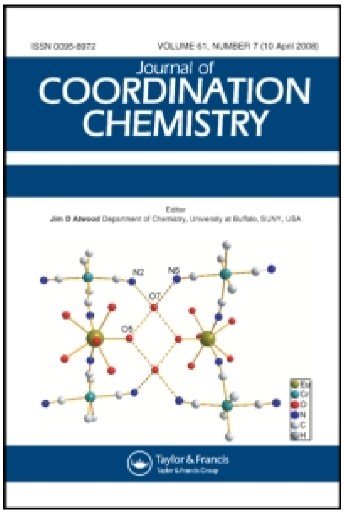

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# PROTONATION OF DIAZA CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION STUDIED BY MEANS OF POTENTIOMETRIC AND CALORIMETRIC TITRATIONS

H. -J. Buschmann[a]; C. Carvalho[a]; E. Cleve[a]; G. Wenz[a]; E. Schollmeyer[a]
[a] Deutsches Textilforschungszentrum Nord-West e.V., Krefeld, Germany

**To cite this Article** Buschmann, H. -J. , Carvalho, C. , Cleve, E. , Wenz, G. and Schollmeyer, E.(1994) 'PROTONATION OF DIAZA CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION STUDIED BY MEANS OF POTENTIOMETRIC AND CALORIMETRIC TITRATIONS', Journal of Coordination Chemistry, 31: 4, 347 — 352

**To link to this Article: DOI:** 10.1080/00958979408024228

**URL:** http://dx.doi.org/10.1080/00958979408024228

*J. Coord. Chem.*, 1994, Vol 31, pp. 347–352
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# PROTONATION OF DIAZA CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION STUDIED BY MEANS OF POTENTIOMETRIC AND CALORIMETRIC TITRATIONS

H.-J. BUSCHMANN,* C. CARVALHO, E. CLEVE, G. WENZ and
E. SCHOLLMEYER

*Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany*

*(Received November 16, 1993)*

Protonation of diazacrown ethers and cryptands in water was studied using potentiometric and calorimetric titrations. The potentimetric titrations were performed in two different ways. Calculated stability constants from both titrations were in good agreement with each other. Values of stability constants and reaction enthalpies give further insight into the structures of the mono- and bisprotonated ligands in solution.

KEYWORDS: Crown ethers, cryptands, protonation, stability constants, thermodynamic properties

## INTRODUCTION

Since the synthesis of nitrogen containing macrocyclic and macrobicyclic ligands such as azacrown ethers[1,2] and cryptands,[2-4] the protonation of these ligands in aqueous solutions has been studied by several authors.[3,5-7] Protonation in the presence of metal ions can be used to calculate stability constants of complexes.[6-8]

Numerous articles have been published dealing in general with potentiometric titrations.[9-12] Different computer programs for the calculation of stability constants of the protonated complexes are known from the literature.[13-15] However, only relatively few experimental results have been published up to now.[16,17] In some cases the agreement between the published data is not very good. Variations of experimental conditions may be responsible. Two different ways to perform these titrations are possible; a solution containing the ligand and a suitable base is neutralized using an acid or a solution containing the ligand and a base is neutralized using a base. Using different macrocyclic and macrobicyclic ligands the validity of both methods should be tested and compared. By combination of the stability constants with thermodynamic data some further insight into the structure of mono- and bisprotonated diaza crown ethers and cryptands in solution is expected.

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* Author for correspondence.

## EXPERIMENTAL

Chemical structures of the macrocyclic and macrobicyclic ligands (all Merck) are given in Figure 1. Tetramethylammonium hydroxide (Fluka) and hydrochloric acid (Merck) were used. All solutions were prepared with doubly distilled water.

Potentiometric titrations were performed using a pH-electrode (Metrohm, 6.0203.100) with internal reference. The electrode was calibrated before the titrations using aqueous solutions of hydrochloric acid. Ionic strength was kept constant during the titration at $I = 0.05$ mol dm$^{-3}$ using tetramethylammonium perchlorate.

