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The Macrocyclic and Cryptate Effect.
2. Complexation of Silver(I) by Different Ligands in Methanol*

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Abstract

The complex formation of Ag^+ with a variety of noncyclic ligands, crown ethers, aza crown ethers and cryptands has been studied in methanol by potentiometric and calorimetric titrations. From the measured reaction enthalpies with different noncyclic ligands it is deduced that the bond strength between the silver ion and different donor atoms decreases in the order: $N > S > O$. A macrocyclic effect for ligands containing only oxygen as donor atoms was found, caused by a favourable entropic change. Complexes of aza crowns and their noncyclic analogues have the same stabilities. The existence of different conformations of the cyclic ligands is mainly responsible for the absence of the macrocyclic effect. A cryptate effect for the complexation of Ag^+ was observed, due to an increase in ΔH.

Introduction

The concept of a 'macrocyclic effect' was used to explain the high stability of metal complexes with cyclic ligands compared with their noncyclic analogues [2]. Studying the complex formation of 18C6 and PG, Frensdorff hypothesized that noncyclic ligands are unable to surround the cation completely because of electrostatic repulsion between the terminal oxygens. Beyond that an unfavourable entropy change occurs during wrapping the ligand around the cation [3]. More experimental results have been published, but no explanations for the cause of the macrocyclic effect have been reported [4].

Using bicyclic ligands, cryptands, there is a further increase in stability for some complexes. From the formation reaction of some cryptands with K^+ it was concluded that the 'cryptate effect' is caused by enthalpic changes [5]. Both effects were found for the reaction of Pb(II) with crown ethers and cryptands [1]. Monocyclic ligands containing oxygen and nitrogen atoms are as stable as their noncyclic analogues. But for the complexation of Hg^{2+}, Cd^{2+} and Ag^+ in water with noncyclic, cyclic and bicyclic ligands, neither a macrocyclic nor a cryptate effect was observed [6]. Comparing the stability constants of the silver ion with mono and bicyclic ligands in methanol, other authors have found a cryptate effect [7]. In order to get more information about these two effects, the complex stability and thermodynamic values for the complex formation of Ag(I) with different ligands in methanol were studied.

Experimental

The noncyclic ligands (see Fig. 1) 1,5-diaminopentane (DAP; Merck); 1,8-diaminooctane (DAO; Merck); 2,2′-iminodiethanol (DEA; Merck); 1,8-diamino-3,6-dioxaoctane (DAOO; Merck); N-(2-aminoethyl)-1,2-ethanediamine (DAAP; Ega); N,N′-*bis*(2-

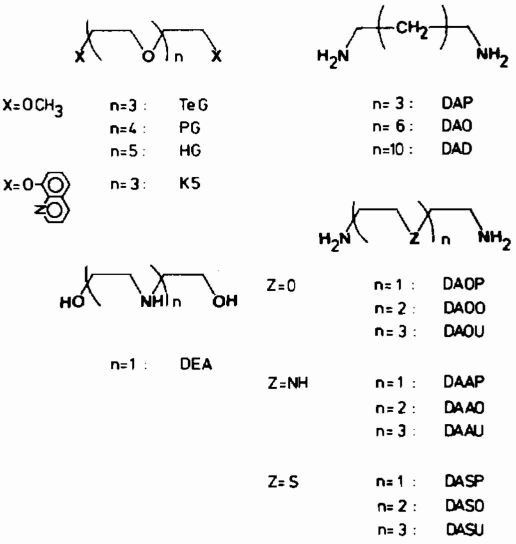

Fig. 1. Noncyclic ligands studied in this work.

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*For Part 1, see ref. [1].

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aminoethyl)-1,2-ethanediamine (DAAO; Ega); tetraethylenpentamine (DAAU; Ega), bis-(2-aminoethyl)-sulfide (DASP; ICN), and 2,5,8,11,14,17-hexaoxaoctadecane (PG; Riedel-de Haen) were distilled under vacuum. Using published procedures 1,8-diamino-3,6-dithiaoctane (DASO; [8]) and 1,11-diamino-3,6,9-trithiaundecane (DASU; [9]) were synthesized. The remaining noncyclic ligands, crown ethers and cryptands, see Fig. 2, were used without further purification.

Stability constants smaller than 10^5 and the reaction enthalpies were determined by titration calorimetry. All experimental conditions have been described previously in detail [1]. The other complex stabilities were measured by potentiometric titration of a $AgNO_3$ (Merck) solution (9×10^{-4}–1.5×10^{-3} M) with the ligand (1.5×10^{-2}–2.5×10^{-2} M) in anhydrous methanol (Merck). The concentration of the uncomplexed silver ions was measured by a silver electrode (Metrohm EA 282). The ionic strength was kept constant at $I = 0.05$ M by adding tetraethylammoniumperchlorate as supporting electrolyte.

