, 23.

12 Y. Liu, T.-B. Lu, M.-Y. Tan, T. Hakushi and Y. Inoue, *J. Phys. Chem.*, 1993, **97**, 4548.

13 Y. Liu, B.-H. Han, Y.-M. Li, R.-T. Chen, M. Ouchi and Y. Inoue, *J. Phys. Chem.*, 1996, **100**, 17361.

14 (*a*) L. D. Hansen and E. R. Lewis, *J. Chem. Thermodyn.*, 1971, **3**, 35; (*b*) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet and J. J. Christensen, *J. Am. Chem. Soc.*, 1976, **98**, 7620.
15 F. Arnaud-Neu, *Chem. Soc. Rev.*, 1994, **23**, 235.
16 N. Sabbatini, M. Guardigli, A. Mecati, V. Balzani, R. Uagaro, E. Ghidini, A. Casnati and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1990, 878.
17 J. J. Christensen, J. Ruckman, D. J. Eatough and R. M. Izatt, *Thermochim. Acta*, 1972, **3**, 202.
18 D. J. Eatough, J. J. Christensen and R. M. Izatt, *Thermochim. Acta*, 1972, **3**, 219.