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Intramolecular Sandwich Complexation of Light Lanthanoid Nitrates with Bis(benzo-12-crown-4)s: Enhanced Selectivity for Eu^{3+}

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Abstract. Spectrophotometric titrations performed in anhydrous acetonitrile at 25°C give the complex stability constants (log K_S) and the Gibbs free energy changes ($-\Delta G°$) for the stoichiometric 1 : 1 intramolecular sandwich complexation of light lanthanoid (III) nitrates (La∼Gd) with the polymethylene-bridged bis(benzo-12-crown-4)s **1**, the corresponding dioxo derivative **2** and its dihydroxy analogue **3**. The complex stability sequence as a function of reciprocal ionic radius of lanthanoids showed similar profiles in stability constants (log K_S) and maximum stabilities were obtained at Eu^{3+} for the complexation of light lanthanoids with the three bis(benzo-12-crown-4)s **1**–**3**. The cation binding abilities and relative selectivities for the trivalent lanthanoid ions of these structurally related bis(benzo-12-crown-4)s **1**–**3** are discussed according to the derivatization of the bridging.

Key words: bis(benzo-12-crown-4)s, lanthanoids, complexation, stability constant, spectrophotometry, selectivity.

1. Introduction

Bis(crown ether)s, possessing two crown ether moieties linked by a bridged chain in a ligand molecule, were originally designed and indeed known to enhance the binding abilities of the parent mono crown ethers toward some cations, especially large cations [1–4], through intramolecular sandwich complexation. Therefore, a good deal of effort has been devoted to the synthesis of various bis(crown ether)s and the studies of their complexation with cations in order to compare and examine the cation binding ability of crown ether and bis(crown ether)s and to gain insight into factors governing complexation phenomena between host and guest [5]. However, the work on the complexation with various bis(crown ether)s has been concentrated mainly on alkali and some heavy metal salts [6–10]. So far, less attention has been paid to the complexation with trivalent lanthanoids [11–20], in

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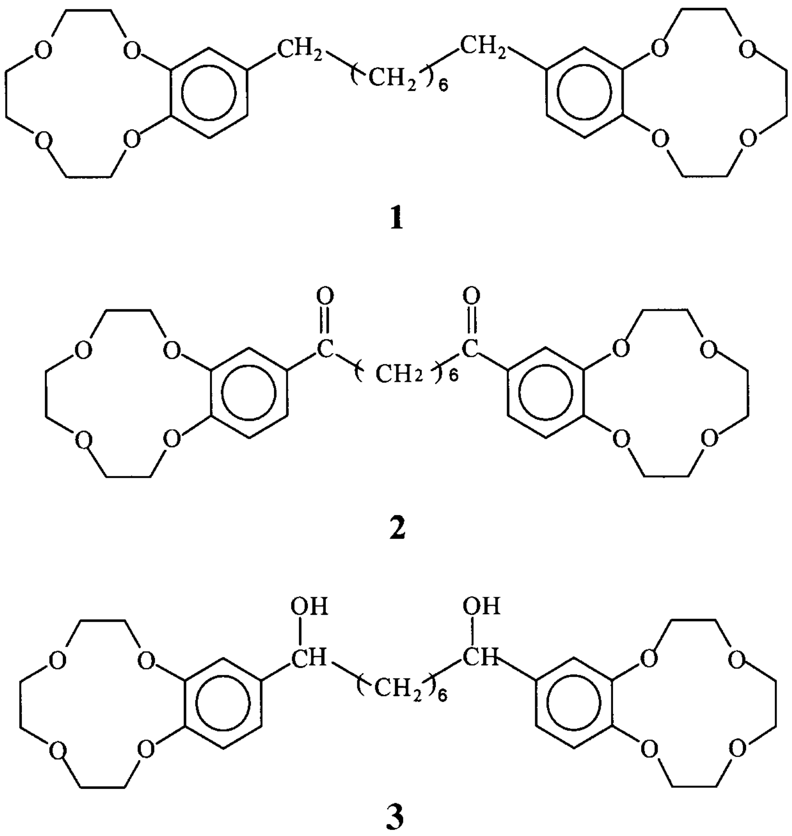

Chart I.

spite of the potential importance of such studies in discussing and understanding the complexation behavior of bis(crown ether)s [1].

