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Macroheterocycles.
46. Complexing Properties of Bis(benzo-15-crown-5) with Acylhydrazide Fragments in the Linking Chain

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Abstract

Complex stability of bis(benzo-15-crown-5) with acylhydrazide fragments in the linking chain with Na^+, K^+, Rb^+ and Cs^+ in 95% aqueous methanol has been determined by spectrophotometric titrations. In all cases the formation of 1:1 complexes was observed. The studied bis-crown ethers form more stable complexes than benzo-15-crown-5. The stability of bis-crown ethers complexes is substantially determined by the length of the linking chain. Bis-crown ethers with a glutaric acid residue in the linking chain exhibit striking potassium selectivity. High selectivity and stability of the complexes are due to the increase of their sandwich structure rigidity resulting from the formation of H bonds between acylhydrazide fragments.

Introduction

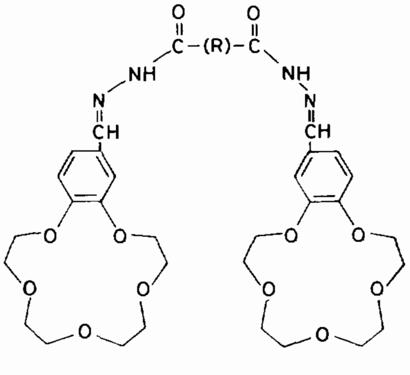
Bis-crown ethers in which two polyether cycles are connected by a relatively short chain are structurally ready for the formation of intramolecular sandwich type complexes. In many cases this results in an increase of the complexes selectivity and stability [1–3]. In general, complexing abilities of bis-crown ethers are determined by the nature of the polyether cycles and the linking chain. It has been recently shown that moieties able to form H bonds in this chain may result in a sharp increase in complexation selectivity [4]. In order to get more information about this effect we have studied stabilities of complexes of Na^+, K^+, Rb^+ and Cs^+ with bis(benzo-15-crown-5) with acylhydrazide fragments in the linking chain.

Experimental

Bis(benzo-15-crown-5) (see Fig. 1) were prepared as described earlier [5–7]. All the used salts were of reagent grade. ^1H NMR spectra were recorded on a Bruker AM-250 spectrometer.

Typical UV absorption spectra of bis-crown ethers (**1**–**9**) have a band characteristic of the aromatic *ortho*-diether portion at *ca.* 292 nm (ϵ *ca.* 42 000 $dm^3\ mol^{-1}\ cm^{-1}$) and one characteristic of azomethine at *ca.* 315 nm (ϵ *ca.* 45 000 $dm^3\ mol^{-1}\ cm^{-1}$). In the UV spectrum of compound **9** one broad band is observed at 330 nm. The intensity of these absorptions decreases with the addition of alkali metal salts.

Stability constants of the complexes were determined by spectrophotometric titration of ligand



1 : $R = CH_2$
2 : $R = (CH_2)_2$
3 : $R = (CH_2)_3$
4 : $R = (CH_2)_4$
5 : $R = (CH_2)_5$
6 : $R = (CH_2)_6$
7 : $R = (CH_2)_7$
8 : $R = (CH_2)_8$
9 : $R = o\text{-}C_6H_4$

Fig. 1. Ligands studied in this work.

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solutions (3×10^{-5} M) with metal chlorides (5×10^{-3} M) in 95% aqueous methanol at 25 °C. Ratio of concentrations of salts and ligand (C_M/C_L) varied from 0.5 to 25. Measurements of the absorbance changes due to complex formation were carried out at 280, 316 and 320 nm (for compound **9** at 290, 328 and 335 nm) using a Specord M-40 spectrophotometer. Experimental values of absorbance obtained for three wavelengths were used jointly for the calculation of the stability constants of the complexes. The calculation was carried out using a non-linear least-squares method by the program given in ref. 8. When calculating the stability constants the possibility was taken into account of the formation of complexes of ligand/cation ratios 1:1, 1:2 and 2:1 (eqns. I, II and III respectively), as well as the possibility of successive complex formation 1:1, 2:1 and 1:1, 1:2 (eqns. I, IV and I, V).

