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# Various aspects of enantiomeric recognition of (*S,S*)-dimethylpyridino-18-crown-6 by several organic ammonium salts

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**Factors responsible for complex stability and enantiomeric recognition for the interactions of (*S,S*)-dimethylpyridino-18-crown-6 with several organic ammonium salts were examined using an $^1$H NMR technique. The results indicate that cation structures have a significant effect on enantiomeric recognition; solvents play a very important role in the stability of the complexes, and anions can compete with ligands for the ammonium cations.**

## INTRODUCTION

In the past decade, our interest in enantiomeric recognition has focused on the interactions of chiral macrocycles with chiral organic ammonium salts.[1–10] In an effort to identify, understand, and quantitate the factors responsible for these host-guest interactions, we have chosen the chiral pyridino-18-crown-6 ligand as a probe to study enantiomeric recognition under a variety of conditions such as at different temperatures and by changing the structure of the organic ammonium cation. The pyridino-crown system was chosen because pyridino-crowns form strong complexes with organic ammonium salts[11] and their chiral forms exhibit recognition for the enantiomers of chiral organic ammonium salts.[1–3]

Over thirty pyridine-containing chiral crown ethers with different substituents at the chiral centers have been prepared. These chiral crowns can have different functional groups on the ring, different donor atoms in the ring, and different substituents on the 4-position of the pyridine subunit.[4] The interactions of these chiral ligands with several chiral organic ammonium salts have been reported.[12–14]

An extensive study of enantiomeric recognition of one chiral organic ammonium salt, [α-(1-naphthyl)ethyl] ammonium perchlorate, by many different chiral ligands has been carried out.[12–14] The companion study of recognition by one chiral pyridino-18-crown-6 ligand with chiral organic ammonium salts with varying organic structures and various anions and in different solvents has not been reported.

This paper describes the effects of cation structure and of varying the anions and solvents on the interaction of chiral dimethylpyridino-18-crown-6 ($Me_2$P18C6, see Figure 1) with chiral organic ammonium salts. These effects were evaluated from the log $K$ values. $\Delta G$, $\Delta H$, and $\Delta S$ values were also determined for one of the reactions. An NMR structural analysis of the complexes of $Me_2$P18C6 with (*R*)- and (*S*)-[α-(1-naphthyl)ethyl] ammonium perchlorate (NapEtHClO$_4$) has been reported.[9] This ligand ($Me_2$P18C6) was chosen because it is stable in various solvent systems and it exhibited enantiomeric recognition in previous studies.

## RESULTS AND DISCUSSION

*Effect of cation structure.* In a complex of a macrocyclic ligand and an organic ammonium ion, there are hydrogen bonding, electrostatic, π-π, and steric interactions between the ligand and the guest. The bulkiness of the guest molecule, the size of the π system, and the extent of charge distribution in the guest molecule influence the stability of the complex and enantiomeric recognition. In order to study the effect of cation structure on the magnitude of enantiomeric recognition, the interactions of (*S,S*)-$Me_2$P18C6 with the enantiomeric forms of NapEtHClO$_4$, (α-phenylethyl)ammonium perchlorate

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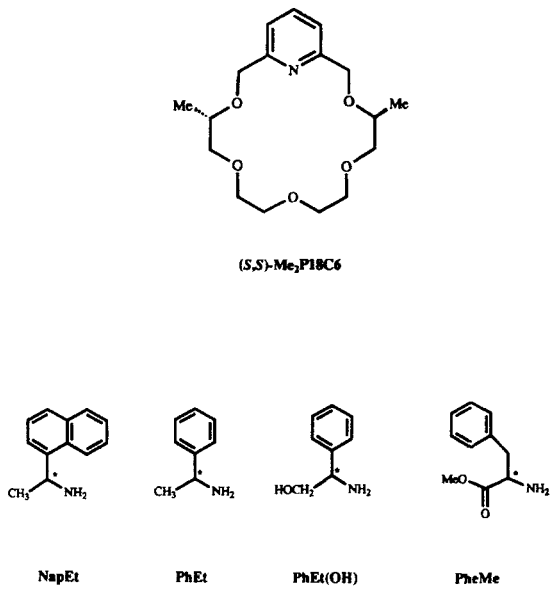


**Figure 1** Structures of (*S,S*)-dimethylpyridino-18-crown-6 and chiral organic amines.

($PhEtHClO_4$), the hydrogen perchlorate salt of methyl phenylalaninate ($PheMeHClO_4$), and the hydrogen perchlorate salt of 2-amino-2-phenylethanol ($PhEt(OH)HClO_4$) (see chiral amine structures in Figure 1) were investigated. $NapEtHClO_4$ was selected because it has a more extended $\pi$ system than $PhEtHClO_4$ allowing a comparison of the complex stability and enantiomeric recognition with different $\pi$ systems. $PhEt(OH)HClO_4$ was selected in order to study the effect of the hydroxyl group on enantiomeric recognition. $PheMeHClO_4$ was used because it has a larger group ($-CO_2CH_3$) at its chiral center which could change enantiomeric recognition relative to other systems studied.