Our recent study has shown that the intramolecular sandwich complexation of bis(benzo-15-crown-5)s demonstrates higher cation selectivity for the light lanthanoid series [1], but insufficient data were available to us to discuss their complexation behavior. These results prompted us to investigate the intramolecular sandwich complexation behavior of bis(benzo-12-crown-4)s with different bridges with lanthanoid nitrates. In the present study, we synthesized the polymethylene-bridged bis(benzo-12-crown-4) **1**, dioxo derivative **2** and its dihydroxy analogue **3** (Chart I) and investigated the intramolecular sandwich complexation with light lanthanoid (III) (La, Ce, Pr, Nd, Sm, Eu, Gd) nitrates in acetonitrile by the three bis(benzo-12-crown-4)s, using differential UV spectrometry. It is found that the derivatization of the bridge connecting two crown ether units influenced directly the intramolecular sandwich complexation with cation and leads to significant change in its cation-binding ability.

2. Experimental

2.1. MATERIALS

Dioxobis(benzo-12-crown-4) **2** was synthesized by the reaction of benzo-12-crown-4 with the respective alkanedioic acid in polyphosphoric acid. Catalytic hydrogenation over Raney nickel or reduction with lithium aluminum hydride of α, α'-dioxobis(benzo-12-crown-4) **2** gave the corresponding polymethylene-bridged bis(benzo-12-crown-4) **1** or α, α'-dihydroxypolymethylene-bridged bis(benzo-12-crown-4) **3**. The full description of the synthetic procedures for these bis(benzo-12-crown-4)s has been presented previously [21]. Analytical grade acetonitrile was dried over P_2O_5 powder and then fractionally distilled to give the anhydrous solvent ($<5 \times 10^{-7}$ S cm^{-1}) for spectrophotometry. Light lanthanoid (III) (La $\sim$ Gd) nitrates were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemicals Co.) in 50% aqueous nitric acid while heating for a certain amount of time. After evaporation and temperature decrease, crystals appeared. Storing in vacuo with P_2O_5 for several weeks gave powdery products. Lanthanoid nitrates were dissolved in anhydrous acetonitrile and refluxed for 24 hours over molecular sieves for further removal of water. The exact concentrations of lanthanoid nitrate solution in acetonitrile were determined by EDTA titrations using xylenol orange as an indicator. The conductometric measurements showed that these light lanthanoid nitrates behave as nonelectrolytes in anhydrous acetonitrile [22].

2.2. SPECTRAL MEASUREMENTS

The stability constants for the complexation of bis(benzo-12-crown-4)s **1**–**3** with lanthanoid (III) (La$\sim$Gd) nitrates were determined using differential UV spectrometry. Differential absorption spectra were obtained directly by using a Shimadzu UV-2401 spectrophotometer connected to a personal computer for controlling and data processing. The quartz cells (1cm) were kept at constant temperature (25.0 ± 0.1°C) with circulating water from a constant-temperature water bath.

3. Results and Discussion

3.1. SPECTRAL TITRATIONS

As can be seen from Fig. 1, in the titration experiments using UV spectrometry, the absorbance of the aromatic groups, originally perched on the two crown ether units, gradually increased upon the addition of various concentrations of Ln (III) (La$\sim$Gd) (0.4–3.0×10^{-3} mol dm^{-3}), and there was one characteristic absorption at 277 nm (ϵ = 4839, 25817, 4991 for **1**–**3**, respectively), indicating that bis(benzo-12-crown-4)s must suffer substantial conformational change upon complexation with cation, and form complexes with lanthanoids. This substantial conformational change is used to determine complex stability constants [10, 23, 24]. Although

