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COMPLEX FORMATION OF COBALT(II) AND COPPER(II) WITH MACROCYCLIC POLYETHERS IN PROPYLENE CARBONATE

HANS-JÜRGEN BUSCHMANN *

Physikalische Chemie, Universität-GH Siegen, Postfach 101240, D-5900 Siegen (F.R.G.)

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ABSTRACT

By means of potentiometric and calorimetric titrations, the complex formation of Co^{2+} and Cu^{2+} with different crown ethers has been studied in propylene carbonate. 15C5-crown ethers form the most stable complexes with both cations. The reaction enthalpies and entropies measured for the complexation of both cations by different 18-crown-6 ligands were quite unusual. One possible explanation is the differences in the fluctuations of these ligands around the complexed cations.

INTRODUCTION

Many results for the complexation reactions of crown ethers in different solvents have been reported during recent years [1]. However, very little is known about the reactions of transition metal ions with macrocyclic and macrobicyclic ligands. Normally only the complexation reactions between ligands containing nitrogen and other donor atoms and these cations have been reported [1,2]. To our knowledge, only Dickert and his coworkers have studied the reaction of Co^{2+} with different crown ethers in methanol [3] and other solvents [3,4]. Their results for the reaction of 15-crown-5 with Co^{2+} in methanolic solution show that the complex formation is an endothermic process. Thus, the formation of Co^{2+}–crown ether complexes in this solvent can only be attributed to entropic factors. In order to obtain more information about the complex formation of crown ethers with Co^{2+} and other ions another solvent has to be used. The reduction of the cation–solvent interactions should result in an exothermic reaction which can more easily be studied by the normal calorimetric titrations technique. The solvent propylene carbonate was accordingly chosen for the present study. Owing to solubility problems with nickel(II) salts only the complexation of Co^{2+} and Cu^{2+} could be studied.

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* Present address: Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-4150 Krefeld 1, F.R.G.

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EXPERIMENTAL

The crown ethers (see Fig. 1) 12-crown-4 (12C4; Merck), 15-crown-5 (15C5; Merck), benzo-15-crown-5 (B15C5; Merck), benzo-18-crown-6 (B18C6; Parish), dibenzo-18-crown-6 (DB18C6; Merck), and dicyclohexano-18-crown-6 (DC18C6; Ega) were used without further purification. The salt solutions were prepared by dissolving $Co(NO_3)_2 \cdot 6H_2O$ (Ventron) or $Cu(ClO_4)_2 \cdot 6H_2O$ (Johnson Matthey) in propylene carbonate (PC; Merck; p.a.) and drying the solutions using molecular sieves.

All stability constants, with the exception of the Co^{2+}–12C4 complex, were determined indirectly by means of disproportion reactions with Ag^+ [5]

$$ML^{n+} + Ag^+ \rightleftharpoons AgL^+ + M^{n+}$$

Using the known stability constant for the corresponding silver complex [6] the stability of the M^{n+} complex can be calculated according to the following equilibrium

$$M^{n+} + L \rightleftharpoons ML^{n+} \qquad K = \frac{[ML^{n+}]}{[M^{n+}][L]}$$

During the potentiometric titrations the ionic strength was kept constant at $I = 0.05$ mol dm^{-3} using tetraethylammonium perchlorate as the supporting electrolyte.

All reaction enthalpies and the stability of the Co^{2+} complex with 12C4 were measured using a Tronac Model 450 calorimeter. Only the reaction

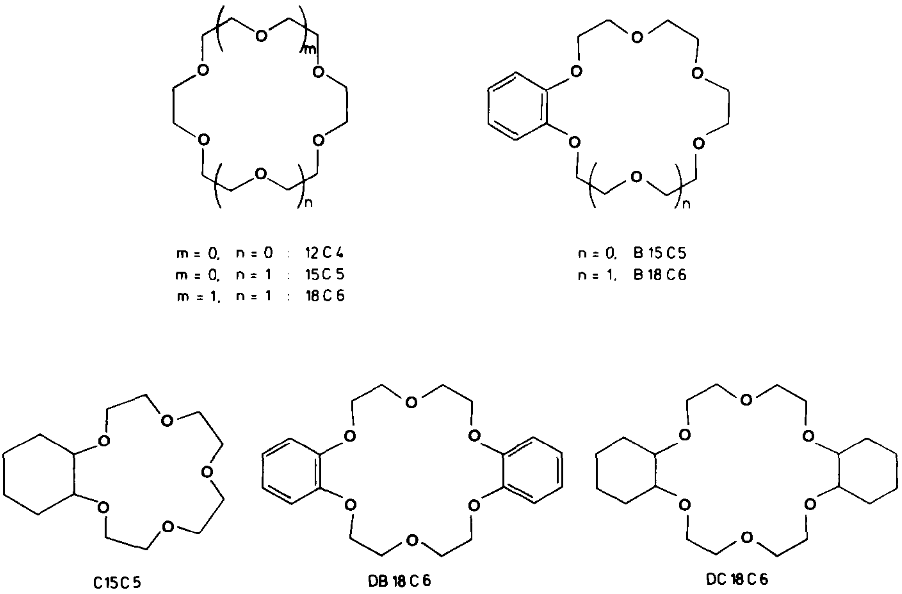

Fig. 1. Crown ethers used in this study.