Table 1 lists the log $K$ values determined at 25°C by an $^1H$ NMR technique[7] together with $\Delta\log K$ values for the interactions of (*S,S*)-$Me_2P18C6$ with the four guests in a mixed $CD_3OD$-$CDCl_3$ (1M/1C, v/v) solvent system. The largest log $K$ values and the highest enantiomeric recognition ($\Delta\log K = 0.54$) were found for the interactions of (*R*)- and (*S*)-$NapEtHClO_4$ with the ligand. The interactions of the ligand with the enantiomers of $PhEtHClO_4$ gave a lesser amount of enantiomeric recognition ($\Delta\log K = 0.33$), indicating that the $\pi$ system in the guest plays an important role in enantiomeric recognition. The presence of $\pi$-$\pi$ stacking in these complexes has been illustrated by $^1H$ NMR NOESY spectra and molecular mechanics calculations.[9] The $\pi$-$\pi$ interaction has also been illustrated in other systems.[15] Interactions of the ligand with the enantiomers of $PhEt(OH)HClO_4$ gave little or no enantiomeric recognition ($\Delta\log K = -0.06$). As mentioned above, $\pi$-$\pi$ stacking is very important for enantiomeric recognition. The hydroxyl group in the $PhEt(OH)HClO_4$ guest could weaken the $\pi$-$\pi$ stacking in this system by hydrogen bonding to one of the oxygen atoms on the ring leading to poor recognition. Interactions of the ligand with the enantiomers of $PheMeHClO_4$ also gave little or no enantiomeric recognition ($\Delta\log K = -0.09$). In this case, the $\pi$ system of $PheMeHClO_4$ is one carbon unit away from its chiral center resulting in poor or no $\pi$-$\pi$ stacking in the complex. Also, there is a larger group ($-CO_2CH_3$) in $PheMeHClO_4$ which could weaken the $\pi$-$\pi$ interaction.

**Table 1** Log $K$ values for the interactions of (*S,S*)-$Me_2P18C6$[a] with the enantiomers of several organic ammonium perchlorates in a 1M/1C[b] mixed solvent at 25°C

| *Cation*[c] | *Salt Config.* | *log K*[d] | *Δ log K* | *Ref.* |
|---|---|---|---|---|
| $NapEtHClO_4$ | *R* | 3.96(5) | | |
| | *S* | 3.42(5) | 0.54 | |
| $PhEtHClO_4$ | *R* | 3.62(5) | | |
| | *S* | 3.29(5) | 0.33 | 12 |
| $PhEt(OH)HClO_4$ | *R* | 3.21(5) | | |
| | *S* | 3.27(5) | -0.06 | 12 |
| $PheMeHClO_4$ | *R* | 3.02(5) | | |
| | *S* | 3.11(5) | -0.09 | 12 |

[a](*S,S*)-$Me_2P18C6$ = (*S,S*)-Dimethylpyridino-18-Crown-6. [b]M = $CD_3OD$, C = $CDCl_3$. [c]$NapEtHClO_4$ = [α-(1-naphthyl)ethyl]ammonium perchlorate; $PhEtHClO_4$ = α-phenylethyl-ammonium perchlorate; $PhEt(OH)HClO_4$ = the hydrogen perchlorate salt of 2-amino-2-phenylethanol; $PheMeHClO_4$ = the hydrogen perchlorate salt of methyl phenylalaninate. [d]Uncertainties are indicated in the parentheses following each value.