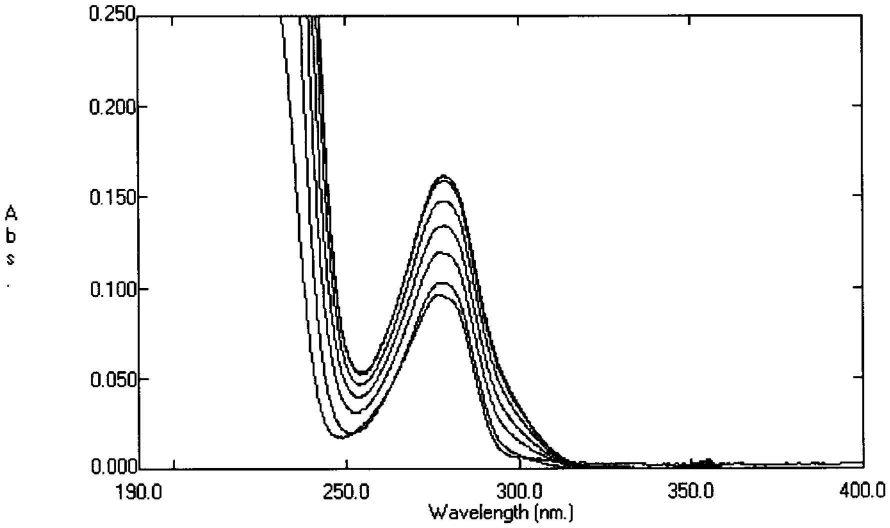

Figure 1. UV spectra of the bis(benzo-12-crown-4) **3** (1.964×10^{-5} mol dm^{-3}) in the presence of Nd^{3+} in different concentrations ($\times 10^{-4}$ mol dm^{-3}) at 25°C. (a) 0.000, (b) 3.923, (c) 7.853, (d) 11.784, (e) 15.707, (f) 17.676, (g) 19.637 (from bottom to top).

there was a slight shift in the absorbance wavelength at the characteristic absorption maximum due to the complexation of the bis(benzo-12-crown-4)s with the lanthanoids, the K_s was calculated on the basis of the original absorption maximum at 277 nm.

Assuming 1 : 1 stoichiometry [1, 10, 25] for the complexation of $Ln(NO_3)_3$(Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) with the bis(benzo-12-crown-4)s, the complexation of host bis(crown ether)s (BCE) with guest lanthanoid ions (Ln) can be expressed by Equation (1):

$$\mathrm{BCE} + \mathrm{Ln} \overset{K_s}{\rightleftharpoons} \mathrm{BCE.\ Ln} \tag{1}$$

Under the experimental conditions, the concentration of bis(benzo-12-crown-4)s (3.0–5.0×10^{-5} mol dm^{-3}) is much smaller than that of the lanthanoids, i.e., $[\mathrm{BCE}]_0 \ll [\mathrm{Ln}]_0$. Therefore, the stability constant (K_s) of the intramolecular sandwich complexation can be calculated according to the modified Hildebrand–Benesi [26, 27] Equation (2):

$$\frac{[\mathrm{BCE}]_0[\mathrm{Ln}]_0}{\Delta A} = \frac{1}{K_s\,\Delta\varepsilon} + \frac{[\mathrm{Ln}]_0}{\Delta\varepsilon} \tag{2}$$

where $[\mathrm{Ln}]_0$ and $[\mathrm{BCE}]_0$ refer to the total concentration of light lanthanoid and bis(benzo-12-crown-4)s, $\Delta\varepsilon$ is the difference between the molar extinction coefficient for free and complexed bis(crown ether)s, and ΔA denotes the changes in the absorbance of the bis(crown ether)s upon addition of Ln (III). For all guest