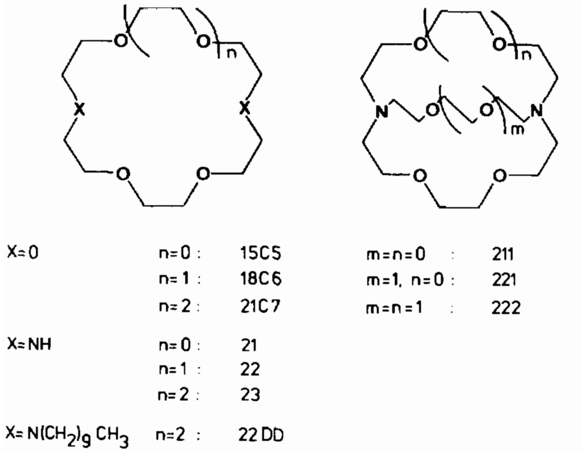

Fig. 2. Crowns, azacrowns, and cryptands studied in this work.

Normally, one would expect the reaction described by eqn. (1) takes place:

$$Ag^+ + L \rightleftharpoons AgL^+ \qquad K = \frac{[AgL^+]}{[Ag^+][L]} \tag{1}$$

The stoichiometry of the titration with DEA however indicates the following reaction (eqn. 2)

$$Ag^+ + 3L \rightleftharpoons AgL_3^+ \qquad \beta_3 = K_1 \cdot K_2 \cdot K_3 = \frac{[AgL_3^+]}{[Ag^+][L]^3} \tag{2}$$

Results and Discussion

The values of $\log K$, ΔH, and $T\Delta S$ for the reaction of Ag^+ with noncyclic ligands are summarized in Table I. Ligands which only contain oxygen donor atoms form the weakest complexes. Substitution of both methyl groups of TeG through chinoline groups causes an increase in stability of about 10^5. The interaction between the additional nitrogen atoms in K5 give rise to a greater value of ΔH due to covalent bonding of Ag^+. In contrast the nitrogen-containing noncyclic ligands complex the silver ion strongly. The reaction enthalpy of DEA has about half the value of that of the unsubstituted diamines DAO and DAD. Thus it is obvious that both nitrogen atoms of the diamines take part in complex formation. Using these values it is possible to calculate a mean value of 23 kJ mol^{-1} for a single Ag–N bond.

TABLE I. Stability Constants ($\log K$; K in M^{-1}) and Thermodynamic Parameters for the Reaction of Ag^+ with Noncyclic Ligands in Methanol at 25 °C.

Ligand	$\log K$	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
DAP	6.74	58.4	−20
DAO	6.93	47.2	−8
DAD	7.24	49.4	−8
DEA	>5 (10.5)[a]	22.1	
DAOP	7.14	61.5	−21
DAOO	9.59	58.3	−4
DAOU	8.55	58.4	−10
DAAP	8.07	55.2	−9
DAAO	10.12	69.4	−12
DAAU	10.59	81.5	−21
DASP	8.51	66.4	−18
DASO	10.06	64.9	−8
DASU	10.97	77.8	−15
TeG	[b]	>0	
K5	7.02	37.8	2
PG	1.80	15.8	−6
HG	1.82	23.0	−13

[a] $\log \beta_3$. [b] Measured value of Q is too small for evaluation.

The smallest diamine ligand DAP involves considerable stress if the usual 180° bond angle of Ag^+ has to be satisfied [10]. This is reflected by the entropy. Inserting a further hetero atom at the 3-position of the ligand does not change the situation. With increasing chain length the additional donor atoms of the substituted diames also take part in complexation.

Enthalpies for the reaction of DAOO and DAOU with Ag^+ are identical. Only two oxygens are involved in the reaction. The strength of a Ag–O bond is of the order of 6 kJ mol^{-1}. In the case of the ligands with only nitrogen atoms it is possible to decide how many donor atoms participate in complex formation, by using the known value for a Ag–N bond. The measured reaction enthalpies of DAAO and DAAU confirm that one nitrogen atom less than possible takes part in the reaction. This is necessarily accompanied by more negative entropic changes, because of increasing steric strain. Therefore the stability constants of DAAO and DAAU are nearly constant. Only for the case that all sulfur atoms of DASO and DASU take part in complexation a reasonable Ag–S bond strength of 10 kJ mol^{-1} can be calculated. The interaction of silver ions with the donor atoms examined decreases in the order N > S > O.

Stability constants and thermodynamic values for the reaction of Ag^+ with cyclic and bicyclic ligands are summarized in Table II. There is reasonable agreement with the literature data for the stability constants [7, 11]. On the other hand, a big difference in ΔH is found for the reaction of Ag^+ with (211) and (222). These values were not directly measured but were determined from a plot of log K *vs.* $1/T$. All crown ethers form more stable complexes than the noncyclic glymes. A macrocyclic effect is obvious. However, without the information from the reaction of the noncyclic ligands with the silver ion there is no discussion possible about its origin. The ionic radius of Ag^+ (r = 1.15 Å) [12] match best the cavity size of 18C6 (r = 1.4 Å) [13] so the interaction between the cation and the donor atoms of the ligand should be optimal.

TABLE II. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters for the Reaction of Ag^+ with Mono- and Bicyclic Ligands in Methanol at 25 °C.

