# Influence of the ligand structure of macrocyclic diaza crown ethers on the complexation of Ag(I) in methanol

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(Received 17 April 1992)

## Abstract

Potentiometric and calorimetric methods were used to measure the stability constants and thermodynamic values for the complexation of $Ag^+$ with different diaza crown ethers in methanol solvent. The ligands were modified by different substituents at the nitrogen donor atoms. The substituents used have no additional donor atoms. However, for all reactions studied the substituted ligands give higher values of the reaction enthalpies than the unsubstituted ligands. The origin has to be assumed to be due to the differences in the solvation strengths of the ligands.

## INTRODUCTION

The complexation of cations by uncharged ligands in different solvents has been the subject of numerous articles. All known data were summarized recently by Izatt et al. [1]. The most frequent ligands studied are 18-crown-6 and the cryptand (222). In spite of the large number of experimental data it is mainly stability constants that are known. Less thermodynamical data are known. Without the knowledge of these thermodynamical parameters it is not possible to discuss whether the stability constants are influenced by the reaction enthalpies or by the reaction entropies when compared with other ligands.

In the case of the lariat ethers, changes in the stability constants due to additional donor atoms fixed in side chains of the macrocyclic ligands are discussed in terms of a lariat effect [2]. With few exceptions no thermodynamic data for the complexation reactions of these ligands have been published [3]. These results show only small enthalpic contributions to the measured reaction enthalpies. They are integrated as additional

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interactions of the complexed cations with the donor atoms in the side chains of the ligands.

To study the effect of different side chains on the complex stability we started to measure stability constants and thermodynamic data for the reaction of different substituted diaza crown ethers with silver(I). It is known that strong interactions between nitrogen donor atoms and silver ions take place. Therefore substitutions at the nitrogen donor atoms may result in measurable changes in the strengths of interactions if the charge distribution at this donor atom is being influenced.

EXPERIMENTAL

*Materials*

Anhydrous $AgNO_3$ of the highest purity (Merck) was used for all experiments.

The ligands (see Figs. 1 and 2) (22) (22DD) and (22DL) (all Merck) were used without further purification. The ligands (21TT) [4, 5], (22TT) [4, 5], (22BuBu) [6], (22OcOc) [6], ($22TT_p(NO_2)_2$) [7] and ($22TT_o(NO_2)_2$) [7] were synthesized and purified according to published procedures. The ligand (22BzBz) was synthesized by the reaction of ligand (22) with benzoyl chloride. The experimental details were identical with those reported for the synthesis of the ligand (22TT) (yield 81%) [4, 5]. The ligand (21DD) was synthesized according to published procedures [8].

As solvent anhydrous methanol (Merck; $H_2O$ content less than 0.01%) was used.
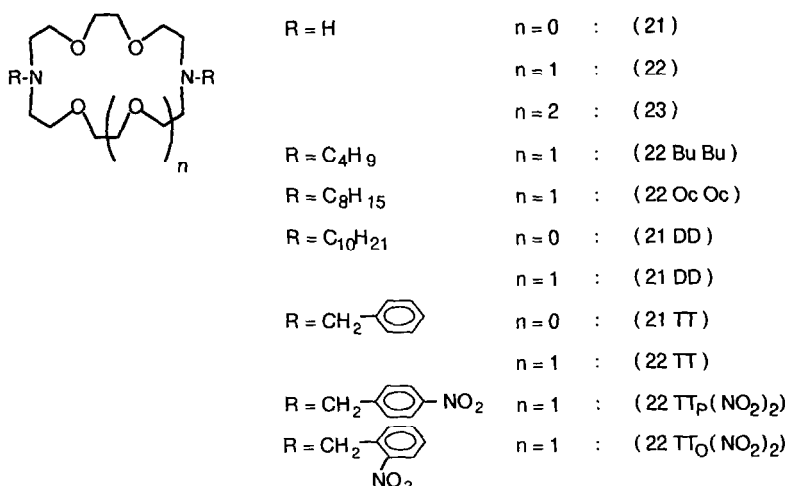


| | | |
|---|---|---|
| R = H | n = 0 | : (21) |
| | n = 1 | : (22) |
| | n = 2 | : (23) |
| R = $C_4H_9$ | n = 1 | : (22 Bu Bu) |
| R = $C_8H_{15}$ | n = 1 | : (22 Oc Oc) |
| R = $C_{10}H_{21}$ | n = 0 | : (21 DD) |
| | n = 1 | : (21 DD) |
| R = $CH_2$—⟨○⟩ | n = 0 | : (21 TT) |
| | n = 1 | : (22 TT) |
| R = $CH_2$—⟨○⟩—$NO_2$ | n = 1 | : ($22 TT_p(NO_2)_2$) |
| R = $CH_2$—⟨○⟩ $NO_2$ | n = 1 | : ($22 TT_o(NO_2)_2$) |

