

**THERMODYNAMIC STABILITIES OF COMPLEXES OF SYNTHETIC MACROCYCLIC
VALINOMYCIN MIMICS WITH ALKALI, BARIUM, AND GUANIDINIUM CATIONS**

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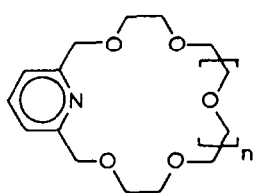
Abstract— Association constants of the 1:1 complexes of a series of pyrido crown ethers **1** ($n=0-6$) and a number of large ring (27-33 ring atoms) benzo and dibenzo crown ethers **2,3** with alkali, barium and guanidinium chlorides have been determined potentiometrically in MeOH. For most of the ions besides a global maximum for 18-membered rings, a local maximum for the complexation with 30-membered rings is observed. The appearance of local maxima is attributed to the tennisball-seam like conformations that large macrocycles can adopt. The larger crown ethers show a remarkably high K^+/Na^+ selectivity similar to the antibiotic valinomycin, a structurally related 36-membered macrocycle. Therefore, these large ring crown ethers can be regarded as synthetically easy to modify valinomycin mimics. The effects of the solvation of the hosts, guests and complexes on the overall (co-)complexation is discussed. Comparison of data from extraction experiments with association constants clearly shows that differences in the distribution of the complexes between the aqueous and organic phases may be a dominating factor for the selective extraction of cations.

The ability of biochemical systems to recognize and selectively bind guest species, represents one of their most important properties. In order to mimic the selective binding properties of the natural ionophores, several classes of macrocyclic ligands have been designed and synthesized. Cram and co-workers have recently compared these classes and they concluded that there seems to be a relation between the thermodynamic stability of host-guest complexes and the binding selectivity of the hosts towards the guests.¹ The following order was observed: spherands > cryptahemispherands > cryptands > hemispherands > chorands (crown ethers) > podands, for both the stability of the complex and selectivity of the host.

Most of the work in the host-guest chemistry has been focussed on the relatively small crown ethers with 12-21 ring atoms and an overwhelming number of thermodynamic data on the complexation of spherical cations by these ligands has been collected.² For the optimal complexation of polyfunctional cations such as (thio)uronium,^{3,4} and guanidinium salts,⁵ we have shown that larger ligands with 27-33 ring atoms are needed, because otherwise relatively weak perching complexes⁶ are formed. We are currently interested in the selective transport of such polyfunctional cations through membranes in competition with other, spherical cations.⁷ Therefore, we decided to study the thermodynamics of complexation of macrocycles with 27 to 33 ring atoms towards several cations because hardly any data are available in the literature.^{8,9}

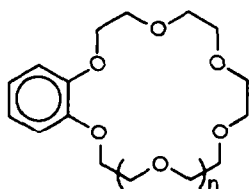
Other reasons to perform a systematic study originate from our work on the design of ion-selective field-effect transistors (ISFETs).¹⁰ The aim of that work is the selective conversion of chemical information into electrical signals. Until now natural ionophores exhibiting a high K^+/K^{Na} selectivity for one ion amongst other ions (e.g. valinomycin: $K^+/K^{Na} = 6700$, MeOH)^{2a} were used in the sensing components of ISFETs.¹¹ Since valinomycin (36 ring atoms) is structurally related to large ring crown ethers¹² we wanted to explore the possible selective complexation behaviour of the large ring crown ethers, hoping to

barium cations generally show the following trend: $K^{\text{Li}} < K^{\text{Na}} < K^{\text{K}}, K^{\text{Rb}}, K^{\text{Cs}} < K^{\text{Ba}}$ (see Table I).



