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Complexation thermodynamics of crown ethers. Part 4 [1]. Ring-enlargement effects upon cation complexation with dibenzo-18 to dibenzo-22-crown-6 ☆

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Abstract

Calorimetric titrations have been performed in methanol and acetonitrile at 25°C to give the complex stability constants (K) and the thermodynamic parameters for the complexation of sodium thiocyanate and potassium thiocyanate with the dibenzo-crown ethers: 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6) (1); 2,3,12,13-dibenzo-1,4,7,10,15,18-hexaoxacycloeicosa-2,12-diene(dibenzo-20-crown-6) (2); 2,3,12,13-dibenzo-1,5,8,11,15,18-hexaoxacycloeicosa-2,12-diene) (dibenzo-20-crown-6) (3); and 3,4,14,15-dibenzo-1,6,9,12,17,20-hexaoxacyclodocosa-3,14-diene) (dibenzo-22-crown-6) (4). Data analyses assuming 1:1 stoichiometry were successfully applied to all of the crown ether–cation combinations employed. The complex stability constants, reaction enthalpies and entropies were calculated directly by using a calorimeter connected to a CA-033 microcomputer. The thermodynamic parameters obtained and the examination of CPK molecular models reveal that the less-symmetrical arrangement of donor oxygen is induced by increasing methylene in the dibenzo-18-crown-6 molecule and leads to an unfavorable conformation for complexation compared with the parent crown ether. The complex stability constants are lower than those of dibenzo-18-crown-6 (1) for the ligands (2)–(4) with Na^+

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and K^+, but the relative cation selectivity for K^+/Na^+ is increased respectively. The effects of the molecular structure of crown ether and the cation diameter, and of solvent upon complex stability are discussed from a viewpoint of thermodynamics.

Keywords: Cation; Complexation; Crown ether; Ether; Stability

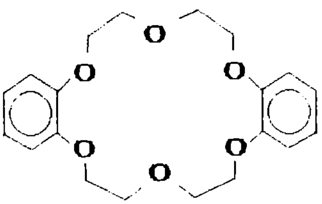
1. Introduction

The complexation thermodynamics of a host crown ether and a guest cation has been the subject of investigations since the first synthesis of the ligand in order to elucidate the nature of the cation-binding behavior in terms of free energy, and the enthalpy and entropy changes [2]. Extensive thermodynamic studies on cation–crown ether complexation have shown that the cation-binding ability of the containing benzo groups crown ether is lower than that for the parent crown ether [3]. It has been demonstrated that, in general, the diminished complex stability is due to the decreased electron density of donor oxygens produced by the electron-withdrawing aromatic ring. Curiously, little attention has been paid so far to the fact that the introduction of extra methylene groups into the ring of crown ethers reduces the influence of the electron-withdrawing effect of the aromatic ring upon complexation of the crown ether with cations. However, the cation-binding ability and selectivity of crown ether is related to the ligand's cavity size, softness, spatial arrangement, and other major factors governing cation–ligand complexation [4]. Our recent investigations have shown that the introduction of extra methylene groups into the relatively rigid skeleton of crown ethers such as 12-crown-4 and 15-crown-5, leads to much higher cation selectivities for lithium and sodium ions, respectively, than the parent crown ethers. Hence, the tailoring of the crown ether's ring size by introducing extra methylene group is a convenient and powerful tool with which to design and synthesize host crown compounds processing high cation selectivity [5–7]. In order to study extensively the ring enlargement and solvent effects upon introduction of extra methylene groups into the crown ether ring containing the same number of donor atoms on complexation with cation, in the present communication we report our results of the thermodynamic study on the complexation of dibenzocrown ethers (1)–(4) with sodium and potassium ions in methanol and acetonitrile using titration calorimetry, in order to enable us to elucidate the effect of the crown-6 cavity size, molecular symmetry and solvent used upon their cation binding ability/selectivity after the introduction of 1–4 methylene groups into parent crown ether ring.