Fig. 1. Various diaza crown ethers used in this work.
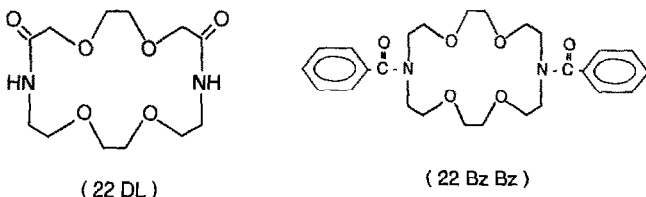
(22 DL)                    (22 Bz Bz)

Fig. 2. Various dilactam crown ethers used in this work.

## Procedure

Stability constants were measured by means of an ion selective electrode for silver(I) (Methrom EA 282). The experimental set-up has already been described in detail [4]. From the measured potentials during the titrations the activity of the uncomplexed $Ag^+$ ion was calculated using the Nernst equation [9]. The ionic strength is kept constant at $I = 0.05$ M using tetraethylammonium perchlorate as supporting electrolyte.

With the exception of the ligand (21) all ligands formed 1:1 complexes. Thus the following reaction between an $Ag^+$ ion and a ligand molecule L takes place
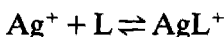
$$Ag^+ + L \rightleftharpoons AgL^+$$

The stability constant $K$ is given by

$$K = \frac{[AgL^+]}{[Ag^+][L]}$$

To estimate the reaction enthalpies calorimetric titrations using a Tronac Model 450 calorimeter were performed. A solution of the ligand (0.04–0.08 N) was titrated continuously into a solution containing the cation ($1 \times 10^{-3}$ to $5 \times 10^{-3}$ N). After correction for all non-chemical heat effects the reaction enthalpy can easily be calculated from the thermograms. Owing to the fact that all stability constants measured are higher than $10^5$ $M^{-1}$, the number of moles of the ligand added to the salt solution is equal to the number of moles $\Delta n$ of the complex formed. The measured heat $Q$ is related to the reaction enthalpy by

$$Q = \Delta H \cdot \Delta n$$

## RESULTS AND DISCUSSION

Values of the stability constants, reaction enthalpies and entropies for the complexation of $Ag^+$ with different ligands are summarized in Table 1.

No complex formation is observed with the ligands (22DL) and (22BzBz). The amide structure of both ligands are obviously responsible for this observation. No difference is found whether the amide group is part of the macrocyclic ligand or not. Owing to the electron withdrawing

TABLE 1

Log $K$ ($M^{-1}$), $\Delta H$ (kJ mol$^{-1}$), and $T\Delta S$ (kJ mol$^{-1}$) for the reaction of different ligands with $Ag^+$ in methanol at 25°C

| Ligand | log $K$ | $-\Delta H$ | $T\Delta S$ |
|---|---|---|---|
| (21) [a] | 7.63 | 34.6 | 8.8 |
| (22) [a] | 10.02 | 44.9 | 12.0 |
| (23) [a] | 9.60 | 53.4 | 1.1 |
| (22BzBz) | – | – | – |
| (22DL) | – | – | – |
| (21DD) | 9.78 | 65.0 | −9.4 |
| (21TT) | 8.95 | 54.6 | −3.7 |
| (22BuBu) | 10.01 | 60.5 | −3.6 |
| (22OcOc) | 10.20 | 62.3 | −4.3 |
| (22DD) [a] | 10.28 | 61.1 | −2.7 |
| (22TT) | 9.70 | 68.5 | −13.4 |
| (22TT$_p$(NO$_2$)$_2$) | 7.92 | 62.4 | −17.4 |
| (22TT$_o$(NO$_2$)$_2$) | 5.26 | 51.1 | −21.2 |

[a] From ref. 12.

effect of the carbonyl group the basicity of the nitrogen donor atoms is reduced. However, the ether donor atoms should be able to interact with the silver(I) cation. Under these circumstances it is surprising that no complex formation is observable. A possible explanation is that a mesomeric structure of the ligand with a partial positive charge at the nitrogen atom and a partial negative charge at the carbonyl group is stabilized by the formation of hydrogen bonds with the solvent methanol. This interpretation is supported by the experimental values of the reaction enthalpies for the diprotonation of both ligands: for ligand (22), $\Delta H = -113.7$ kJ mol$^{-1}$; for ligand (22BzBz), $\Delta H < 1$ kJ mol$^{-1}$ [10].