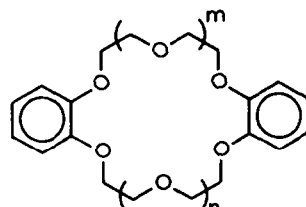
1

n=0 : P15C5
1 : P18C6
2 : P21C7
3 : P24C8
4 : P27C9
5 : P30C10
6 : P33C11



2

n=1 : B18C6
4 : B27C9
5 : B30C10
6 : B33C11



3

n=0, m=5 : [2,7]DB27C9
1 5 : [3,7]DB30C10
2 5 : [4,7]DB33C11

0 6 : [2,8]DB30C10
1 1 : [3,3]DB18C6
3 3 : [5,5]DB30C10

For ligands 2 and 3 the association data are collected in Table II. For most ions the 30-membered ligands form relatively stable complexes when compared with the 27- and 33-membered macrocycles. Surprisingly the association constants of the complexes of Na^+ and crown ethers 2 and 3 are 50–800 fold smaller than with the K^+ , Rb^+ , and Cs^+ cations. [4,7]DB33C11 exhibits a relatively strong preference for Ba^{2+} and Cs^+ .

Association constants of the complexes of guanidinium (Gu^+) cations with several crown ethers are also given in both Table I and II. The binding of the polyfunctional Gu^+ cation is rather weak compared to the binding of the centrosymmetrical cations.

Table II. Log K values^a and K^+/Na^+ selectivity for 1:1 complexes of crown ethers 2 and 3 in MeOH (0.1 M Et₄NCl) at 25.0 °C

ligand	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Gu^+	$\text{K}^{\text{K}}/\text{K}^{\text{Na}}$
B18C6 ^b	4.2	5.28	4.86	3.88	5.35		10
B27C9	1.88 ^c	4.00	3.88 ^c	4.57	3.93	1.77 ^d	132
B30C10	1.93	4.28	4.49	4.35	5.01	1.83	224
B33C11	1.91	3.57	4.27	3.88	4.30	1.37	46
[2,7]DB27C9	1.90	4.36	4.31	4.35	2.83	<1	288
[3,7]DB30C10	1.98 ^e	4.47	4.69 ^e	4.38	3.94	1.50 ^f	309
[4,7]DB33C11	1.82	3.79	4.55	4.72	>5.5	1.37	93
[2,8]DB30C10	1.98	4.62	4.89	4.79	2.99	1.62	437
[3,3]DB18C6 ^b	4.36	4.96	4.23	3.23	4.28		4
[5,5]DB30C10 ^b	2.11	4.57	4.64	4.2			288

^aThe log K values for Na^+ , K^+ , and Rb^+ were determined directly (s.d. 0.04), and the others in competition experiments (s.d. 0.2). ^bThe values for these ligands, taken as the average of the association constants reported in the literature, Ref. 2a, were included for comparison. ^cRef 19, by polarography: 2.01 (Na^+), and 3.78 (Rb^+). ^dRef 19, by conductometry at 20.0 °C: 1.70 (GuSCN). ^eRef 19, by polarography: 2.18 (Na^+), and 5.09 (Rb^+). ^fRef 19, by conductometry at 20.0 °C: 2.00 (GuCl).

find valinomycin mimicry and with that a much higher cation selectivity than was found for small ring crown ethers.

Finally it is noted that in order to fully comprehend the ion complexing properties of synthetic ionophores in transport or extraction systems one has to correlate the relative thermodynamic stabilities of complexes and the partition of the complexes and its components over aqueous and organic phases. It is known from X-ray data that [5,5]DB30C10 3 ($n=m=3$) wraps around K^+ and Rb^+ ions.¹³ The resulting conformation of the complex resembles to some extent a tennisball-seam. The complexes formed in this way show a more pronounced lipophilicity than the corresponding complexes with 18-crown-6, in which the guest is still partly solvated as theoretical studies indicate.¹⁴ Therefore, the degree of desolvation of the guest cation, which is an important contribution to the overall free energy of complexation,^{2b} is expected to be very large in the case of the 27-33 membered macrocycles.

This paper describes the thermodynamics of complexation of 15 to 33-membered crown ethers both with centrosymmetrical and with polyfunctional cations. The association constants were determined potentiometrically in methanol (0.10 M Et_4NCl) at 25.0 °C, using direct¹⁵ and competition¹⁶ methods.

Results

In order to study systematically the effect of an increasing ring size of the crown ethers on the stabilities of the complexes, we have measured the association constants (K) of alkali cations with a series of pyrido crown ethers 1 ($n=0-6$)^{5b} (see Table I).

