Inorganica Chimica Acta, 108 (1985) 241–245

The Macrocyclic and Cryptate Effect.
4. Complexation of Cobalt(II) and Nickel(II) by Noncyclic, Monocyclic and Bicyclic Ligands in Methanol

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Received August 2, 1985

Abstract

The complex formation of Co^{2+} and Ni^{2+} with various noncyclic ligands, aza crown ethers and cryptands has been studied in methanol by means of calorimetric and potentiometric titrations. The reactions of both cations with aza crown ethers were endothermic. This surprising result can be explained by structural changes of the ligand during the complexation process. The thermograms for the titration of Ni^{2+} solutions with cryptands show two different reactions. On the basis of further results from potentiometric titrations, a two-step reaction mechanism is discussed. The macrocyclic and the cryptate effect are only caused by favourable entropic changes.

Introduction

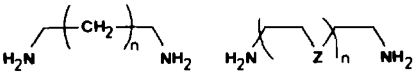
In macrocyclic chemistry the transition metal cations play an extremely important role. This is particularly true for the synthesis of ligands which contain nitrogen donor atoms [1]. The complexation reaction between Cu^{2+} and cyclic tetramines led to the discovery of the macrocyclic effect [2]. This effect was explained to be mainly caused by entropic factors [3, 4]. Most of the published experimental results deal with the complexation of the copper ion [5]. Only very few data are available for the reaction of Co^{2+} and Ni^{2+} with these ligands [6].

Until now, experimental results with ligands containing nitrogen, sulfur and or oxygen as donor atoms are rather rare. Some results are reported in the literature for the reaction of cobalt and nickel cations with noncyclic [7], monocyclic [8, 9] and bicyclic ligands [10] in aqueous solution or in a mixture of methanol and water [11].

Continuing our work on the macrocyclic and cryptate effect [12], the complex stabilities and thermodynamic values for the complexation of Co^{2+} and Ni^{2+} with different ligands were studied in methanol solutions by calorimetric and potentiometric methods.

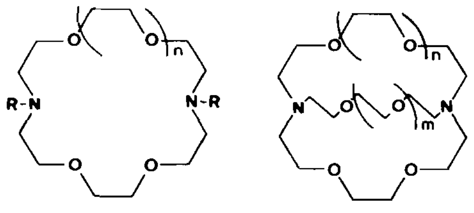
Experimental

The noncyclic ligands, shown in Fig. 1, 1,2-diaminoethane (DAE; Merck); 1,3-diaminopropane (DAP; Merck); 1,4-diaminobutane (DAB; Merck); 1,5-diaminopentane (DAPe; Merck); 1,6-diaminohexane (DAH; Merck); 1,8-diaminooctane (DAO; Merck); 1,9-diaminononane (DAN; Merck); 1,12-diaminododecane (DAD; Merck); 1,8-diamino-3,6-dioxaoctane (DAOO; Merck); N-(2-ethanediamine) (DAAP; EGA), and bis-(2-aminoethyl)sulfide (DASP; ICN) were distilled under vacuum prior to use. All other noncyclic ligands, azacrown ethers and cryptands (all Merck), see Fig. 2, were used without further purification. The salt solutions were prepared by dissolving anhydrous $CoCl_2$ (Ventron) or $NiBr_2$ (Ventron) in methanol (H_2O contents less than



n = 2	DAE	Z = O	n = 1	DAOP
n = 3	DAP		n = 2	DAOO
n = 4	DAB		n = 3	DAOU
n = 5	DAPe			
n = 6	DAH	Z = NH	n = 1	DAAP
n = 8	DAO			
n = 9	DAN	Z = S	n = 1	DASP
n = 12	DAD			

Fig. 1. Noncyclic ligands studied in this work.



R=H	n=0 :	21	m=n=0 :	211
	n=1 :	22	m=1, n=0 :	221
	n=2 :	23	m=n=1 :	222
$R=(CH_2)_9CH_3$	n=1 :	22DD		

Fig. 2. Aza crowns and cryptands studied in this work.

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0.01%; Merck) or by drying the solutions of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Ventron) with molecular sieves. Stability constants smaller than 10^5 and the reaction enthalpies were determined by titration calorimetry, using a Tronac Model 450 calorimeter [13].

Higher stability constants were measured by means of a disproportionate reaction with the silver ion [14]. Tetraethylammoniumnitrate (TEAN, Fluka) has been used as supporting electrolyte and the ionic strength was kept constant at $I = 0.05$ M. In some cases, the drying process of the solutions in the presence of TEAN leads to insoluble precipitations. Thus, the actual concentrations were calculated from the equivalent point. In other cases, the titrations were performed without drying the solution.