*Effect of solvent.* The effect of solvent on complex stability is pronounced. The macrocyclic ring replaces solvent molecules in the solvation shell of the cations, and solvent must be regarded as a reagent participating in the complexation reaction. The effect of solvent on interactions of macrocycles with metal cations has been reported.[16–18] The effect of solvent on complex stability and enantiomeric recognition for the interactions of other chiral macrocycles with chiral organic ammonium salts has also been reported.[19] In this work, the interactions of (*S,S*)-$Me_2P18C6$ with the enantiomers of $NapEtHClO_4$ were examined using a number of different solvents and one solvent mixture. The choice of solvents was primarily dictated by the desire to compare several media of different donor ability as well as to have complexes in the correct stability range so that the $^1H$ NMR titration procedure can give accurate results. As shown in Table 2, the log $K$ values clearly illustrate the important influence of the solvent on complex stability. As expected,[14] the magnitude of the dielectric constant does not seem to have a notable effect on the stability of the complexes. On the other hand, the donor number of the solvent expressed by the Gutmann donor number[20,21] is in-

**Table 2** Log $K$ values for the interaction of the $(S,S)$-$Me_2P18C6$[a] with the enantiomers of $NapEtHClO_4$[b] in various solvents and one solvent mixture at 25°C

| Solvent[c] | Salt Config. | log $K$[f] | $\Delta$ log $K$ | Ref. | Solvent Parameters[g] $\varepsilon_r$ | $E_T$ | DN | AN |
|---|---|---|---|---|---|---|---|---|
| DMSO | R | N/O[d] | | | 46.45 | 0.444 | 29.8 | 19.3 |
| | S | N/O | | | | | | |
| M | R | 3.12(5) | | | 32.66 | 0.762 | 19.0 | 41.5 |
| | S | 2.72(6) | 0.40 | | | | | |
| DM[e] | R | 3.46(5) | | | | | | |
| | S | 3.20(5) | 0.26 | | | | | |
| C | | | | | 4.81 | 0.259 | 4.0 | 23.1 |
| 1M/1C | R | 3.96(5) | | | | | | |
| | S | 3.42(5) | 0.54 | | | | | |
| AN | R | 4.64(6) | | | 35.94 | 0.460 | 14.1 | 18.9 |
| | S | 4.10(5) | 0.54 | 12 | | | | |

[a]See footnote a in Table 1. [b]See footnote b in Table 1. [c]DMSO = Deuterated dimethylsulfoxide; M = $CD_3OD$; C = $CDCl_3$; DM = $CD_2Cl_2$; AN = $CD_3CN$. [d]N/O = no observable interaction. [e]NapEtHTs {[α-(1-naphthyl)ethyl]ammonium tosylate} was used because $NapEtHClO_4$ was not soluble in DM. [f]Uncertainties are indicated in the parentheses following each value. [g]$\varepsilon_r$ = dielectric constant, $E_T$ = empirical polarity, DN = Gutmann donor number, AN = Gutmann acceptor number.

versely proportional to complex stability. No interaction could be observed in DMSO which has the largest donor number (29.8). The strongest interaction was observed in acetonitrile which has the smallest Gutman donor number (14.1). Solvents of higher donicity have a stronger solvation ability towards ammonium cations. Hence, they destabilize the complexes formed between the macrocycle ligands and the ammonium cations.

*Effect of anion.* Anions affect the complexation of macrocycles with metal cations.[22–25] The effect is probably due to the difference in the types of ion pairs in solution. It is believed that anions in contact ion pairs can compete with ligands for the cations, which would lower complex stability. In the case of interactions of macrocycles with organic ammonium cations, if the anion and ammonium cation form contact ion pairs, the anion will undoubtedly compete with the ligand for the ammonium cation leading to a decrease in complex stability. In most cases, the effect of the anion can be ignored for the interactions of macrocycles with ammonium salts. First, anion-ammonium cation contact ion pairs are not the primary species in most solutions. Second, an ion pair is formed between the anion and the cation-ligand complex. This balances the negative effect of the anion-ammonium cation ion pair. Experimentally, when the effect of anions is negligible, the observed chemical shifts (paramagnetic or diamagnetic) vary linearly with the mole ratio of the ligand and the ammonium cation until a mole ratio of 1:1 is reached. Further addition of the ligand does not change the chemical shifts indicating the formation of a strong 1:1 complex. For weak complexation, the chemical shifts do not reach a limiting value even at fairly high mole ratio values. However, the experimental data fit a simple 1:1 single reaction model in both cases. When the anion effect is significant, the data do not fit a simple model implying that a complicated reaction occurs.