enthalpy was calculated using a thermogram, a ligand solution (0.02–0.04 N) being titrated continuously into the salt solution (0.01–0.015 N). Under these conditions the heat produced during the titration is related to the reaction enthalpy, after correction for all non-chemical heat effects, by

$$Q = \Delta n \times \Delta H$$

Since the complex formation is complete, at any time the number of moles of the complex formed is identical to the number of moles of the ligand which is added to the salt solution. The experimental conditions and the procedure for estimating stability constants and reaction enthalpies from one thermogram have already been described in detail [7].

RESULTS AND DISCUSSION

The values of log K, ΔH and $T\Delta S$ for the complexation of Co^{2+} and Cu^{2+} by different crown ethers in propylene carbonate are summarized in Table 1. A comparison is not possible as there are no other data available. The validity of the experimental techniques used to estimate the stability constants and reaction enthalpies has been proved in the past [8,9].

The most stable complexes of both cations are formed with the ligand 15C5. This ligand obviously has an optimal size for accommodating these cations. Other factors influencing the stability constants, reaction enthalpies and reaction entropies of the remaining ligands are quite difficult to interpret.

In the case of the 15-crown-5 ligands, one benzo group attached to the ligand reduces the cavity dimensions of the ligand and the basicity of the ether donor atoms in its vicinity. The reaction enthalpies measured confirm

TABLE 1

Stability constants (log K; K in M^{-1}) and thermodynamic parameters (ΔH, $T\Delta S$ in kJ mol^{-1}) for the reaction of crown ethers with Co^{2+} and Cu^{2+} in propylene carbonate at 25 ° C

Ligand	Co^{2+} ($r = 0.57$ Å)			Cu^{2+} ($r = 0.73$ Å)		
	Log K	$-\Delta H$	$T\Delta S$	Log K	$-\Delta H$	$T\Delta S$
12C4 ($r = 0.6$ Å)	3.25	6.8	11.7	> 5	5.0	
15C5 ($r = 0.9$ Å)	4.55	29.1	−3.2	> 6.3	65.8	
B15C5	1.24	16.0	−9.0	> 5	32.9	
C15C5	5.63	24.4	7.6	> 5	66.2	
18C6 ($r = 1.4$ Å)	3.95	47.8	−25.4	6.35	51.0	−14.9
B18C6	2.97	43.1	−26.2	4.51	54.5	−28.9
DB18C6	2.40	61.2	−47.6	3.26	94.0	−75.5
DC18C6	4.71	35.0	−8.2	6.48	31.7	5.1

this phenomenon. In contrast, the cyclohexano group reduces only the flexibility of the ligand. As a result the increase in complex stability for the Co^{2+}–C15C5 complex is caused by changes in the reaction entropy on comparison with the unsubstituted crown ether 15C5.

The different 18-crown-6 ligands behave quite unexpectedly. The results are not in agreement with what one would expect from the experimental data in the literature for the complexation of other cations by these ligands [10].

The reaction enthalpies for the complex formation of Co^{2+} with the ligands 18C6 and B18C6 are rather similar. The same is true for the reaction entropies. In the case of the copper complexes both reaction enthalpies agree very well. Only the reaction entropy found for the ligand B18C6 inhibits the complexation of Cu^{2+} more than the crown ether 18C6. The formation of the corresponding DB18C6 complexes is favoured by the high reaction enthalpies, however, these are overcompensated for by strong negative reaction entropies. As a result, the stability constants of the DB18C6 complexes are the smallest values found for all 18C6 ligands.

One possible explanation for these unusual observations can be given from the results reported by Dickert et al. [4]. They observed a fluctuation in the donor atoms of some crown ethers around the complexed Co^{2+}. Not all donor atoms of the ligands 12C4 and 18C6 are interacting with the cation. This is also confirmed by the structure of a solid 18C6–Ni^{2+} complex [11]. The benzo groups reduce the cavity dimensions of the crown ethers, thus the interactions of all donor atoms with the complexed Co^{2+} are increased. Another perhaps even more important factor is the reduction of the ligand flexibilities. As a result of this the fluctuations of the ligand is less likely. This leads to an increase in the values of the reaction enthalpies. On the other hand, rigidity of the ligand leads to unfavourable contributions to the complex stability by the reaction entropy. The same may be true for the Cu^{2+} complexes. The ligand DC18C6 is more flexible than the corresponding dibenzo crown ether and it behaves in a similar way to 18C6. On comparison with the other 18-crown-6 ligands one finds that its higher stability constants are due only to entropic factors.

A further insight into this unusual complexation behaviour is expected from NMR measurements and from analyses of the structure of the solid complexes.

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