

- (34) It is unlikely that Co-Cl charge transfer would appear below $3.4 \mu\text{m}^{-1}$.
- (35) Spectrum 4A shows incomplete formation of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and deviation from the isobestic point because PhS^- is deficient.
- (36) Other possible complexes are $[\text{Co}_n(\text{SPh})_{3n}]^{n-}$.
- (37) This experiment included solutions with $\text{PhS}^-/\text{CoBr}_4^{2-}$ ratios at close intervals; representative key spectra only are drawn in Figure 5.
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A Calorimetric Titration Study of the Reaction of Several Organic Ammonium Cations with 18-Crown-6 in Methanol^{1a}

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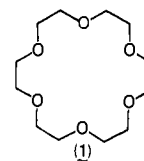
Abstract: Log K , ΔH , and $T\Delta S$ were determined by titration calorimetry for reaction of over 30 organic ammonium cations (guests) with 18-crown-6 (host) in methanol at 25 °C. The number of hydrogen atoms on the ammonium group available for bonding to the crown ether was the most important factor in determining complex stability. Steric hindrance of the approach of the guest to the host was also influential. Electronic factors showed no significant effect. Separation of charges on diammonium cations of varying chain length also had little effect on complex stabilities.

Introduction

Host-guest interaction has been termed² "a complementary stereoelectronic arrangement of binding sites in host and guest". In the chemical sense the host is usually an organic molecule containing specific receptor sites while the guest is normally a metal or organic cation. Host-guest interactions have recognized importance in many biological processes, including enzyme catalysis and inhibition, antibody-antigen interactions, and membrane transport. A particularly fruitful field of organic synthesis during the past several years has been the design and preparation of macrocyclic molecules of the cyclic polyether type with the intent to mimic certain biological host-guest interactions.²⁻¹¹ Cram and his co-workers⁴ as well as others^{6,7} have incorporated chiral barriers in host compounds which make possible "chiral recognition" between guest and host. By this means, the total optical resolution of host by guest and of guest by host has been accomplished.⁴ Several workers have reported the attachment of organic ammonium¹³ or sulfonium⁹ groups to hosts which are analogues of 18-crown-6 with the subsequent enhancement of a reaction between host and guest components away from the site of primary binding. Because of their ability to differentiate among inorganic cations and organic stereoisomers, these "functionalized crown ethers" have been suggested as model compounds for the investigation of mechanisms of enzyme action. Indeed Chao and Cram¹³ have reported a system which mimics transacylation.

We have attempted to define and investigate the parameters which determine the magnitude of log K for the formation of host-guest complexes from their constituents. Our earlier

studies have involved primarily metal cation guests. However, we have now embarked on a systematic thermodynamic study of these host-guest parameters as they apply to organic cations.¹⁴ Host parameters of importance in binding both metals and organic ammonium cations include cavity size, donor atom number and type, ring number and type, ring substituents, and ring conformation. Guest parameters for organic ammonium cations differ from those of metal cations because of the different binding mechanisms involved for the two types of guest. Metal cations are sequestered within the macrocyclic ring, whereas ammonium cations hydrogen bond to the ring donor atoms. Thus, guest parameters significant to organic ammonium cation binding include (1) number of hydrogen atoms available for hydrogen bonding, (2) steric hindrance of host-guest approach by the guest organic moiety, (3) electronic effects, and (4) separation of charges on diammonium cations of the type $^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$. In this paper we illustrate the effect of these four guest parameters on log K , ΔH , and $T\Delta S$ data for the reaction in methanol of over 30 organic ammonium cation guests with 18-crown-6 host (1).



The importance to host-guest interaction of the guest and host parameters listed has been alluded to previously by other workers. Log K values for the interaction of several derivatives

Table I. Log K , ΔH , and $T\Delta S$ Values^a for Reaction of 18-Crown-6 with Several Organic Ammonium Cations^b in Methanol at 25 °C