The data for the interactions of $(S,S)$-$Me_2P18C6$ with four different anion salts of NapEt shown in Table 3 indicate that the simple 1:1 reaction model works well for all four systems. This indicates that the anion effect is too small to have a significant impact in this solvent. However, the anion effect was clearly observed in $CDCl_3$ for the interaction of the ligand with the enantiomers of NapEtHTs because the experimental data do not fit the simple 1:1 reaction model. It is possible that contact ion pairs are formed in this solvent because $CDCl_3$ has a lower dielectric constant which favors contact ion pair formation. As shown in Table 3, changing the counteranion of the ammonium salt does affect complex stability (3.96-3.48) and enantiomeric recognition (0.54- 0.35) in these systems. We are not sure why these changes in stability are occuring.

*Free energy, enthalpy and entropy changes for the complexation reactions.* In order to determine the free energy, enthalpy and entropy changes, complex stability constants were measured as a function of temperature in 1M/1C (v/v). The data are given in Table 4. Obviously, lowering the temperature increases the stabilities of the complexes. A plot of log $K$ vs. $1/T$ for this interaction is shown in Figure 2. The changes in enthalpy and entropy were obtained in the usual manner from the slopes and the intercepts of the plots and the results are given in Table 5. The data show that the complex is enthalpy stabilized and entropy destabilized for the interaction of $(S,S)$-$Me_2P18C6$ with $(R)$-$NapEtHClO_4$ [$(S,S)$-$(R)$] and is both enthalpy and entropy stabilized for the interaction of the $(S,S)$-$Me_2P18C6$ with $(S)$-$NapEtHClO_4$ [$(S,S)$-$(S)$].

**Table 3** Log $K$ values for the interactions of the $(S,S)$-$Me_2P18C6$[a] with the enantiomers of $NapEtH^+$[b] with different anions in 1M/1C[c] at 25°C

| Anion[d] | Salt config. | log $K$[e] | $\Delta$ log $K$ |
|---|---|---|---|
| $ClO_4^-$ | R | 3.96(5) | |
| | S | 3.42(5) | 0.54 |
| $tBuSO_3^-$ | R | 3.48(5) | |
| | S | 3.02(5) | 0.46 |
| $Ts^-$ | R | 3.61(5) | |
| | S | 3.17(5) | 0.44 |
| $Pic^-$ | R | 3.73(5) | |
| | S | 3.38(5) | 0.35 |

[a]See footnote a in Table 1. [b]See footnote c in Table 1. [c]See footnote b in Table 1. [d]$Ts^-$ = Tosylate; $Pic^-$ = Picrate. [e]Uncertainties are indicated in the parentheses following each value.

**Table 4** Log $K$ values for the interactions of $(S,S)$-$Me_2P18C6$[a] with the enantiomers of $NapEtHClO_4$[b] in 1M/1C[c] at different temperatures

| $T(^\circ K)$ | *Salt Config.* | *log K*[d] | *Δ log K* |
|---|---|---|---|
| 283 | *R* | 4.18(5) | |
| | *S* | 3.58(5) | 0.60 |
| 298 | *R* | 3.96(5) | |
| | *S* | 3.42(5) | 0.54 |
| 313 | *R* | 3.65(5) | |
| | *S* | 3.24(5) | 0.41 |
| 323 | *R* | 3.38(5) | |
| | *S* | 3.17(5) | 0.21 |

[a]See footnote a in Table 1. [b]See footnote c in Table 1. [c]See footnote b in Table 1. [d]Uncertainties are indicated in the parentheses following each value.

Although the uncertainty of the data obtained through this procedure is relatively high,[7] some useful information can be obtained from these results. It is well known that a free ligand is more flexible than the complexed one. The conformation changes from the free to the complexed ligand should result in a negative $\Delta S$ value. Because the $(S,S)$-$(R)$ complex has a better fit than the $(S,S)$-$(S)$ complex, a greater negative $\Delta S$ value was obtained for the $(S,S)$-$(R)$ complexation reaction. The almost zero $\Delta S$ for the $(S,S)$-$(S)$ complexation reaction means that the conformation change of the ligand in this complexation reaction is small. In other words, the $(S,S)$-$(S)$ complex is much looser than the $(S,S)$-$(R)$ complex.