$$L + M^+ \rightleftharpoons LM^+ \qquad K_1 = \frac{[LM^+]}{[L][M^+]} \qquad (I)$$

$$L + 2M^+ \rightleftharpoons LM_2^{2+} \qquad K_2 = \frac{[LM_2^{2+}]}{[L][M^+]^2} \qquad (II)$$

$$2L + M^+ \rightleftharpoons L_2M^+ \qquad K_3 = \frac{[L_2M^+]}{[L]^2[M^+]} \qquad (III)$$

$$LM^+ + L \rightleftharpoons L_2M^+ \qquad K_4 = \frac{[L_2M^+]}{[LM^+][L]} \qquad (IV)$$

$$LM^+ + M^+ \rightleftharpoons LM_2^{2+} \qquad K_5 = \frac{[LM_2^{2+}]}{[LM^+][M^+]} \qquad (V)$$

The scheme of complexation which describes the experimental titration curve in the best way was considered true.

Results and Discussion

Analysis of the titration curves has shown that all the studied ligands **1–9** form 1:1 complexes with Na^+, K^+, Rb^+ and Cs^+. Stability constants (log K) are given in Table 1. For comparison the corresponding data for benzo-15-crown-5 (B15C5) from the literature [9] are also cited.

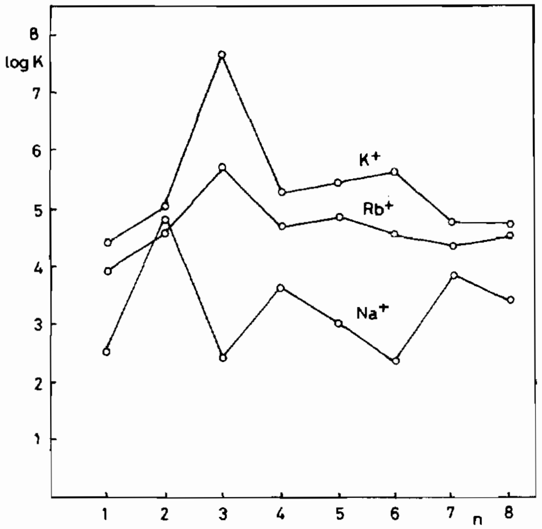

Fig. 2. Dependence of the stability of complexes of bis(benzo-15-crown-5) (1–8) on the length of the chain linking two polyether cycles $(CH_2)_n$.

Bis(benzo-15-crown-5) **1–8** form more stable complexes with K^+, Rb^+ and Cs^+ than B15C5. The stability of these complexes depends considerably on the length of the chain connecting two polyether cycles (Fig. 2). This dependence varies considerably – bis-crown ether **3** forms the most stable complexes. The high stability of bis-crown ether **1–8** complexes and its clearly expressed dependence on the linking chain length provide evidence of their sandwich structure.

The stability of complexes of the studied bis-crown ethers with Na^+ with the exception of compound **2** is similar to the corresponding value for B15C5 and does not have any clear dependence on

TABLE 1. Stability Constants (log K; K in M^{-1}) of Complexes of Na^+, K^+, Rb^+ and Cs^+ with Bis(benzo-15-crown-5) in 95% Aqueous Methanol at 25 °C

Ligand	Na^+	K^+	Rb^+	Cs^+
1	2.48 ± 0.53	4.40 ± 0.08	3.92 ± 0.02	2.24 ± 0.08
2	4.77 ± 0.31	5.02 ± 0.07	4.61 ± 0.08	3.00 ± 0.11
3	2.41 ± 0.44	7.65 ± 0.11	5.68 ± 0.09	3.67 ± 0.05
4	3.61 ± 0.22	5.26 ± 0.06	4.67 ± 0.05	2.19 ± 0.21
5	3.04 ± 0.21	5.47 ± 0.05	4.84 ± 0.04	3.30 ± 0.10
6	2.32 ± 0.42	5.60 ± 0.04	4.53 ± 0.03	2.34 ± 0.23
7	3.82 ± 0.40	4.75 ± 0.05	4.33 ± 0.06	3.98 ± 0.32
8	3.39 ± 0.31	4.68 ± 0.08	4.61 ± 0.09	2.17 ± 0.38
9	3.02 ± 0.14	3.61 ± 0.25	<2	<2
B15C5[a]	3.05[b]	3.17[b]	1.97	1.91[b]

[a] From ref. 9; for K^+ and Rb^+ stability constants of 2:1 complexes are given. [b] In CH_3OH.