Table I. Log K values^a and K^+/Na^+ selectivities for 1:1 complexes of 2,6-pyrido crown ethers 1 in MeOH (0.1 M Et_4NCl) at 25.0 °C

ligand	Li^+	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Gu^+	K^K/K^{Na}
P15C5	2.19	3.34	3.01	2.63	2.44	5.05	b	0.5
P18C6	3.01	4.25 ^c	5.30 ^c	4.66 ^c	4.08	>5.5	b	11
P21C7	<1	1.91	3.79	4.36	2.81	5.37	b	76
P24C8	<1	2.27	2.89	3.25	3.28	2.91	b	4
P27C9	2.02	1.60	3.23	3.08	3.20	5.45	1.18	42
P30C10	2.12	1.71	3.15	3.44	3.51	>5.5	1.32	27
P33C11	2.55	1.44	3.00	3.28	3.24	2.97	1.44	36

^aThe log K values for Na^+ , K^+ , and Rb^+ were determined directly (s.d. 0.04), and the others in competition experiments (s.d. 0.2). ^bNot measured. ^cRef 17, by calorimetry at I=0.005: 4.09 (Na^+), 5.35 (K^+), and 4.56 (Rb^+).

From the data in Table I it is concluded that for all the cations a global maximum in the stability constants of the complexes is observed for the 18-membered ligand. This observation seems to be rather surprising since the ionic radii of the guests vary from 0.78 Å (Li^+) to 1.65 Å (Cs^+).¹⁸ According to the so-called 'hole-size cation-diameter' relationship^{2,16f} one would expect that the larger ligands would preferentially bind the larger cations. However, it is known that besides the ring size more factors contribute to the binding of cations, e.g. (de)solvation, conformational flexibility, the number, spatial arrangement, and electron density of the binding sites, and the type of the anion.

When the ring size is gradually increased to 24 ring atoms the association constants of the complexes decrease. Further increasing the ring size leads to an enlargement of the association constants for most of the complexes. Noteworthy a sort of local maximum in the stability constants of the complexes with ligands possessing 27 to 33 ring atoms is observed. The association constants of the pyrido crown ethers 1 with the alkali and

Discussion

Ring Size. The stability constants of the complexes of pyrido crown ethers 1 having ring sizes of 15-33 ring atoms, with the alkali and barium cations provide an excellent data set to verify the hole-size cation-diameter relationship. Hitherto only studies with relatively small ring macrocycles (12-24 ring atoms) have been performed.^{16f} The global maximum in binding ability towards the cations is found for the 18-membered ligand. This has previously been explained in terms of a favourable binding enthalpy that is due to the the symmetric and planar geometry of the ligand.^{2a,c}

Local maxima that we observe for hosts possessing 27 to 33 ring atoms, can be explained by the 'tennisball-seam' like conformations. According to X-ray studies 30-membered ligands are able to adopt such a conformation.¹³ In the complexes of [5,5]DB30C10 with potassium^{13a,c,d} and rubidium^{13b} salts the macrocycles wrap around the guest ion in such way that the donor atom - cation distances are minimalized and the electrostatic interactions are most favourable. It is known from NMR studies that also in solution crown ethers possessing (hetero)aromatic rings can adopt twisted conformations in which the size of the cavity is adjusted to the size of the cation.²⁰

From the data in Table I and II it may be deduced that the 30-membered cycles seem to be somewhat favoured in comparison to the 27- and 33-membered ligands with respect to the thermodynamic stabilities of the complexes formed. Possibly crown ethers with 30 ring atoms possess relatively favourable conformational properties. An alternative explanation could be that the 30-membered crown ethers are able to simultaneously complex a cation and one solvent molecule. Previously we have shown for pyrido crown ethers that macroring-assisted solvation of a proton can be a stabilizing factor and leads to a basicity of the ligand that is ring size dependent.²¹ Recently Stoddart and coworkers²² reported complexes of 30- and 36-membered dibenzo crown ethers with lithium picrate and water.