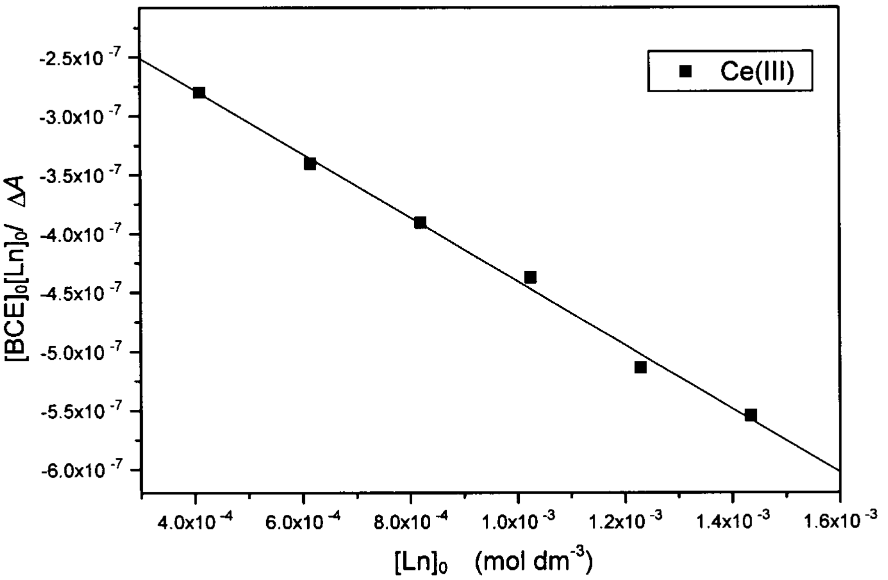

Figure 2. Typical plot of $[\mathrm{BCE}]_0[\mathrm{Ln}]_0/\Delta A$ vs $[\mathrm{Ln}]_0$ for the intramolecular sandwich complexation of bis(benzo-12-crown-4) **2** with Ce^{3+} at 25°C.

lanthanoid nitrates examined, the plots of calculated $[\mathrm{BCE}]_0[\mathrm{Ln}]_0/\Delta A$ values as a function of $[\mathrm{Ln}]_0$ give good straight lines. A typical plot is showed in Figure 2. The experiments were performed at 25°C and the stability constant (log K_s) calculated from the slope and intercept are listed in Table I.

3.2. BINDING CONSTANTS AND SELECTIVITY

Extensive studies of cation binding by bis(crown ether)s have shown that an important characteristic of the complexation is two crown ether units in a ligand molecule cooperatively binding one cation to form the intramolecular "1 : 2" sandwich complex [9, 10]. This should depend on the chain length and/or flexibility of the bridge connecting the two crown ether units and the relative size between the mono crown ether's cavity and the cation's diameter. In order to visualize the cation-binding properties of the bis(benzo-12-crown-4)s **1**–**3**, the changing profile of the complex stability constant (log K_s) is plotted as a function of the reciprocal ionic radius of lanthanoids in Figure 3.

As shown in Figure 3, a similar tendency in the complexation with the bis(benzo-12-crown-4)s **1**–**3** is seen in the complex stability constants (K_s) for all the light lanthanoid nitrates examined, i.e., the complex stability constants increased in the order of $\mathrm{La}^{3+} < \mathrm{Ce}^{3+} < \mathrm{Pr}^{3+} \leq \mathrm{Nd}^{3+} < \mathrm{Sm}^{3+} < \mathrm{Gd}^{3+} < \mathrm{Eu}^{3+}$, probably owing to the similar bridge-chain length, cavity size and analogous donors' orientations. Simultaneously, the result obtained also indicates that Eu^{3+} possesses the best fitting ion diameter in the "size-match" sandwich complexation with the bis(benzo-

Table I. Stability Constants (log K_S) and Gibbs Free Energy Changes ($\Delta G°$) for Molecular Sandwich Complexation of Light Lanthanoid (III) Nitrates with bis(benzo-12-crown-4)s **1**–**3** in Anhydrous Acetonitrile at 25°C[a]

Ligand	Cation	log K_S	$-\Delta G/\text{kJ} \cdot \text{mol}^{-1}$
1	La^{3+}	2.97	16.98
	Ce^{3+}	3.37	19.26
	Pr^{3+}	3.41	19.44
	Nd^{3+}	3.53	20.13
	Sm^{3+}	3.46	19.75
	Eu^{3+}	4.27	24.40
	Gd^{3+}	3.80	21.69
2	La^{3+}	2.91	16.69
	Ce^{3+}	3.20	18.28
	Pr^{3+}	3.05	17.43
	Nd^{3+}	3.18	18.13
	Sm^{3+}	3.12	17.81
	Eu^{3+}	3.39	19.36
	Gd^{3+}	3.28	18.74
3	La^{3+}	3.31	18.88
	Ce^{3+}	3.41	19.48
	Pr^{3+}	3.42	19.54
	Nd^{3+}	3.42	19.54
	Sm^{3+}	3.55	20.25
	Eu^{3+}	4.07	23.25
	Gd^{3+}	3.66	20.89

[a] The log K_S values are the average of two or more independent runs, error <5% of the reported value.

12-crown-4)s. CPK molecular model examination indicated that the two crown ether units in the bis(benzo-12-crown-4)s molecule can be cooperated to bind one lanthanoid ion to form a “clamlike” intramolecular sandwich complex, as studied previously [8, 9].