Two different experimental setups were chosen to determine the protonation constants of aza crown ethers and cryptands:

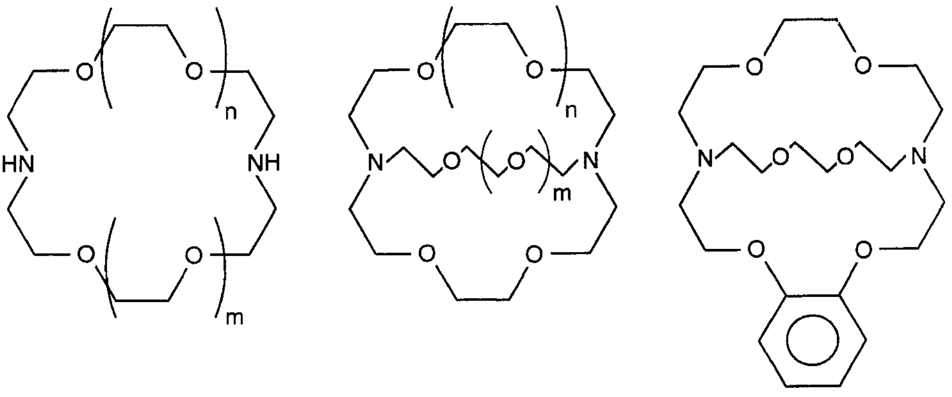
a) a solution of hydrochloride acid (0.1 mol dm$^{-3}$) was titrated into 20 cm$^3$ of a solution containing the ligand ($7–8 \cdot 10^{-3}$ mol dm$^{-3}$) and tetramethylammonium hydroxide ($2 \cdot 10^{-2}$ mol dm$^3$) or

b) a solution of tetramethylammonium hydroxide ($5.5 - 6.5 \cdot 10^{-2}$ mol dm$^{-3}$) was titrated into 20 cm$^3$ of a solution containing the ligand ($7.5 \cdot 10^{-3} - 1.25 \cdot 10^{-2}$ mol dm$^{-3}$) and hydrochloric acid ($2.0 - 2.5 \cdot 10^{-2}$ mol dm$^{-3}$).

The ionic product of water, $K_W$, was measured under the given experimental conditions. The calorimetric titrations were performed using a Tronac Calorimeter (Model 450). The heat, Q, produced during titration is related to reaction enthalpy, $\Delta H$, after correction for non-chemical heat effects by the following equation,

$$Q = \Delta H \, \Delta n$$

with $\Delta n$ being the number of moles of the complex formed during the titration. The experimental set-up for calorimetric titrations and the evaluation of the data has already been described in the literature in detail.[18-20] Due to the fact that all



n = 0, m = 0 : (11)
n = 0, m = 1 : (21)
n = 1, m = 1 : (22)

n = 0, m = 0 : (211)
n = 0, m = 1 : (221)
n = 1, m = 1 : (222)

(222 B)

**Figure 1** Chemical structures of macrocyclic and macrobicyclic ligands used in this study.

protonation constants are several order of magnitude higher than $10^5$ (dm$^3$/mol], the number of moles added to the solution is equal to the number of complexes formed. Again two different types of titrations were performed:

a) a solution of hydrochloric acid (0.1 mol dm$^{-3}$) was titrated continously over a short period into 40 cm$^3$ of the ligand solutions ($5\cdot10^{-2}$ mol dm$^{-3}$). Under these experimental conditions the ligand concentration in the reaction vessel during the titration is always much higher than the proton concentration. Thus only monoprotonation of the ligands takes place.

b) a solution of the ligand ($3\text{-}4\cdot10^{-2}$ mol dm$^{-3}$) was titrated into 40 cm$^3$ of hydrochloric acid ($5\cdot10^{-2}$ mol dm$^{-3}$). In this case the proton concentration in the reaction vessel is much higher than the ligand concentration. Under these experimental conditions two protons react with the ligand. Using the prior measured value of the reaction enthalpy for the monoprotonation, the reaction enthalpy for the second protonation can be calculated.