For calorimetric titrations, it is essential that the measured reaction is in equilibrium at any time during titration. This condition was not fulfilled for the complexation reaction of Co^{2+} by DAE and DAP and of Ni^{2+} by DAB, DAPe, DAH, DAO, DAN and DAD due to a second slow reaction. Under these circumstances, only the reaction enthalpies could be calculated from the initial slopes of the thermograms.

The amount of heat produced during the titration of Co^{2+} with (22DD) was too small to calculate ΔH and the stability constant K of the complex so formed. Even the disproportionate reaction with silver(I) could not be used because (22DD) and $Co(NO_3)_2$ in 0.005 M TEAN form a precipitate. A calorimetric competitive reaction with Ba^{2+} was successful to obtain values of K and ΔH [15]. On the other hand, this method failed for the determination of stability constants with the bicyclic cryptands, due to the slow decomposition reactions of the complexes with Co^{2+} and Ni^{2+}. Only the reaction enthalpy for the formation of $(222Co^{2+})$ could be checked by calorimetric titration with Na^+.

All measurements evaluated for the direct complexation of Co^{2+} and Ni^{2+} could be described by the following equation:

$$M^{2+} + L \rightleftharpoons ML^{2+} \qquad K = \frac{[ML^{2+}]}{[M^{2+}]\,[L]} \qquad (1)$$

Results and Discussion

The values of log K, ΔH, and $T\Delta S$ for the complexation reaction of Co^{2+} and Ni^{2+} by noncyclic ligands are summarized in Table I. It can be seen that the diamines containing two or three methylen groups show the strongest interaction with the complexed cations. With increasing chain length, the measured reaction enthalpies drop to a constant value for all other diamines. ΔH values for the complexation of Ni^{2+} by diamines with a longer alkyl chain could only be calculated from the initial slope of the thermogram. Thus, it is obvious that, under these conditions, only the formation of one Ni^{2+}–N bond is observed. It is known that the complexation reaction of Ni^{2+} with a noncyclic ligand is rather slow [16]. Therefore, it can be assumed that the strength of a single Co^{2+}–N bond can be calculated giving 13.4 ± 0.5 kJ mol^{-1} and that of a single Ni^{2+}–N bond with 11.2 ± 0.9 kJ mol^{-1}.

After inserting further donor atoms such as oxygen, nitrogen, and sulfur into the diamines, changes in the reactions are observed. The smallest ligands DAOP, DAAP, and DASP, which are analogous to DAPe, form complexes of unknown composition

TABLE I. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters for the Reaction of Co^{2+} and Ni^{2+} with Noncyclic Ligands in Methanol at 25 °C.

Ligand	Co^{2+} cation			Ni^{2+} cation		
	log K	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	log K	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
DAE		39.1[a]		>5	32.7	
DAP		29.7[a]		>5	23.5	
DAB	2.36	18.5	-5.1	–	8.7[a]	
DAPe	2.49	25.7	-11.6	–	10.6[a]	
DAH	2.48	26.7	-12.6	–	11.3[a]	
DAO	2.47	26.4	-12.4	–	11.7[a]	
DAN	2.48	28.2	-14.1	–	9.8[a]	
DAD	2.49	26.6	-12.5	–	12.1[a]	
DAOP	–[b]	–		–[b]	–	
DAOO	2.51	7.2	7.1	5.88		
DAOU	2.25	16.2	-3.4	5.32	9.3	20.9
DAAP	–[b]	–		–[b]	–	
DASP	–[b]	–		–[b]	–	

[a] Calculated from the initial slope of the thermogram. [b] No 1:1 complex formed.

TABLE II. Stability Constants (log K_{ov}; K_{ov} in M^{-1}) and Thermodynamic Values for the Complexation of Co^{2+} and Ni^{2+} by Aza Crown Ethers and Cryptands in Methanol at 25 °C.