2. Experimental

2.1. Materials

Commercially available dibenzo-18-crown-6 (1) (Merck) and Cica-grade sodium thiocyanate and potassium thiocyanate (Kanto Chem. Co.) were used without



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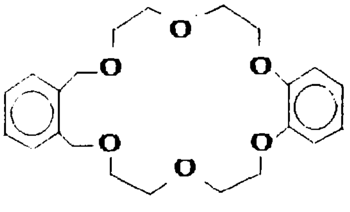

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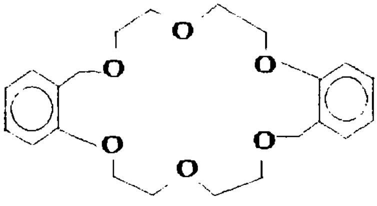

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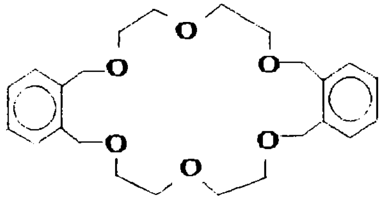

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further purification. The dibenzo-20-crown-6 (2) (2,3,12,13-dibenzo-1,4,7,10,15,18-hexaoxacycloeicosa-2,12-diene) and dibenzo-22-crown-6 (4) (3,4,14,15-dibenzo-1,6,9,12,17,20-hexaoxacyclodocosa-3,14-diene) were prepared according to the procedures reported previously [8]. Dibenzo-20-crown-6 (3) (2,3,12,13-dibenzo-1,5,8,11,15,18-hexaoxacycloeicosa-2,12-diene) was synthesized in the reaction of diethylene glycol bis(toluene-*p*-sulphonate) with salicyl alcohol in the presence of sodium hydroxide in DMF; subsequent recrystallization of the product from acetone gave white crystals [9]. Analytical grade acetonitrile and methanol were dried and then distilled fractionally to give the anhydrous acetonitrile ($< 5 \times 10^{-7} \Omega^{-1}$ cm^{-1}) and methanol solvents for calorimetric use, respectively. The dibenzo-crown ethers were dissolved in acetonitrile or methanol to make a 1.1–1.5 mmol dm^{-3} solution. Sodium thiocyanate and potassium thiocyanate were dissolved in solvents to make a 0.1–0.15 mmol dm^{-3} solution.

2.2. Apparatus and procedures

Calorimetric titrations were performed under atmospheric pressure in a water bath thermostated at 25.0°C, using a calorimeter assembled in this laboratory connected to a CA-033 microcomputer for automated titration and data processing [10–12]. The temperature change detectable in the calorimeter is 5.60×10^{-3}°C/V^{-1}. The principle of the measurement and the detailed experimental procedures have been reported elsewhere [13–16]. The alkali metal salt solution (0.1–0.15 mmol · dm^{-3}) was introduced continuously at a rate of 0.0152 ml s^{-1} into a dibenzo-crown ether solution (1.0–1.5 mmol dm^{-3}) placed in the calorimeter. A titration curve was obtained by plotting the temperature change (measured as E/V) against the amount of KSCN solution added, from which the values of K and ΔH were calculated. One titration gives a set of complex stability constant (K) and enthalpy change (ΔH) values simultaneously. The reliability of the whole system was checked by test runs using the reported reaction system [17]: the enthalpy change ($\Delta H = -14.77$ kJ mol^{-1} at 25.0°C) upon complexation of dibenzo-18-crown-6 with sodium thiocyanate anhydrous acetonitrile solution was consistent with that reported in the literature, -14.31 and -15.02 kJ mol^{-1} [18,19].

3. Results and discussion

In a typical experiment, a potassium thiocyanate (0.1 M) solution in anhydrous acetonitrile is added continuously to the ligand in acetonitrile solution which is placed in the calorimeter, giving the calorimetric titration curve as shown in Fig. 1

As can be seen from Fig. 1, the ascending temperature curves in the before (before point x) and after (behind point y) periods appear to be excellent straight