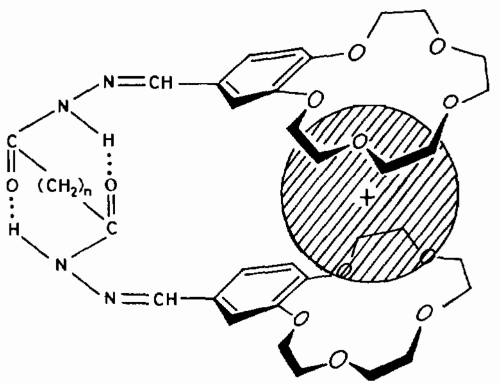

Fig. 3. Suggested structure of bis(benzo-15-crown-5) complexes stabilised by H bonds.

the length of the linking chain. In this case only one polyether cycle seems to take part in complex formation. ^1H NMR spectra prove this suggestion. Addition of an equimolar amount of NaI to a solution of ligand 3 in CD_3OD shifted the ligand signals downfield similar to that observed at the formation of 1:1 complexes of Na^+ with B15C5 [10]. In contrast, equimolar amounts of KI shifted the ligand signals upfield which proves the formation of sandwich complexes [10]. Bis-crown ether **2** forms a more stable complex with Na^+ than B15C5 which is probably due to the formation of an intramolecular sandwich complex.

Compound **3** is of the most interest. The stability of this ligand complex with potassium and its K^+/Na^+ and K^+/Rb^+ selectivity exceed the corresponding parameters of all the known crown ethers, bis-crown ethers and even cryptands. For **3** $\log(K_{K^+}/K_{Na^+}) = 5.24$, $\log(K_{K^+}/K_{Rb^+}) = 1.97$; for [2.2.2] cryptand $\log(K_{K^+}/K_{Na^+}) = 2.54$, $\log(K_{K^+}/K_{Rb^+}) = 1.35$ [9].

We suggest that the unusually high stability of the complexes and the selectivity of the studied bis-crown ethers are due to the increase of rigidity of intramolecular sandwich complexes resulting from the formation of H bonds between acylhydrazide fragments in the linking chain as shown in Fig. 3. This suggestion can be proved by the significant decrease of the stability of bis-crown ether **9** complexes with K^+, Rb^+ and Cs^+ as compared with other bis-crown ethers. The complexing ability of ligand **9** is about the same as that for B15C5 (Table 1). A CPK models analysis has shown the phenyl group in the linking chain of **9** prevents the formation of H bonds between acylhydrazide fragments which probably results in the decrease of stability of the intramolecular sandwich complexes.

References

1 K. Kimura, T. Maeda and T. Shono, *Talanta, 26* (1979) 945.
2 K. H. Wong and H. L. Ng, *J. Coord. Chem., 11* (1981) 49.
3 H. Sakamoto, K. Kimura, Y. Koseki, M. Matsuo and T. Shono, *J. Org. Chem., 51* (1986) 4974.
4 E. Lindner, K. Toth, M. Horvath, E. Pungor, B. Agai, I. Bitter, L. Toke, Z. Hell and Z. Frezenius, *Anal. Chem., 332* (1985) 157.
5 *GDR Patent WPC 07 D/288 7278 DDR* (1986) to H.-J. Holdt and J. Teller.
6 *GDR Patent WP C 07 D/299 194 4 DDR* (1986) to H.-J. Holdt, J. Aurich, J. Teller and G. Kuntosch.
7 *GDR Patent WP C07 D/303 028 1 DDR* (1987) to H.-J. Holdt, J. Aurich, J. Teller and G. Kuntosch.
8 N. G. Lukyanenko, V. I. Vetrogon, N. Yu. Nazarova and A. S. Reder, *Zh. Obshch. Khim., 58* (1988) 214.
9 R. M. Izatt, J. S. Bradshaw, A. N. Steven, J. D. Lamb and J. J. Christensen, *Chem. Rev., 85* (1985) 271.
10 J. C. Lockhart, A. C. Robson, M. E. Thompson, P. D. Tyson and I. H. M. Wallace, *J. Chem. Soc., Dalton Trans.,* (1978) 611.