cation ^b	anion ^c	log K	ΔH , kcal/mol	$T\Delta S$, kcal/mol
RNH ₃ ⁺ Cations				
NH ₄ ⁺ (99.3 ± 0.9)	I ⁻	4.27 ± 0.02	-9.27 ± 0.18	-3.44
HONH ₃ ⁺ (97.6 ± 2.2)	Cl ⁻	3.99 ± 0.03	-9.01 ± 0.21	-3.57
NH ₂ NH ₃ ⁺ (98 ± 2)	Cl ⁻	4.21 ± 0.02	-10.43 ± 0.09	-4.69
CH ₃ NHNH ₃ ⁺ (97.2 ± 0.3)	Cl ⁻	3.41 ± 0.02	-9.49 ± 0.21	-4.84
CH ₃ NH ₃ ⁺ (96.3 ± 0.9)	I ⁻	4.25 ± 0.04	-10.71 ± 0.17	-4.91
CH ₃ CH ₂ NH ₃ ⁺ (98.3 ± 1.0)	I ⁻	3.99 ± 0.03	-10.65 ± 0.10	-5.21
CH ₃ CH ₂ OC(O)CH ₂ NH ₃ ⁺ (98.4 ± 1.0)	Cl ⁻	3.84 ± 0.04	-9.20 ± 0.09	-3.96
CH ₃ (CH ₂) ₂ NH ₃ ⁺ (98.9 ± 1.2)	I ⁻	3.97 ± 0.07	-10.06 ± 0.06	-4.64
CH ₃ (CH ₂) ₂ NH ₃ ⁺ (98.1 ± 0.8)	CH ₃ SO ₃ ⁻	3.90 ± 0.04	-9.85 ± 0.19	-4.53
CH ₂ CHCH ₂ NH ₃ ⁺ (97.9 ± 0.6)	CH ₃ SO ₃ ⁻	4.02 ± 0.03	-10.52 ± 0.17	-5.04
CHCCH ₂ NH ₃ ⁺ (97.6 ± 2.2)	CH ₃ SO ₃ ⁻	4.13 ± 0.02	-10.39 ± 0.17	-4.76
(CH ₃) ₂ CHNH ₃ ⁺ (96 ± 2)	I ⁻	3.56 ± 0.03	-9.65 ± 0.17	-4.79
CH ₃ CH ₂ OC(O)- CH(CH ₃)NH ₃ ⁺ (96.5 ± 0.8)	Cl ⁻	3.28 ± 0.02	-8.25 ± 0.21	-3.77
2 (95.4 ± 0.9)	I ⁻	3.90 ± 0.01	-10.12 ± 0.06	-4.80
(CH ₃) ₃ CNH ₃ ⁺ (96.8 ± 1.9)	I ⁻	2.90 ± 0.03	-7.76 ± 0.08	-3.80
PhCH(CH ₃)NH ₃ ⁺ (95.6 ± 0.9)	I ⁻	3.84 ± 0.01	-9.52 ± 0.13	-4.28
PhNH ₃ ⁺ (98.5 ± 0.8)	Br ⁻	3.80 ± 0.03	-9.54 ± 0.14	-4.36
2-CH ₃ C ₆ H ₄ NH ₃ ⁺ (96.0 ± 2.0)	Br ⁻	2.86 ± 0.03	-7.59 ± 0.15	-3.69
4-CH ₃ C ₆ H ₄ NH ₃ ⁺ (97.7 ± 1.6)	Br ⁻	3.82 ± 0.04	-9.92 ± 0.22	-4.71
2,6-(CH ₃) ₂ C ₆ H ₃ NH ₃ ⁺ (99.5 ± 0.3)	Br ⁻	2.00 ± 0.05	-5.65 ± 0.27	-2.92
3,5-(CH ₃) ₂ C ₆ H ₃ NH ₃ ⁺ (98.6 ± 0.8)	I ⁻	3.74 ± 0.02	-9.07 ± 0.06	-3.97
R ₂ NH ₂ ⁺ Cations				
NH ₂ C(NH ₂)NH ₂ ⁺ (98.1 ± 1.2)	I ⁻	1.7 ± 0.2	-2.41 ± 0.22	-0.1
(CH ₃) ₂ NH ₂ ⁺ (97.5 ± 1.0)	I ⁻	1.76 ± 0.02	-6.67 ± 0.23	-4.27
(CH ₃ CH ₂) ₂ NH ₂ ⁺	I ⁻		<i>d</i>	
3 (99.4 ± 0.2)	I ⁻	1.98 ± 0.01	-7.36 ± 0.11	-4.66
4 (96.3 ± 0.7)	I ⁻	2.05 ± 0.02	-6.83 ± 0.19	-4.03
R ₃ NH ⁺ Cations				
(CH ₃) ₃ NH ⁺	I ⁻		<i>d</i>	
5	I ⁻		<i>d</i>	
R ₄ N ⁺ Cations				
(CH ₃) ₄ N ⁺	I ⁻		<i>d</i>	