Ligand	Co^{2+} cation			Ni^{2+} cation					
	log K_{ov}	$-\Delta H_{ov}$ (kJ mol^{-1})	$T\Delta S_{ov}$ (kJ mol^{-1})	log K_{ov}	$-\Delta H_{ov}$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})	log K_i[a]	$-\Delta H_1$ (kJ mol^{-1})	$-\Delta H_2$ (kJ mol^{-1})
21	6.9[b]	−5.2	44.4	4.90[b]	−23.8	51.6	–	–	–
22	3.56	−11.4	31.6	3.90, 4.13[b]	−24.7	46.9	–	–	–
22D	2.36	−2.8	16.2	2.54	−11.2	25.6	–	–	–
23	3.59	−8.4	28.8	4.04	−16.5	39.5	–	–	–
211	6.38[c]	–	–	9.3[b]	−11.6	64.4	4.53	22.4	−34.0
221	13.40[c]	–	–	9.6[b]	−11.2	65.7	4.64	26.6	−37.8
222	2.47	−8.1	22.1	6.9[b]	−13.5	52.7	2.93	25.5	−39.0

[a] $i = 1$ or 2. [b] From a potentiometric titration. [c] From a potentiometric titration without supporting electrolyte, water content approx. 0.1 M.

with both cations. Obviously, the additional oxygen donor atoms in DAOO and DAOU do not participate in complex formation. In contrast, they seem to weaken the bond strength between the complexed cations and the nitrogen donor atoms.

Stability constants and thermodynamic values for the reaction of Co^{2+} and Ni^{2+} with cyclic and bicyclic ligands are summarized in Table II. All measured reaction enthalpies for the complexation of these cations by aza crown ethers have a positive sign. During the calorimetric titrations the temperature decreases in the reaction vessel as show in Fig. 3. Thus, no important increase of the complex stabilities compared with the noncyclic ligands is found although the reactions are favoured by high positive values of the reaction entropy.

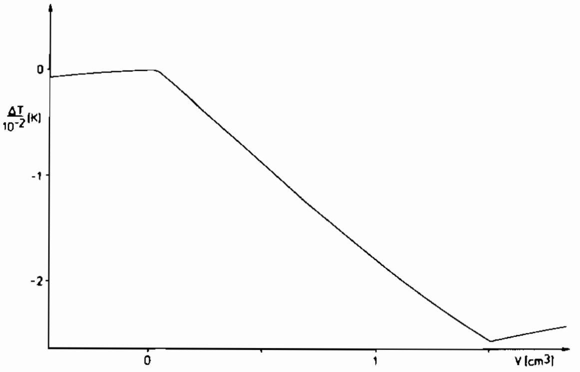

Fig. 3. Thermogram for the titration of nickel(II) with (22).

Using the estimated bond energies between a single nitrogen atom and Co^{2+} and Ni^{2+}, it is possible to calculate theoretical reaction enthalpies. The difference between calculated and measured reaction enthalpies, as a function of the ratio of the ligand to cation radii, is shown in Fig. 4. The measured reaction enthalpies of aza crown ethers are almost 40 kJ mol^{-1} smaller than the calculated values. This difference is slightly higher, as was found for the reaction of Ag^+ and Ba^{2+} with these ligands [12]. The existence of the monocyclic ligands in different conformational forms was made responsible for the observed discrepancy between calculated and measured reaction enthalpies.

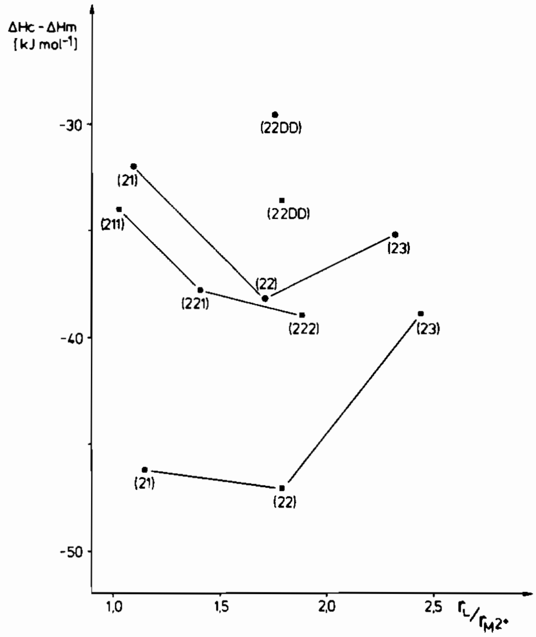

Fig. 4. Difference between calculated (ΔH_c) and measured reaction enthalpies (ΔH_m) as a function of the ratio of the ligand to metal ion radii (Co^{2+} ● and Ni^{2+} ■).