Ligand	log K	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
15C5[a]	3.65	26.9	−6
18C6[a]	4.58	39.1	−13
21C7[b]	2.46	28.8	−15
21	7.63	34.6	9
22	10.02	44.9	12
22DD	10.28	61.1	−3
23	9.60	53.4	1
211	10.46	54.6	5
221	14.44	81.9	0
222	12.22	68.3	1

[a]From ref. [17]. [b]From ref. [18].

Assuming equal bond strength one gets 6.5 kJ mol^{-1} from the reaction enthalpy for the strength of a single Ag–O bond. This is in excellent agreement with the value calculated earlier. The cavity of 15C5 (r = 0.9 Å) is too small, and of 21C7 (r = 1.9 Å) [13] too large, for the silver ion. Therefore an interaction with all donor atoms is not possible. The reaction enthalpies indicate that 4 oxygens of 15C5 and 5 oxygens of 21C7 are involved in the complex formation. In the case of the crown ethers the macrocyclic effect is only produced by favourable entropic changes.

The situation becomes more difficult for the reactions of azacrowns and cryptands. In contrast to the crown ethers no increase in complex stability with the ligands (21), (22), (22DD) and (23) is found compared to noncyclic nitrogen containing ligands. Even the reaction enthalpies of these cyclic ligands are equal or smaller than those of similar linear ligands.

For bicyclic diamines [14] and cryptands [15] it is known that they exist in different conformational forms. This is also possible for monocyclic azacrowns, see Fig. 3. To estimate the importance of the various ligand conformations for the complexation reactions it is necessary to know their concentrations and the reaction enthalpies for transformation. These values have not yet been estimated. The only approach is to use the values estimated above for the strength of a single Ag–N and Ag–O bond, in order to calculate a theoretical value of ΔH. The difference between calculated and measured reaction enthalpies, as a function of the ratio of the ligand to silver radii, is shown in Fig. 4. The measured reaction enthalpies of the monocyclic azacrowns are nearly 30 kJ mol^{-1} smaller than the calculated values. This is in excellent agreement with the measured activation energy of the nitrogen inversion of bicyclic diamines [14]. As expected the difference decreases with increasing ring size.

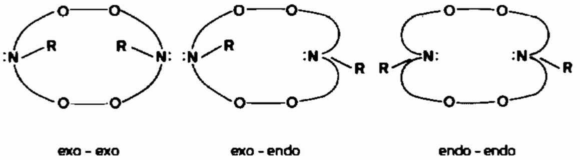

Fig. 3. Different conformational forms of uncomplexed azacrowns.

Substitution of the protons of the amino groups of (22) by long alkyl chains (22DD) leads to a considerable increase of the reaction enthalpy. The difference between calculated and measured ΔH values is now smaller than 10 kJ mol^{-1}. Obviously the equilibrium between the different conformers is influenced by the substituents. Space-filling groups at the nitrogen atoms cause an increase of endo-endo-conformation. Thus less energy is necessary to reach the best arrangement of all donor atoms during complexation. The disappearance of the macrocyclic effect for the azacrowns can mainly be ascribed to the existence of different ligand conformers.

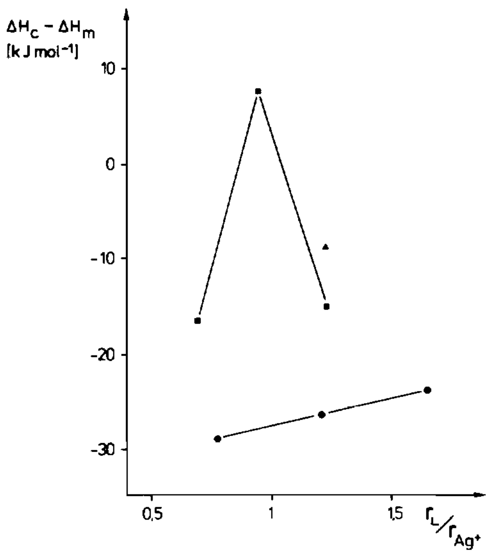

Fig. 4. Difference between calculated (ΔH_c) and measured reaction enthalpies (ΔH_m) as a function of the ratio of the ligand to silver radii. ● (21, 22, 23); ▲ (22DD); ■ (211, 221, 222).

The stability of silver complexes with the bicyclic ligands (221) and (222) is higher than with all other ligands examined. This is mainly caused by an increase in reaction enthalpies. The smallest cryptand (211) (r = 0.8 Å) [16] is deformed during the reaction with the silver ion (r = 1.15 Å), leading to a lower value of ΔH. Nevertheless the difference between calculated and measured reaction enthalpies is smaller for all cryptands in comparison to the azacrowns, see Fig. 4. The reaction of (221) with Ag^+ even leads to a positive difference. The enhancement of ΔH may be explained by the fixed geometry of the bicyclic ligands causing stronger interactions between donor atoms and the complexed metal ion. As in the reaction of Pb^{2+} with cryptands [1], ΔS does not play an important role for the cryptate effect.

Acknowledgements

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