The substitution of the protons of the nitrogen donor atoms of the macrocyclic ligands by alkyl chains of different lengths or by the $-CH_2C_6H_5$ group leads in all cases to an increase in the values of the reaction enthalpies. Owing to the fact that these side chains do not contain additional donor atoms, no influence upon the reaction enthalpies is expected despite the possible inductive effect of the alkyl substituents. Thus, changes in the ligand solvation can be mainly responsible for these observations. The side chains at the nitrogen donor atoms obviously reduce the interactions between the diaza crown ethers and the solvent molecules. Therefore less energy is consumed during the complex formation with $Ag^+$ for the partial desolvation of the ligands with side chains.

If this explanation is correct, the values of the reaction entropies should also be influenced. As it can easily be seen from Table 1 the complex formation of the substituted ligands is not favored by the reaction

entropies. Owing to the reduced solvation of these ligands, fewer solvent molecules are liberated during the complex formation.

Too many different contributions to the overall observed reaction entropies have to be taken into account, so no information can be obtained from the measured values. In most cases these contributions cannot be calculated or measured separately. However, from the differences between the reaction entropies obtained for different ligands some conclusions can be drawn, because all contributions to the reaction entropies (e.g. the desolvation of the cation due to complex formation) can be assumed to be equal if the ligands compared have identical cavity dimensions. Taking into account the entropy of fusion of methanol at 298.1 K $(T\Delta S_{fusion} = 5.4\,kJ\,mol^{-1}$ [11]) it is possible to calculate the difference between the number of moles of the solvent liberated during complex formation by both ligands and the differences between the corresponding reaction energies. This is shown as an example for the ligands (22) and (22DD), with $n$ as the number of moles of additional liberated solvent molecules

$$n = \frac{T\Delta S_{(22)} - T\Delta S_{(22DD)}}{T\Delta S_{fusion}} = 2.7$$

During the complex formation three additional solvent molecules are set free in the case of the ligand (22) compared to ligand (22DD), with the assumption that all other contributions to the reaction entropies are constant for both ligands. The values of $n$ obtained in this way are given in Table 2.

In all cases the number of solvent molecules set free during the complex formation is higher for the unsubstituted diaza crown ethers compared to the corresponding substituted ligands. In most cases three solvent molecules are liberated if the nitrogen donor atom is substituted by an alkyl chain. The length of the alkyl chain has no influence on the ligand solvation. Aromatic substituents in the case of diaza crown ether (22) give higher values, indicating that these ligands show the weakest solvation.

TABLE 2

Difference between the reaction entropy at 25°C for the complexation of $Ag^+$ with diaza crown ether and the corresponding substituted diaza crown ether, and the corresponding difference in the number of solvent molecules $n$ $(M^{-1})$ set free during the complexation reaction

| Ligands | $\Delta(T\Delta S)$ | $n$ | Ligands | $\Delta(T\Delta S)$ | $n$ |
|---|---|---|---|---|---|
| (21) – (21DD) | 18.2 | 3.4 | (22) – (22DD) | 14.7 | 2.7 |
| (21) – (21TT) | 12.5 | 2.3 | (22) – (22TT) | 25.4 | 4.7 |
| (22) – (22BuBu) | 15.6 | 2.9 | (22) – (22T$_p$(NO$_2$)$_2$) | 29.4 | 5.4 |
| (22) – (22OcOc) | 16.3 | 3.0 | (22) – (22TT$_o$(NO$_2$)$_2$) | 33.2 | 6.1 |

The substitution of the proton at the nitrogen donor atoms reduces the interactions between the ligands and the solvent molecules. The experimental data clearly demonstrate the absence of any lariat ether effect for the ligands examined. The observed changes of the stability constants, reaction enthalpies and entropies are explained by changes in the ligand–solvent interactions. Without the knowledge of the reaction enthalpies and entropies no realistic interpretation of the stability constants is possible. Further work is necessary to obtain data for crown ethers with different side chains with and without additional donor atoms.

## ACKNOWLEDGMENTS

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