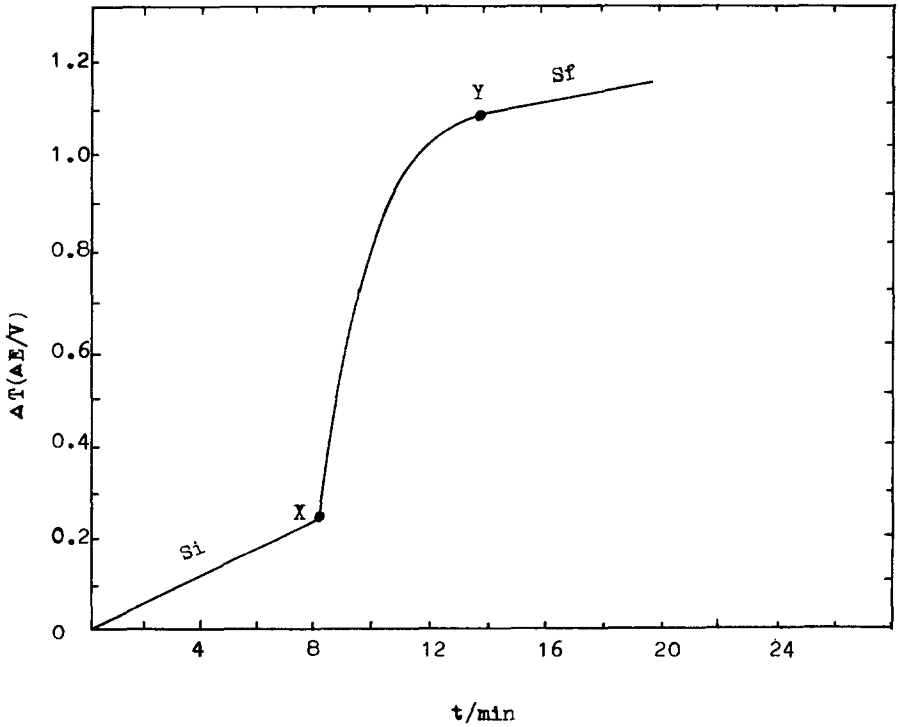

Fig. 1. Calorimetric titration curve of 1.204 mmol dm^{-3} dibenzo-20-crown-6 (2) with 0.1 mmol dm^{-2} potassium thiocyanate in acetonitrile at 25°C.

Table 1
Calorimetric titration data and heat corrections for 1.204 mmol dm^{-3} dibenzo-20-crown-6 (2) with 0.1 mmol dm^{-3} potassium thiocyanate in acetonitrile at 25°C

t/min	$-Q_p$/J	$-Q_{\mathrm{D}}$/J [a]	$-Q_{\mathrm{HL}}$/J	$-Q_{\mathrm{Tc}}$/J	$-Q$ (exp)/J
0.40	0.707	0.048	0.183	0.000	0.476
0.80	1.537	0.064	0.360	0.000	1.113
1.20	2.285	0.081	0.523	0.001	1.680
1.60	2.852	0.092	0.638	0.001	2.121
2.00	3.259	0.150	0.692	0.001	2.416
2.40	3.554	0.223	0.716	0.001	2.614
2.80	3.802	0.282	0.735	0.001	2.784
3.20	4.016	0.358	0.755	0.002	2.964
4.00	4.332	0.516	0.806	0.002	3.008
4.40	4.473	0.590	0.831	0.002	3.050
4.80	4.550	0.641	0.858	0.003	3.048
5.20	4.589	0.662	0.884	0.003	3.040

[a] The average value of three dilution heats.

lines, giving the initial equilibrium slope ($S_{\mathrm{i}} = 0.03125$ V min^{-1}) at point x and the final equilibrium slope ($S_{\mathrm{f}} = 0.0112$ V min^{-1}) at point y respectively. These slopes indicate the heat rise due to stirring, the heat flow between the vessel and its surroundings, and the resistance heating by the thermistor used. The net heat of complexation at any point p is given by

$$Q_{\mathrm{c},p} = Q_p - Q_{\mathrm{HL},p} - Q_{\mathrm{Tc},p} - Q_{\mathrm{D},p} \tag{1}$$

where Q_p denotes the total formal heat, $Q_{\mathrm{HL},p}$ the non-chemical contributions (determined by the rate of heat loss), $Q_{\mathrm{Tc},p}$ the temperature difference between the titrant and the titrate, and $Q_{\mathrm{D},p}$ refers to the heat correction for the dilution of titrant determined by separate experiment. The calorimetric titration data and heat corrections for the complexation of ligand (2) with KSCN are listed in Table 1. Data for the complexation of ligands (1)–(4) with the other alkali metal salts are omitted.

In the treatment of the experiment data, assuming a 1 : 1 stoichiometry for the complexation of sodium and potassium ions with all the crown ethers, the complex stability constant (K) and the enthalpy change (ΔH) were determined calorimetrically using the least-squares method to minimize the error square sum (U) [20–22]

$$\mathrm{L} + \mathrm{M} \overset{\mathrm{K}}{\rightleftharpoons} \mathrm{LM} \tag{2}$$

$$U(K,\Delta H) = \sum_{i=1}^{m} (Q_t - N_t \Delta H)^2 \tag{3}$$

where Q_s refers to the net heat of complexation measured at time t in min, and N_t denotes the number of moles of the complex formed at time t and is directly related to the complex stability constant K. The stability constant K and the enthalpy change ΔH of complexation were calculated by computer simulation by continuously changing K, i.e., N_t, to minimize the U value. For each cation–ligand