However, the binding abilities of light lanthanoid nitrates by the three bis(benzo-12-crown-4)s **1**–**3** are completely different. It can be noted that the polymethylene-bridged bis(benzo-12-crown-4)s **1** gave the highest K_s for Eu^{3+} and the lowest K_s for La^{3+} among the light lanthanoid ions, eventually showing the highest cation selectivity for Eu^{3+} (Fig. 3). It is noted that the relative cation selectivity of Eu^{3+}/La^{3+} (K_s (bis(crown ether)s-Eu^{3+} complex)/K_s(bis(crown ether)s-La^{3+} complex)) for compound **1** is 19.95 ($\Delta\Delta G° = -7.42$ kJ.mol^{-1}), and for compounds **2** and **3**, are 3.02 ($\Delta\Delta G° = -2.67$ kJ.mol^{-1}) and 5.75 ($\Delta\Delta G° = -4.37$ kJ.mol^{-1}), respectively.

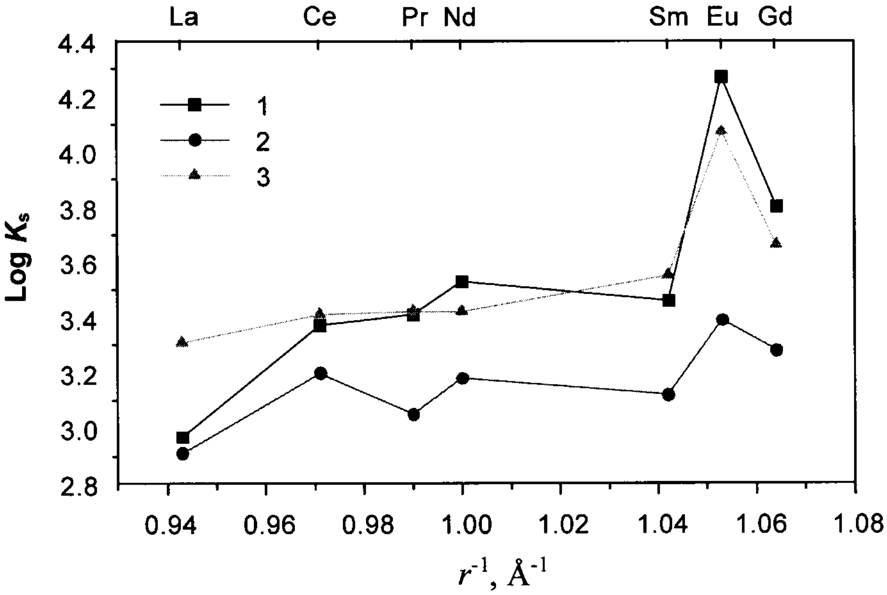

Figure 3. Complex stability constant (log K_S) at 25°C as a function of reciprocal ionic radius (r^{-1}, Å^{-1}) for the intramolecular sandwich complexation of light lanthanoids with bis(benzo-12-crown-4)s **1**–**3** in acetonitrile.

Therefore, it is interesting to compare the derivatization of the chain connecting the two crown ether units upon complexation with lanthanoid ions. The presence of two carbonyl groups in compound **2** as compared with the bis(benzo-12-crown-4) **1**, shows a relative lower cation-binding ability and selectivity for all the light lanthanoid nitrates examined. The decreased cation-binding constants for **2** are distinctly attributed to the electron-withdrawing carbonyl, which decreases the electron density of the donor oxygens attached to the aromatic ring. On the other hand, the dihydroxyl bis(benzo-12-crown-4) **3** forms much more stable complexes with most of the lanthanoid nitrates employed compared with the bis(benzo-12-crown-4) **1** and dioxo derivatives **2**. One possible explanation for the enhanced complex stability would be the intramolecular hydrogen bonding in host compound **3**, which helps the dihydroxyl bis(benzo-12-crown-4) **3** to form a parallel face-to-face sandwich structure [8], which possibly benefits the intramolecular sandwich complexation, although we do not have any direct evidence to date [9]. These results indicate that the derivatization of the bridge connecting the two crown ether units influences directly the intramolecular sandwich complexation with the trivalent lanthanoid ions and leads to significant changes in its cation-binding ability.

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