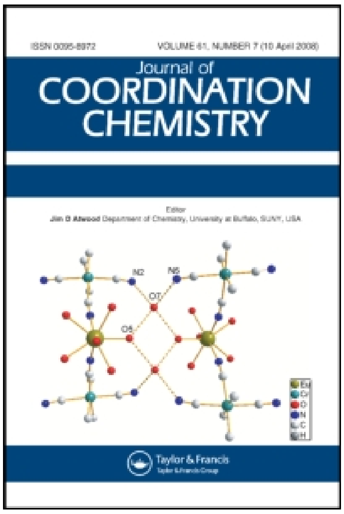

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COMPLEX FORMATION OF NONCYCLIC, MONOCYCLIC AND BICYCLIC LIGANDS WITH NICKEL(II) AND COBALT(II) IN ACETONITRILE

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Equilibrium constants and thermodynamic parameters for the complexation of nickel(II) and cobalt(II) by noncyclic, monocyclic and bicyclic ligands in acetonitrile have been determined by calorimetric titrations. The donor atoms and the ring size of the ligands play an important role for the stabilities of the complexes formed. An increasing number of nitrogen atoms in the crown ether favours complex formation. The number of nitrogen donor atoms of the macrocyclic ligands examined has a direct influence on the values of the reaction enthalpies.

Keywords: Complex formation; crown ethers; azacrown ethers; thiacrown ethers; cryptands; acetonitrile

INTRODUCTION

Crown ethers and cryptands are known to selectively form complexes with cations in different solvents.[1-3] It is known that the exchange of oxygen donor atoms by nitrogen or sulfur atoms results in an increasing ability to form complexes with transition metal ions. Complex formation between diazacrown ethers and cryptands with transition metal cations in aqueous solution has been studied in some detail.[4-6] There are only a few data available for the formation of such complexes in non-aqueous solutions.

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Till now, only few experimental data for the complexation of nickel(II) and cobalt(II) by azacrown ethers are known in the literature.[7] However, no thermodynamic data for these have been reported. Without their knowledge no discussion about factors influencing complex formation is possible. In this paper we present some stability constants together with thermodynamic data for complex formation between nickel(II) and cobalt(II) with noncyclic ligands, crown ethers and cryptands.

EXPERIMENTAL

The ligands used in this work are shown in Figure 1. The noncyclic ligands 1,8-diamino-3,6-dioxaoctane (DADO, Merck), Kryptofix 5 (K5, Merck), the ligands 15-crown-5 (15C5, Merck), 18-crown-6 (18C6, Merck), the monoazacrown ethers MA15C5 (Aldrich), MA18C6 (Aldrich), the dithiacrown ether DT18C6 (Parish), the diazacrown ethers (21), (22), (22DD) (Merck) and the cryptand (222) (Merck) are used without further purification. The diazacrown ether (22TT) and the dithiacrown ether DT15C5 were prepared and purified according to published procedures.[8,9] Salt solutions were prepared by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa Products) or $Co(ClO_4)_2 \cdot 6H_2O$ (Alfa Products) in acetonitrile (Rathburn Chemicals Ltd.) and drying the solutions with molecular sieves (4 Å).

Stability constants and reaction enthalpies were determined from calorimetric titrations using a Tronac Modell 450 calorimeter. A ligand solution ($0.08\,\mathrm{mol\,dm^{-3}}$) was titrated into the salt solution ($5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$). The heat, Q, produced during the titration is related to the reaction enthalpy, ΔH, after correction for all non-chemical heat effects, *e.g.*, stirring of the solution, by Equation (1),

$$Q = \Delta n \cdot \Delta H \qquad (1)$$

with the number of moles, Δn, of the complex formed at any time during the titration. Δn depends on the stability of the complex formed. The procedure for estimating stability constants and reaction enthalpies from thermograms has already been described in detail in the literature.[10] The reliability of the results obtained from calorimetric titrations has been shown.[11]

RESULTS AND DISCUSSION

The values of $\log K$, ΔH and $T\Delta S$ for the complexation of Ni^{2+} and Co^{2+} by the different ligands in acetonitrile are given in Table I. Few data