Table 2
Comparison of experimental and calculated data for the calorimetric titration of complexation of 1.204 mmol dm^{-3} dibenzo-20-crown-6 (2) with 0.1 mmol dm^{-3} potassium thiocyanate in acetonitrile at 25°C

t/min	$-Q_t$ (net)/J Experiment	log K assumed	$N_{ML} = [ML]_t V_t$ (mmol)	$-\Delta H$/(kJ mol^{-1}) Calcd.	$-Q_t$/J Calcd.
0.40	0.476	3.23	0.0227	30.33	0.686
0.80	1.113	3.23	0.0416	30.33	1.263
1.20	1.680	3.23	0.0566	30.33	1.715
1.60	2.121	3.23	0.0681	30.33	2.067
2.00	2.416	3.23	0.0768	30.33	2.330
2.40	2.614	3.23	0.0834	30.33	2.531
2.80	2.784	3.23	0.0884	30.33	2.686
3.20	2.901	3.23	0.0923	30.33	2.803
3.60	2.964	3.23	0.0955	30.33	2.900
4.00	3.008	3.23	0.0980	30.33	2.975
4.40	3.050	3.23	0.1001	30.33	3.038
4.80	3.048	3.23	0.1017	30.33	3.088
5.20	3.040	3.23	0.1032	30.33	3.134

combination, the measurement was repeated more than three times and the U value obtained was minimized satisfactorily to give the optimized set of K and ΔH values with their standard deviations. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry of complexation as assumed above. The moles of ligand (2) with K^+ complex formed at each data point are given in Table 2. The calculated Q_t values are compared with the experimentally measured Q_t values at that point. Table 2 gives the results of such a calculation. The free energy change (ΔG) and the entropy change (ΔS) can be calculated from the stability constants (K) and the enthalpy change (ΔH). The complex stability constants and thermodynamics parameters obtained are listed in Table 3, along with those reported for the complexation with dibenzo-18-crown-6 in methanol and acetonitrile [18-19].

As can be seen from Table 3, the complex stability constants, relative cation selectivity and the thermodynanmic parameters for the complexation reactions of potassium and sodium ions with dibenzocrown ethers are influenced by the size ratio of the ligand's cavity to the cation's diameter, softness, spatial arrangement, molecular symmetry, the solvent used and other factors. Before considering the relative cation selectivity is methanol and acetonitrile, we will first discuss the thermodynamics of the ring-enlargement effect on the complexation behavior.

3.1. Complex stability and thermodynamics

In the present study, dibenzo-18-crown-6 was subjected to the introduction of several methylene groups, yielding ligands (2)-(4). It is noted that the introduction of extra methylene groups into the ring of crown ether reduced the influence of the electron-withdrawing effect of the aromatic ring upon complexation between cation

Table 3
Complex stability constants (log K) and thermodynamic parameters in kJ mol^{-1} for complexation of alkali metal ions with ligands (1)–(4) in methanol and acetonitrile at 25°C

Solvent	Cation	log K	$-\Delta G$	$-\Delta H$	$T\Delta S$	Ref.
Ligand (1)						
CH_3OH	Na^+	4.50	25.69	31.30	−5.61	[23]
	K^+	5.12	29.20	40.08	−10.96	[23]
CH_3CN	Na^+	4.93 ± 0.05	28.16	14.77 ± 0.33	13.39	This work
	K^+	4.59 ± 0.4	26.02	18.87 ± 0.07	7.33	This work
	Na^+	5.01	28.62	14.31	14.18	[18]
	Na^+	4.89	27.91	15.02	12.80	[19]
	K^+	4.78	27.28	18.62	8.45	[19]
Ligand (2)						
CH_3OH	Na^+	2.28 ± 0.03	13.01	58.49 ± 0.17	−45.48	This work
	K^+	2.80 ± 0.02	15.98	14.23 ± 0.17	−40.08	This work
CH_3CN	Na^+	3.17 ± 0.07	18.07	25.90 ± 0.38	−7.82	This work
	K^+	3.21 ± 0.02	18.32	30.17 ± 0.17	−11.85	This work
Ligand (3)						
CH_3OH	Na^+	2.03 ± 0.06	11.59	40.25 ± 0.21	−6.85	This work
	K^+	3.61 ± 0.03	20.59	38.24 ± 0.33	−17.66	This work
Ligand (4)						
CH_3OH	Na^+	1.77 ± 0.04	10.08	47.91 ± 0.46	37.82	This work
	K^+	1.95 ± 0.02	11.13	31.76 ± 0.29	−20.63	This work
CH_3CN	Na^+	1.83 ± 0.04	10.46	41.34 ± 0.08	−30.88	This work
	K^+	2.55 ± 0.04	14.55	22.76 ± 0.13	−8.21	This work