Due to the fact that the calorimetric titrations were performed in non-buffered solutions, the formation of water has to be taken into account. Using the stability constants for the protonation reactions the concentration of hydroxyl ions was calculated for each calorimetric titration. Using a value of $\Delta H = -55.84$ kJ mol$^{-1}$ for the formation of water,[21] the experimentally obtained values for both protonation reactions were corrected.

## RESULTS AND DISCUSSION

During the protonation of a ligand L containing two nitrogen atoms as for example diaza crown ethers or cryptands the following reactions take place

$$L + H^+ \rightleftharpoons LH^+ \tag{1}$$

$$LH^+ + H^+ \rightleftharpoons LH_2^{2+}. \tag{2}$$

The corresponding stability constants are given by (*3*) and (*4*).

$$K_1 = \frac{[LH^+]}{[L][H^+]} \tag{3}$$

$$K_2 = \frac{[LH_2^{2+}]}{[LH^+][H^+]}. \tag{4}$$

Writing the mass balances for the total ligand concentration, $C_L$, and for the difference, $C_D$, between the total acid concentration, $C_H$, and base concentration, $C_{OH}$, one obtains (*5*) and (*6*).

$$C_L = [L] + [LH^+] + (LH_2^{2+}] \tag{5}$$

$$C_D = C_H - C_{OH} = [H^+] + [LH^+] + 2[LH_2^{2+}] - [OH^-]. \tag{6}$$

Combination of (*3*), (*4*) and (*5*) with (*6*) results in (*7*).

$$C_D = [H^+] - [OH^-] + C_L\frac{K_1[H^+] + 2K_1K_2[H^+]^2}{1 + K_1[H^+] + 2K_1K_2[H^+]^2} \tag{7}$$

By using (7) the concentration of $[H^+]$ or $[OH^-]$ can be fitted to the experimental data taking into account the ionic product of water, $K_W$. The mathematical treatment of the experimentally observed titration curves is identical for titrations performed using an acid or a base.

Protonation constants obtained are summarized in Table 1. Both experimental methods nearly give the same results. The values are also in accord with most of the published data.[16,17] No data from the literature are included in Table 1 because in many cases no information is given as to which kind of titration was performed. The highest values of the stability constants for the formation of monoprotonated ligands are always observed for the smallest azacrown ether or cryptand. With increasing ring or cavity size, equivalent to increasing distance between both nitrogen donor atoms of the ligands, the stability constants decrease. These results indicate that the other donor atoms of these ligands, especially the second nitrogen donor atom, participate in complex formation. However, in the case of the cryptands (222) and (222B) only the basicity of the ether oxygen atoms attached to the benzo group is reduced. Therefore the decrease in the complex stability of the proton complex with the cryptand (222B) compared with (222) can only be explained if the ether atoms are also involved in complex formation. These results show that the proton of the monoprotonated ligands is obviously located inside the cavities. This interpretation is confirmed by molecular dynamic simulations for the protonation of the cryptand (222).[22]

The stability constants for the reaction of the monoprotonated ligands with a second proton show no great deviations from each other. Thus, the second proton is located outside the cavity. This is probable because the repulsion between two positive charges inside the cavities is high. If both protons are located inside the cavities of the cryptands, as has been shown in crystallographic structures[23,24], the values of the reaction enthalpies should increase with increasing cavity size due to a decrease in repulsion between both protons.

This interpretation should also be supported by the thermodynamic data for the protonation reactions. Values of reaction enthalpies and entropies are summarized in Table 2. With few exceptions the values of the reaction enthalpy for the formation of the protonated ligands are in accord with the values taken from the literature.[16,17] Using the stability constants obtained from titrations of solutions containing the ligand and hydrochloric acid with tetraethylammonium hydroxide the given values of the reaction entropy are calculated.