Cation Selectivity. If the solvation energies for the various cations and ligands would be known, the association data could yield information on the solvation of the complexes and the strength of the mutual interactions between host and guest. Although the solvation energies for most of the cations in MeOH are known,²³ no quantitative data are available for the ligands. The free energies of solvation ($-\Delta G^{\circ}$) of the cations in MeOH increase in the following order: $\text{Cs}^{+} < \text{Rb}^{+} < \text{K}^{+} \ll \text{Na}^{+} \ll \text{Li}^{+}$. The very large value for lithium ions ($\Delta G^{\circ} = -115.0$ kcal/mol) could be the reason that in complexes of Li^{+} a number of solvent molecules are still coordinated to the cation.²² The differences in solvation energies of the cations may dominate the overall complexation process as was illustrated by molecular mechanics^{14a} and distance geometry^{14b} studies of 18-crown-6 and its Na^{+} and K^{+} complexes, performed by Kollman and coworkers. It appeared that the intrinsically more stable 18-crown-6. Na^{+} (1:1) complex actually is in solution less stable than the corresponding complex with K^{+} , due to the differences in solvation energies between K^{+} , Na^{+} , and the complexes.

The driving force for the replacement of the solvation sphere of the cation by the coordinating donor atoms of the larger macrocycles might be due to the favourable entropy associated to the release of a number of solvent molecules upon complexation.

The binding of K^{+} , Rb^{+} , Cs^{+} , and Ba^{2+} by the pyrido crown ethers is rather strong compared to the complexation of Li^{+} , Na^{+} , and Gu^{+} . For the ligands 2 and 3 this preference is even more clear; the free energies of complexation are 3-4 kcal/mol smaller than for the binding of Na^{+} . The $\text{K}^{+}/\text{Na}^{+}$ selectivity is for the 30-membered macrocycles the most clear, with a maximum value of $K^{\text{K}}/K^{\text{Na}} = 437$ for [2,8]DB30C10. X-ray analysis, performed by Owen and Truter,²⁴ of a [5,5]DB30C10.sodium thiocyanate (1:2) complex reveals that in the complex the ligand possesses a somewhat twisted conformation. The authors suggest that very unfavourable non-bonding interactions would be introduced when one sodium ion would be placed in the central cavity of the ligand. Since we observed

only 1:1 stoichiometries, this might be an explanation for the reduced binding abilities of the larger ligands towards Na^+ .

Although the K^+/Na^+ selectivities of the macrocycles 2 - 3 are 15-65 times smaller than the corresponding selectivity of valinomycin, they are substantially higher than one might expect for such simple coronands and they are close to the values measured for the more structured cryptands.² For this reason these large ring macrocycles can be regarded as valinomycin mimics that can be easily functionalized and for instance covalently linked to solid supports.²⁵

Complexation of Barium. The log K values for the complexation of Ba^{2+} show large fluctuations from 2.83 up to >5.5. The ionic radius of Ba^{2+} (1.43 Å) is in between that of K^+ (1.33 Å) and Rb^+ (1.49).¹⁸ However the solvation energy of this doubly charged cation in MeOH is probably much larger than the solvation energies for the monovalent cations, as is the case in aqueous solutions.^{23b} Therefore, desolvation of the barium cation can only be achieved if in the complex the cation is tightly coordinated by the macro ring donor atoms of the ligand.

Pyrido versus Benzo Moiety. All guests used in this study show smaller binding constants for the complexes with the 27-33 membered pyrido ligands 1 (n=4-6) than with the corresponding benzo ligands 2 (n=7-9). At first sight this seems hard to rationalize since the nitrogen atom is a better donor atom than oxygen and in addition the benzo units decrease the electron densities of the catecholic oxygen atoms. However, these effects are more than compensated for by the better solvation in MeOH of the basic pyridine moiety of the free ligands due to the formation of H-bonds.

Structural Isomerism. For the 30-membered ligands with two benzo moieties, data for three different isomers 3 (n=1), 4, and 5 are available. The differences in complexation constants for the isomers are rather small indicating that they form similar complexes. With Rb^+ and Cs^+ the binding decreases in the following order: [2,8]DB30C10 > [3,7]DB30C10 > [5,5]DB30C10. However, with Na^+ the [2,8] isomer exhibits the lowest association constant. The isomers with the two benzo moieties spatially close to each other form more stable complexes and this might be due to the elimination of repulsive interactions between the π -systems of the aromatic rings in the free ligands upon complexation.