and ligand. However the crown ether ring size is enhanced, and therefore, the size-mismatch decreases the ion–dipole interaction, from the perspective of size-fitted combinations. Indeed, the thermodynamic parameters obtained reveal that all the ring-enlargement leads to a gradual reduction in complex stability with increasing methylene groups, although the thermodynamic quantities for each crown-6 behave quite differently in the two solvents. However, examination of CPK molecular models reveals that a less-symmetrical arrangement of the donor oxygen is induced by increasing the methylene groups in the dibenzo-18-crown-6 molecule, leading to an unfavorable conformation for complexation as compared with the parent crown ether. At the same time, examination of CPK molecular models reveals that the compounds possessing larger cavity diameters (3.3 and 3.1 Å, respectively) as compared with dibenzo-18-crown-6 (2.6 Å), dibenzo-20-crown-6 and dibenzo-22-crown-6, may suffer fairly large conformational changes compared with ligand (1) upon complexation with sodium ion (ionic diameter 2.04 Å) and potassium ion (2.76 Å) [24], giving highly negative $T\Delta S$ values and low complex stability constants in methanol and acetonitrile, respectively. The negative $T\Delta S$ value of complexation with sodium ion is increased by 21.21 and 37.38 kJ mol^{-1} for ligand (2) compared with (1) in methanol and acetonitrile, respectively, and is increased by 23.05 kJ mol^{-1} for ligand (3), while the negative $T\Delta S$ values for ligand (4) complexation with Na^+ is increased by 44.27 and 33.22 kJ mol^{-1} in methanol and acetonitrile, respectively.

From the entropic point-of-view alone, the cation–crown ether complex formation is unfavorable, but the entropic loss arising from the cation–crown ether association is often compensated by the gain from the extensive desolvation of cation and ligand, as shown in Table 3, giving rise to the positive $T\Delta S$ value for the parent crown ether (1), and increasing complex stability in acetonitrile. However, in methanol, the complexation stability is totaly enthalpy-driven affording negative $T\Delta S$ values. Maybe it is due to the fact that the dissociated cation and free ligand are both heavily solvated through ion–dipole and hydrogen-bonding interactions, respectively. Under such circumstances, the complexation of cation with crown ether, which is essentially a molecular association process, is driven mainly through the ion–dipole interaction, although accompanying extensive desolving, giving the larger enthalpy changes ΔH and highly negative $T\Delta S$ values [25]. Hence, the complexation enthalpic changes of ligands (1)–(4) with sodium and potassium ions in methanol are larger than those in acetonitrile, while the entropic changes are smaller. However, the cation–ligand combination is methanol or acetonitrile accompanying entropic loss from the structural freezing of the resulting complex and unfavourable desolvation, is often compensated by the enthalpic changes increased through the interaction among ligand, cation and solvent molecules. Therefore, all the ligands used in this study can form stable complexes with cations in anhydrous acetonitrile and methanol. In the whole coordinating process, although the complex formation itself is evidently driven by enthalpy, the complex stability sequence is essentially entropy-governed for ligands (2)–(4).

3.2. Relative cation selectivity

As can be seen from Table 3, although the ring-enlargement of ligands (2)–(4) decreases the complex stability as compared with the parent crown ether, the relative cation selectivity for K^+/Na^+ increases gradually with increasing number of methylene groups in the parent ring. The relative cation selectivity of K^+/Na^+ for ligand (3) (K_{K^+} (crown ether–K^+ complex)/K_{Na^+} (crown ether–Na^+ complex) = 38.02) compared with that of ligand (1) (K_{K^+} (crown ether–K^+ complex)/K_{Na^+} (crown ether–Na^+ complex) = 4.17) is 9.12 times greater. The K^+/Na^+ selectivity for ligand (4) (K_{K^+} (crown ether–K^+ complex)/K_{Na^+} (crown ether–Na^+ complex) = 5.25) is 11.4 times greater than that of ligand (1) (K_{K^+} (crown ether–K^+ complex)/K_{Na^+} (crown ether–Na^+ complex) = 0.46) in acetonitrile solution. It is also interesting to note that the sequence of the thermodynamic parameters between Na^+ and K^+ is in good agreement with that of the crown ether cavity size, i.e., (1) > (2) > (3). This indicates that the size-fit between the cavity and the cation controls the complex stability upon complexation.

4. Conclusions

It can be concluded that the crown-6 series is very sensitive to the solvent used, and the complexation stability constants in acetonitrile are larger than those in methanol. The cation–crown ether size-fit combinations and molecular symmetry play a crucial role in the complex stability. The tailoring of crown ether's ring size by introducing extra methylene groups, as reported in our previous papers [4,5,7], is a convenient and powerful tool with which to design and synthesize host possessing relative cation selectivity.

Acknowledgments

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