^a Values are average of four to six independent determinations; uncertainties are standard deviations. ^b Value in parentheses is calculated purity of salt; see Procedure and Calculations. Uncertainties are standard deviations from the mean value. ^c Our results show no significant anion effect. ^d Heat produced in these reactions is so small that log K and ΔH cannot be calculated, leading to the conclusion that ΔH and/or log K is very small.

of 18-crown-6 with organic ammonium ions in aqueous⁶ and deuterated chloroform⁷ solutions have been reported. In addition, K values have been measured^{3,4} for the extraction of *tert*-butylammonium thiocyanate from water to chloroform using a variety of 18-crown-6 derivatives. Studies¹⁵ have also been made on the effect of the presence of antibiotic macrocycles such as valinomycin, nonactin, and gramicidin on the permeability of lipid bilayer membranes to various organic ammonium cations. It was found that the macrocycles increased permeability in proportion to the number of guest protons available for hydrogen bonding. Likewise, the permeability of bullfrog and rabbit gall-bladder membranes toward protonated organic amines increases according to the number of protons available for hydrogen bonding in the order R₃NH⁺ < R₂NH₂⁺ < RNH₃⁺. Results presented in this paper correlate well with these observations.

Experimental Section

Materials. The following chemicals were obtained from the indicated suppliers: HCl, HBr, HI, CH₃NH₂ (anhydrous gases, Matheson Gas Products); *n*-propylamine, isopropylamine, *o*-toluidine, morpholine, 1,6-hexanediamine, NH₄I, diethylamine (J. T. Baker); allylamine, monopropargylamine, *d*-(+)- α -methylbenzylamine, glycine ethyl ester hydrochloride, α -alanine ethyl ester hydrochloride, cyclopropylamine, 2,6-dimethylaniline, 3,5-dimethylaniline, pyrrolidine, quinuclidine hydrochloride, methylhydrazine monohydrochloride, methylhydroxylamine, 1,4-butanediamine, 1,5-pentanediamine (Aldrich); ethylamine, dimethylamine, trimethylamine, 1,3-pro-

panediamine (Eastman); *tert*-butylamine, *p*-toluidine, guanidine hydrochloride (Matheson Coleman and Bell); NaNO₃, KBr (Mallinckrodt); hydroxylamine (Baker and Adamson); HBF₄, hydrazine monohydrochloride (Ventron); aniline (Merck); Karl Fischer reagent, absolute acetone-free methanol (Fisher); **1** (Parish Chemical).

The ammonium salts used were prepared and/or recrystallized under anhydrous conditions. A typical preparation follows. Approximately 3–5 g of the amine was mixed with 100 mL of anhydrous diethyl ether. Anhydrous hydrogen halide gas was slowly bubbled through the ether solution, causing salt formation and subsequent precipitation. The ammonium salt was filtered from the ether solution under a dry atmosphere, washed with more diethyl ether, and then recrystallized from absolute ethanol/ether. In some cases, anhydrous methanol or 2-propanol was used as recrystallization solvent. The purified salt was washed with ether and dried in vacuo. The purities of the recrystallized ammonium salts were checked by melting points and by calculating end points for the calorimetric data.

Procedure and Calculations. The calorimetric determinations were made at 25 °C using a precision isoperibol titration calorimeter. The calorimeter description, general experimental procedure, and method of calculating log K and ΔH values from the calorimetric data are available.^{16,17}

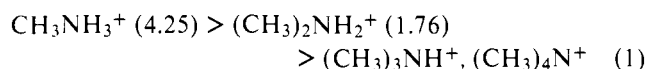
The various guests were allowed to interact with the host (**1**) in absolute, acetone-free methanol. The solution of **1** was standardized calorimetrically against a standardized methanol solution of KBr and found to be better than 99% pure. During data analysis, the concentrations of ammonium salt solutions were adjusted for purity using a computer program which independently determined the best salt concentration. Log K and ΔH results represent the average of four to six independent determinations; reported errors are the standard

deviations from the average. Water content of the methanol was found to be less than 0.05% from a Karl Fischer titration.

Results and Discussion

Log K , ΔH , and $T\Delta S$ for the interaction of 18-crown-6 (**1**) with the organic ammonium cations studied are listed in Table I. The effect of the four guest parameters listed in the Introduction on the strength of host-guest binding will be examined under individual headings. The most notable features of the data are the strength of the complexes formed and the sensitivity of binding strength to the steric properties of the cation. From the fact that changing concentrations and anions caused statistically insignificant changes in the log K or ΔH values, it was concluded that ion pairing effects in methanol were negligible (see Table I, $\text{CH}_3(\text{CH}_2)_2\text{NH}_3^+$).