Comparison with Extraction Experiments. For the pyrido crown ethers 1 (n=0-6) competitive liquid-liquid phase transfer of Li^+ and Gu^+ has been studied previously.^{5b} It appeared that Li^+ was extracted best from an aqueous to a CDCl_3 phase by the 15- and 21-membered ligands. The 18-membered macrocycle preferably transferred water to the organic phase. The larger macrocycles with at least 24 ring atoms (n=3-6) did not extract Li^+ but Gu^+ . These observations seem to contradict the potentiometric data, which show that in MeOH the association constants of the complexes of 1 (n=4-6) with Li^+ are larger than with Gu^+ (the association constants in CDCl_3 could not be determined since no methods are available yet). We feel that an interpretation of this apparent contradiction should be found in the solubilities and distribution between the phases of the two complexes. The encapsulated complexes of the larger pyrido crown ethers with Gu^+ are expected to be more lipophilic than the corresponding Li^+ complexes, in which probably one or two solvent molecules are co-complexed. As a result the solubilities of the Gu^+ complexes increase considerably more than the solubilities of the Li^+ complexes when the polarity of the solvent is decreased. Therefore, Gu^+ is preferentially extracted from aqueous to CDCl_3 phases by the pyrido crown ethers. This specific case clearly shows that caution is required when association constants are determined by extraction methods,²⁶ in which this effect is not evaluated.

Conclusions

The results described in this paper reveal that crown ethers with 27-33 ring atoms show unexpected high selectivities for K^+ , Rb^+ , and Cs^+ amongst other ions like Na^+ and Li^+ . They may therefore be seen as valinomycin mimics, which can be chemically modified rather simple. A careful reexamination of the hole-size cation-diameter relation shows that two maxima in binding abilities towards a number of cations are encountered: a global one, for 18-membered macrocycles, and a local one for 30-membered macrocycles.

Experimental Section

Materials. The pyrido,^{5b} benzo,⁷ and dibenzo⁷ crown ethers were prepared according to literature procedures.

The alkali, barium, and guanidinium chlorides were of Suprapur quality (Merck). Tetraethylammonium chloride (Merck) was recrystallized three times from chloroform/ether and dried for 24 hours at 120°C under low pressure (10-12 mm Hg). Triethylamine (Merck) and Methanol (Merck, 99.8%) were p.a. grade.

Potentiometric Measurements. The stability constants were determined by potentiometric measurements using a Radiometer Copenhagen PHM 26. The K values of the Na^+ , K^+ , and Rb^+ complexes could be determined directly by the Frensdorff method,¹⁶ using a Na^+ (Metrohm, 6.0501.100) or a $K^+(Rb^+)$ (Ingold, pK271) selective electrode, and a $Ag/AgCl$ electrode as a reference electrode. The electrodes were calibrated daily in standard cation solutions.

All solutions were prepared using a methanolic stock solution of constant ionic strength (0.10 M Et_4NCl), to which 5.05 g/L triethylamine was added in order to prevent interference of H^+ ions.

The titrations were carried out in a thermostated cell at 25.0±0.1 °C under a nitrogen atmosphere. In a typical experiment 0.05 M crown ether dissolved in MeOH was added in 10-15 increments from a 250 μ L Hamilton syringe to 20.00 mL of a 0.001 M salt solution. Between every addition a 2 minute waiting time was maintained. Each emf measurement (± 0.1 mV) was obtained at constant stirring speed. In this way at least 10-12 data points were collected which were used for the final iterative calculation of the association constants by the SUPERQUAD program²⁷ on a DEC 2060 computer. 1:1 complexation was observed in all cases and indications for 2:1 or other stoichiometries were absent (SUPERQUAD offers facilities to test various models).

For the Li^+ , Cs^+ , Ba^{2+} , and Ga^{3+} ions a competition method¹⁶ was used with K^+ as indicator ion in solutions with approximately equimolar amounts of cation and potassium chlorides. In the case of the guanidinium salts a 10-fold excess of this salt was used because of the relatively small association constants of the complexes. In general log K values between 1 and 5.5 can be determined by the method described in this paper.

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- (9) Whenever was possible codes were used in order to name the macrocycles and distinguish between the various structural isomers. Abbreviations: D = di, B = benzo, P = pyrido, C = crown. In the presence of several functionalities the numbers of hetero atoms between the functionalities (p,q) are indicated as follows: [p,q].
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