Substituting the protons of the amino groups of (22) by long alkyl chains (22DD) should lead to the preference of the conformational form where both substituents were oriented out of the cavity of the aza crown ether. Thus the lone electron pairs at the nitrogen atoms should be directed inside the cavity leading to an increase of the measured reaction enthalpy. This effect is observed but it is not as strong as for the reaction with Ag^+ and Ba^{2+}.

The disappearance of the macrocyclic effect of aza crown ethers is only caused by infavourable enthalpic changes during the complexation. As in the case of the cyclic tetramines the reaction is favoured by entropic changes. The situation becomes more complicated for the complex formation with bicyclic ligands. The thermograms for the reaction of Co^{2+} with (211) and (221) show two or more different superimposed reactions. Under these circumstances, it is impossible to calculate any meaningful values for the reaction enthalpy. Only in the case of the complexation of Ni^{2+} both effects could be observed separately, see Fig. 5. A two-step mechanism for the complexation of a cation by a cryptand was first suggested by Mei [17]. Using this nomenclature the reaction can be described by the following steps:

$$M^{2+} + L \overset{K_1}{\rightleftharpoons} M^{2+} \cap L \overset{K_2}{\rightleftharpoons} M^{2+} \subset L \qquad (2)$$

An exclusive complex is denoted by ($M^{2+} \cap L$) and an inclusive complex by ($M^{2+} \subset L$).

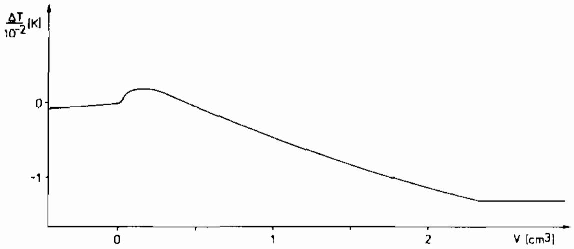

Fig. 5. Thermogram for the titration of nickel(II) with (222).

Such a reaction scheme is supported by experimental results [17, 18]. The calorimetric measured heat Q is the sum of all heats produced by chemical reactions. Thus, for the reaction (2) one obtains

$$Q_t = n_{1,t}\Delta H_1 + n_{2,t}\Delta H_2 \qquad (3)$$

with the number of moles of the exclusive complex $n_{1,t}$ and of the inclusive complex $n_{2,t}$ formed during titration.

Both parts of the observed thermograms were evaluated separately. The first short temperature increase only allows the calculation of a reaction enthalpy. From the second part, values for K and another ΔH were obtained.

These experiments give no direct indication as to which calculated reaction enthalpy belongs to ΔH_1 or ΔH_2, respectively. The same is true for the stability constants K_1 and K_2. Using the estimated bond strength between Ni^{2+} and one nitrogen donor atom, it is possible that the formation of an exclusive complex should be an exothermic reaction. One would expcct a value for $\Delta H_1 \approx -11$ kJ mol^{-1}. Surprisingly, the measured reaction enthalpies from the first part of the thermograms are twice as high. This can only be explained if both nitrogen atoms of the cryptands are involved in formation of the exclusive complexes. The formation of the inclusive complex is connected with structural changes of the complex formed so far. Thus, a positive reaction enthalpy is possible because no additional bonds between Ni^{2+} and the oxygen atoms of the ligand are formed. This assumption is verified for the reaction of DAOO and DAOU with Ni^{2+}. Furthermore the value of ΔH_2 for all cryptands is almost identical with the difference between calculated and measured reaction enthalpies for the complex formation with aza crown ethers.

From potentiometric titrations, different values for the stability constants were calculated. Under the experimental conditions applied ($C_{Ni^{2+}} > C_{Ligand}$), the dissociation of the inclusive complex is measured. No separate stability constant is obtained in this way but the overall complex stability $K_{ov} \cdot K_{ov}$ is related to K_1 and K_2 by the eqn. (4)

$$K_{ov} = K_1 K_2 \qquad (4)$$

Nevertheless, the stability constant calculated from the thermogram may be K_1 or K_2. Only kinetic measurements of the complex formation and dissociation are able to give further information about both stability constants. These investigations have not been completed yet.

The complexation of Co^{2+} by cryptands is very similar to the situation discussed for Ni^{2+}. Due to the experimental conditions only K_{ov} could be measured.

Higher stability constants for the Ni^{2+}-complexes with bicyclic ligands compared to the monocyclic aza crown ether result only from favourable entropic changes. No enthalpic contributions to the cryptate effect can be observed.

Acknowledgement

The ligands DAOP and DAOU were kindly donated by Dr. Klink (Merck, Darmstadt).

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