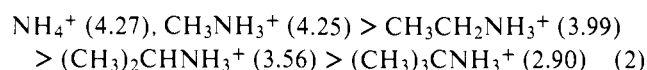
Number of Hydrogen Bonds. The log K data in Table I show that reduction in the number of hydrogen bonds available for host-guest interaction results in decreased stability of the complexes as shown in the sequence



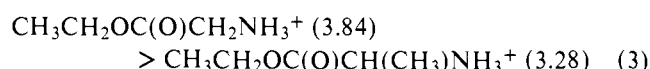
The decrease in log K (values in parentheses) in this series is paralleled by a decrease in ΔH , while $T\Delta S$ remains essentially constant. The biologically important guanidinium cation, $\text{NH}_2\text{C}(\text{NH}_2)\text{NH}_2^+$, behaves similarly to $(\text{CH}_3)_2\text{NH}_2^+$. The unusually small ΔH and $T\Delta S$ values for the formation of the guanidinium complex are likely due to the presence of a more highly ordered and tightly bound solvation shell in the free guanidinium ion which is disrupted upon complexation. This effect should be smaller among the more hydrophobic organic ammonium cations.

A striking feature of the data in Table I is the similarity of log K , ΔH , and $T\Delta S$ for the reaction of NH_4^+ and CH_3NH_3^+ with **1**. Figure 1 illustrates the known mode of binding of the ammonium cation to **1**.¹⁸ Apparently the increased bulk and larger cation size of CH_3NH_3^+ are relatively unimportant to complex formation. Rather, our results lead to the conclusion that the number of hydrogen bonds formed upon complexation is the most important factor in determining complex stability.

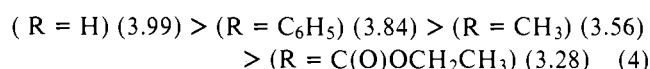
Steric Hindrance of Guest Groups. From the information given above, all cations having the $-\text{NH}_3^+$ group might be expected to complex **1** more or less equally. We tested this hypothesis by reacting a homologous series of aliphatic and aromatic $-\text{NH}_3^+$ -type cations with 18-crown-6. In these series we increased the steric bulk of the R group (Figure 1) attached to the $-\text{NH}_3^+$ group. The trend in log K and ΔH of reaction for the aliphatic species is shown in the sequence



This same trend is seen for the two amino acid esters studied, as shown in the sequence



Increasing steric bulk on the α carbon results in a loss of complex stability. A comparison of the binding of $\text{RCH}(\text{CH}_3)\text{NH}_3^+$ to **1** gives the trend in log K values found in the sequence



This trend is probably the result of steric factors and suggests that the benzene ring can orient itself so as to interfere less with complexation than do the other organic groups.

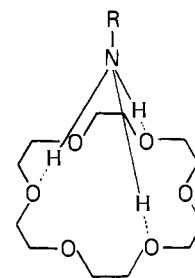
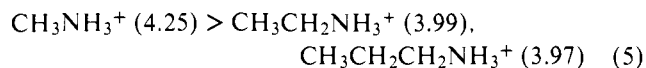
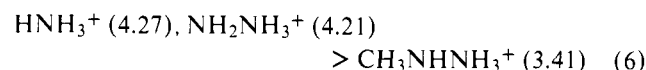


Figure 1. Binding of ammonium cation to 18-crown-6.¹⁸

Sequence 5 illustrates that lengthening the chain of the R group (Figure 1) beyond the α carbon does not appreciably alter complex stability.

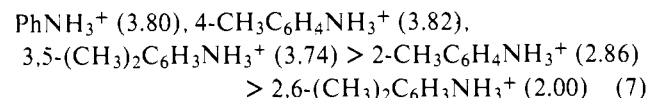


However, for the hydrazinium cation, methyl substitution on the α nitrogen results in a loss of complex stability as shown in the sequence

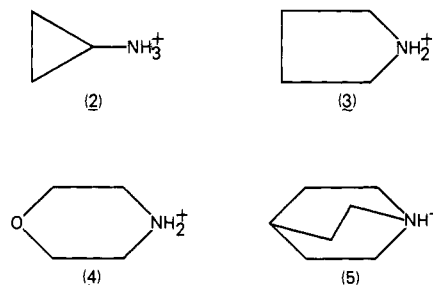
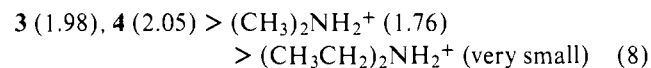


The similarity of NH_4^+ and NH_2NH_3^+ binding constants suggests that electronic effects are unimportant and that the reduced binding of methylhydrazinium ion is a result of steric factors. A curious result is the similarity in log K values for CH_3NH_3^+ (4.25) and NH_2NH_3^+ (4.21) contrasted with the significantly different values for $\text{CH}_3\text{CH}_2\text{NH}_3^+$ (3.99) and $\text{CH}_3\text{NHNH}_3^+$ (3.41). Although these results are difficult to explain, selective solvation by methanol probably is a major factor. This is also the probable cause of the somewhat weaker binding of HONH_3^+ compared to that of either NH_2NH_3^+ or CH_3NH_3^+ .