## EXPERIMENTAL

**Materials**. $(S,S)$-$Me_2P18C6$, $NapEtHClO_4$, $PhEtHClO_4$, $PheMeHClO_4$ and $PhEt(OH)HClO_4$ (see structures in Figure 1) were prepared as reported.[3,7,12] Solvents

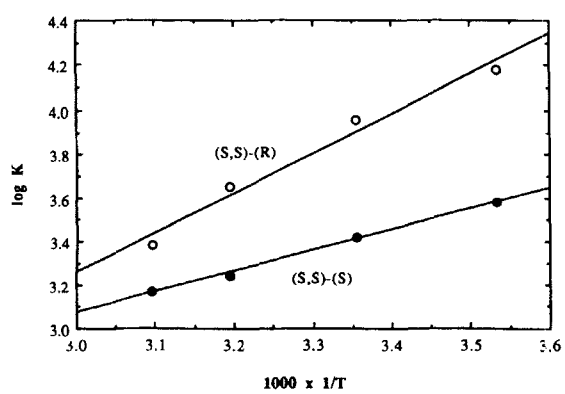


**Figure 2** Plot of log $K$ vs. $T^{-1}$ for the interaction of $(S,S)$-dimethylpyridino-18-crown-6 with $(R)$-[α-(1-naphthyl)ethyl]ammonium perchlorate (circle) and the $(S)$-perchlorate (solid) in a 50% $CD_3OD$ + 50% $CDCl_3$ mixed solvent.

**Table 5** free energy change ($\Delta G$ kcal/mol), enthalpy change ($\Delta H$ kcal/mol) and entropy change($\Delta S$ cal/K.mol) values for the interactions of $(S,S)$-$Me_2P18C6$[a] with the enantiomers of $NapEtHClO_4$[b] in a 1M/1C[c] mixed solvent

| *Salt Config.* | *ΔG (25°C)*[d] | *ΔH*[d] | *ΔS*[d] |
|---|---|---|---|
| *R* | -5.4 | -8.4 | -10.2 |
| *S* | -4.7 | -4.4 | 0.7 |

[a]See footnote a in Table 1. [b]See footnote c in Table 1. [c]See footnote b in Table 1. [d]The estimated uncertainties of the $\Delta G$, $\Delta H$ and $\Delta S$ values are around ±15% according to our previous paper.[7]

$CD_3OD$ (M), DMSO-$d_6$, $CDCl_3$(C) and $CD_3CN_3$(AN) were purchased from Aldrich Chemical Co. and used without further purification. The *t*-butanesulfonate salt of NapEt ($NapEtHtBuSO_3$), tosylate (NapEtHTs), and picrate (NapEtHPic) were prepared according to the procedure described below.

**Synthesis of (*R*)- and (*S*)-α-(1-naphthyl)ethylammonium tert-butanesulfonate** ($NapEtHtBuSO_3$). To a stirred solution of 1.0 g (5.84 mmol) of $(R)$- or $(S)$-α-(1-naphthyl)ethylamine in 20 mL of THF was added dropwise 0.81 g (5.86 mmol) of tert-butanesulfonic acid dissolved in 20 mL of THF at room temperature. After addition, white crystals were separated. The reaction mixture was cooled in a refrigerator for one day and the crystals were filtered. Recrystallization from THF gave the pure ammonium salt. The structure was confirmed by a $^1H$ NMR spectrum.

The $(R)$- and $(S)$-α-(1-naphthyl)ethylammonium tosylate (NapEtHTs) and picrate (NapEtHPic) salts were prepared in a similar manner. Since the picrate salt is more soluble in THF, the THF was removed under reduced pressure after the reaction was completed. The crude picrate salt was recrystallized from methanol to give pure yellow crystals. The structure was confirmed by a $^1H$ NMR spectrum.

**Determination of log *K* values by the $^1H$ NMR method**. The log $K$ values listed in Tables 2, 3 and 4 were determined by a method similar to that reported.[7,26] A sample containing a few milligrams of chiral crown ether in a known volume of solvent was first loaded into the probe and a spectrum was taken. The sample was then unloaded, added to the sample tube with 0.05 mL of standard chiral ammonium salt solution, reloaded into the probe and another spectrum was taken. This procedure was repeated until no significant change was observed in successive $^1H$ NMR spectra. Usually, 8-12 spectra were taken for each log $K$ determination. The original chiral crown ether concentration was about 0.04 M and the ammonium salt concentration was varied from zero to 0.08 M for each experiment. In such an experiment, an accurately weighed quantity of the chiral crown ether was dissolved in a known volume of solvent. The concentrations of chiral ammonium salt and crown ether were calculated according to the volume in the tube and

the original concentration of each material. The log $K$ values were obtained from the variation of the observed chemical shift with the ammonium cation/ligand mole ratio.

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