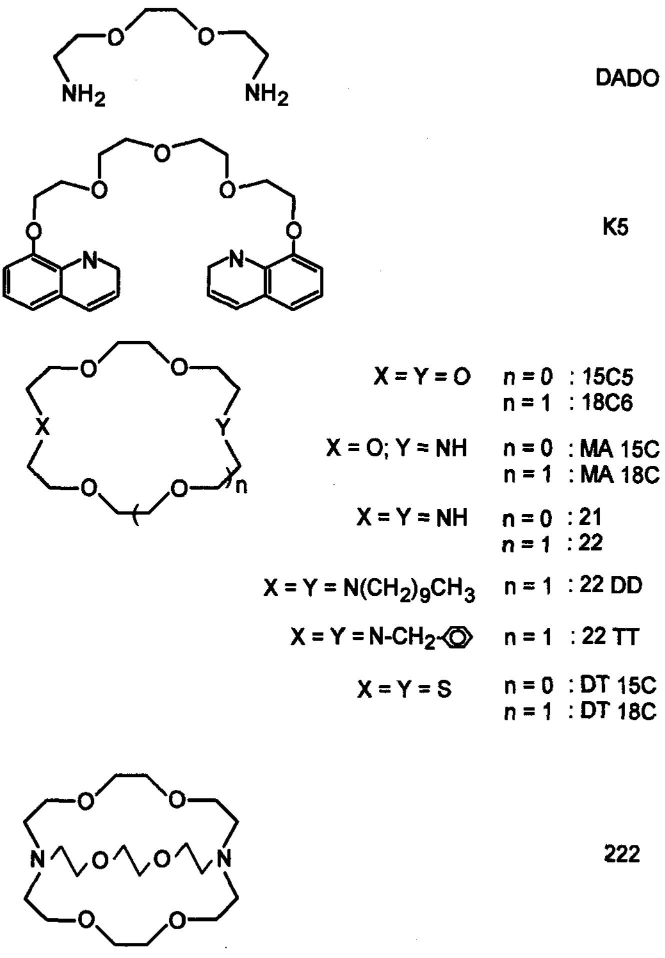

FIGURE 1 Ligands studied in this work.

available from the literature are included. They were measured by polarographic methods.

The noncyclic ligand DADO shows the highest values of the reaction enthalpies with both cations. However, complex formation with this ligand is disfavoured by entropic contributions. The noncyclic ligand K5 contains two pyridino groups which interact with the complexed cations. The basicity of this pyridino group is lower when compared with an amino group. As a result the measured values of the reaction enthalpies of the ligand K5 with both cations are much smaller than for the DADO. In contrast, the stability

TABLE I Stability constants ($\log K$) and thermodynamic parameters ΔH and $T\Delta S$ ($\mathrm{kJ\,mol^{-1}}$) for the formation of 1 : 1 complexes of noncyclic, monocyclic and bicyclic ligands with nickel(II) and cobalt(II) in acetonitrile at 298 K. Errors are ±5%

	Ni^{2+}			Co^{2+}		
	$\log K$	$-\Delta H$	$T\Delta S$	$\log K$	$-\Delta H$	$T\Delta S$
DADO	4.77	77.9	−50.7	3.85	69.5	−47.6
K5	>5	29.3		>5	11.7	
15C5	2.55	16.3	−1.7	4.24	12.9	−11.3
18C6	[a]	<1		[a]	<1	
DT15C5	[a]			[a]		
DT18C6	[a]			[a]		
MA15C5	>5	27.3		>5	36.3	
MA18C6	4.77	20.2	7.0	4.09	13.6	9.7
21	>5 4.89[b]	49.7		4.81	63.9	−36.5
22	>5 3.86[b]	36.8		>5	26.5	
22DD	>5	44.5		>5	35.8	
22TT	3.73	40.7	−19.4	>5	28.4	
222	4.56	59.0	−33.0	3.22	47.7	−29.3

[a]Not enough heat produced during the titration. [b]Ref. 7.

constants of the complexes formed with the ligand K5 are higher when compared with the complexes of DADO. This is only possible if complex formation with K5 is favoured by entropic contributions. From complexation studies of the ligand K5 with alkali and alkaline earth cations, it is known that a preorganization of this noncyclic ligand *via* attractive interactions between both end-groups is possible.[12,13]

The size and the donor atoms of the macrocyclic ligands play an important role for the stabilities of the complexes formed with Ni^{2+} and Co^{2+}. The crown ether 15C5 forms the weakest complex of all ligands examined with Ni^{2+}. The strong interactions between 18C6 and the solvent molecules are responsible for the fact that no complex formation can be observed with either metal cation.[14,15] Between both dithiacrown ethers and Ni^{2+} and Co^{2+} no complex formation is observable. The weak interactions between the sulfur donor atoms and both cations may be responsible.

The stability of complexes with Ni^{2+} and Co^{2+} increases with an increasing number of nitorgen donor atoms of the macrocyclic ligands. For both cations one observes an increase of reaction enthalpy with increasing number of nitrogen donor atoms. In the case of ligands with an identical number of nitrogen donor atoms but different number of oxygen donor atoms the values of the reaction enthalpies are higher in the case of the smaller ligands. The ring size influences the strength of interactions between the nitrogen donor atoms and the complexed cations.

In the case of the substituted diaza crown ethers (22DD) and (22TT) the values of the reaction enthalpies are comparable with the values measured with the ligand (22). The bulky substituents at the nitrogen donor atoms obviously have no influence upon the reaction enthalpies. No further increase of complex stabilities for both cations is observed with the macrobicyclic ligand (222). Increase of values of the reaction enthalpies are compensated by contributions of the reaction entropy. Further investigations are necessary to understand all factors influencing the macrocyclic and macrobicyclic effects for the complexation of these cations.

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