**Table 1** Stability constants (K in $dm^3/mol$) for the protonation reactions of azacrown ethers and cryptands in aqueous solution at 25°C.

| Ligand | $\log K_1{}^a$ | $\log K_2{}^a$ | $\log K_1{}^b$ | $\log K_2{}^b$ |
|---|---|---|---|---|
| (11) | 9.25 | 7.36 | 9.14 | 7.62 |
| (21) | 8.61 | 7.64 | 8.41 | 7.81 |
| (22) | 8.90 | 7.62 | 8.92 | 7.56 |
| (211) | 10.84 | 7.78 | 11.13 | 8.09 |
| (221) | 10.33 | 7.42 | 10.66 | 7.39 |
| (222) | 9.85 | 7.41 | 10.21 | 7.55 |
| (222B) | 9.08 | 6.10 | 9.56 | 6.21 |

[a]Calculated from titrations of solutions containing the ligand and tetramethylammonium hydroxide with hydrochloric acid. [b]Calculated from titrations of solutions containing the ligand and hydrochloric acid with tetramethylammonium hydroxide.

**Table 2** Thermodynamic values $\Delta H$ and $T\Delta S$ (in kJ/mol) for the protonation reactions of azacrown ethers and cryptands in aqueous solution at 25°C.

| Ligand | $-\Delta H_1$ | $T\Delta S_1$ | $-\Delta H_2$ | $T\Delta S_2$ |
|---|---|---|---|---|
| (11) | 48.5 | 3.4 | 28.5 | 14.8 |
| (21) | 35.5 | 12.3 | 46.3 | -1.9 |
| (22) | 38.4 | 12.3 | 53.8 | -10.8 |
| (211) | 49.3 | 13.9 | 31.3 | 14.7 |
| (221) | 56.6 | 4.0 | 22.2 | 19.8 |
| (222) | 51.9 | 6.6 | 29.9 | 13.0 |
| (222B) | 59.0 | -4.7 | 22.2 | 13.1 |

Values of $\Delta H_1$ of the macrocyclic ligands are smaller than those of the macrobicyclic ligands. This result is unexpected because it is known from the literature that the value of the heat of protonation of a secondary amine (dimethylamine, $\Delta H = -50.3$ kJ/mol[25]) is higher than for the corresponding reaction with a tertiary amine (trimethylamine, $\Delta H = -36.9$ kJ/mol[25]). Only additional interactions with the donor atoms of the ligands are responsible for this effect. However, the values of $\Delta H_2$ in the case of the monocylic ligands are comparable with the heat of protonation of a secondary amine. Thus, the interactions between both nitrogen atoms of the monocyclic ligands and the first complexed proton are not very strong. As a result the value of $\Delta H_1$ is smaller as compared with that of a secondary amine.

In the case of the macrobicyclic cryptands the interactions between the first complexed proton and both nitrogen and the ether donor atoms are much stronger (in contrast to the monocyclic ligands). As a result the values of $\Delta H_1$ are higher for these ligands than for the protonation of a tertiary amine and the values of $\Delta H_2$ are lower. These results indicate the interactions of both nitrogens in the case of the cryptands with the first complexed proton. As is known from the literature, the cryptand (111) therefore froms extremely stable 1:1-complexes with $H^+$.[26] If both nitrogen atoms of these ligands are involved in the complexation of the first proton the interactions of both nitrogen atoms with water molecules are interrupted due to the complex formation. Also, a conformational change of the ligand is necessary in order to enable the interactions between both nitrogen atoms and the complexed proton.

## *Acknowledgements*

The diaza crown ether (11) was kindly donated by Dr. R. Klink (Merck). We are grateful to the Forschungskuratorium Gesamttextil for their financial support for this research project (AIF-No. 8824). This support was granted from resources of the Federal Ministry of Economics *via* a supplementary contribution by the Association of Industrial Research Organizations (Arbeitsgemeinschaft Industrieller Forschungsvereinigungen, AIF).

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