In the aromatic anilinium series, increasing the organic bulk in the 2 and 6 positions results in a loss of complex stability. The presence of methyl groups in the 3, 4, and 5 positions has no effect, as illustrated in the sequence



That the binding constant of PhNH_3^+ is 0.4 log K unit smaller than that of CH_3NH_3^+ suggests that even the ortho hydrogen atoms in the phenyl groups weakly destabilize the complex. Trends similar to those in sequences 2-5 for NH_3^+ cations are also observed among $-\text{NH}_2^+$ ammonium cations as shown in the sequence



Sequences 2 and 8 show that steric bulk is a hindrance to complexation only inasmuch as it is allowed to interfere directly with the site of complexation. Space-filling CPK models show

Table II. Log K , ΔH , and $T\Delta S$ Values for the Reaction of Several Diammonium Cations with 18-Crown-6 in Methanol at 25 °C^a

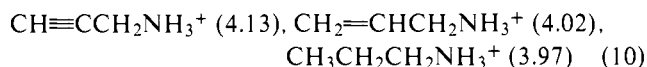
cation	i	log K_i	ΔH_i , kcal/mol	$T\Delta S_i$, kcal/mol
$^+\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3^+$	1	3.05 ± 0.16	-11.8 ± 0.5	-7.7
	2	6.80 ± 0.18	-22.4 ± 0.5	-13.1
$^+\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^+$	1	3.20 ± 0.14	-12.4 ± 0.4	-8.0
	2	6.99 ± 0.13	-21.6 ± 0.4	-12.1
$^+\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3^+$	1	3.51 ± 0.06	-10.0 ± 0.1	-5.2
	2	6.98 ± 0.11	-21.7 ± 0.5	-12.2
$^+\text{H}_3\text{N}(\text{CH}_2)_5\text{NH}_3^+$	1	3.1 ± 0.3	-11.2 ± 1.0	-7.0
	2	6.6 ± 0.6	-21.9 ± 1.3	-12.9
$^+\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3^+$	1	3.3 ± 0.2	-10.7 ± 1.0	-6.2
	2	7.19 ± 0.16	-20.6 ± 0.2	-10.8

^a $\text{Am}^{2+} + i\text{L} = \text{AmLi}^{2+}$; $i = 1, 2$; anion = I^- . Values are average of four to six independent determinations; uncertainties are standard deviations.

that steric bulk close to the $-\text{NH}_2^+$ portion of the molecule increases from left to right in sequence 8. The "tying back" of the alkyl substituents of **3** and **4** restricts their freedom to interfere with complexation. This same stability trend is seen for $-\text{NH}_3^+$ cations in the sequence



Electronic Effects. Unlike those of diazonium cations,¹⁹ the 18-crown-6 complexes of organic anilinium cations studied did not demonstrate a high degree of sensitivity to electronic effects. Similarly, the presence of remote C-C multiple bonds had little effect on the stability constants as illustrated in the sequence



Separation of Charges in Diammonium Cations. Log K , ΔH , and $T\Delta S$ values for the 1:1 and 2:1 ligand-metal reactions of **1** with diammonium cations of the structure $^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$ where $n = 2-6$ are listed in Table II. The 1:1 parameters have values close to those for $\text{CH}_3\text{CH}_2\text{NH}_3^+$. The 2:1 log K and ΔH values are roughly double those for the 1:1 reaction. For this reason, we were unable with the calorimetric titration technique to resolve these quantities to a high degree of accuracy. It may be concluded, however, that the separation of charges in diammonium cations has little effect on complex stability and that each ammonium group complexes with 18-crown-6 more or less independently of the ammonium group at the other end of the molecule. The most interesting cations in this series, $^+\text{H}_3\text{NCH}_2\text{NH}_3^+$ and $^+\text{H}_3\text{NNH}_3^+$, were not studied. We were unable to obtain the former and the latter dissociates to N_2H_5^+ and H^+ under our experimental conditions.

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