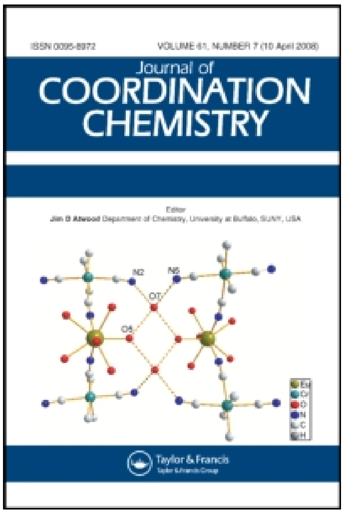

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Note

STABILITY CONSTANTS AND THERMODYNAMIC DATA FOR THE COMPLEXATION OF Pb^{2+} BY NONCYCLIC, MACROCYCLIC AND MACROBICYCLIC LIGANDS IN AQUEOUS SOLUTION

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The complexation of Pb^{2+} by noncyclic, macrocyclic and macrobicyclic ligands in aqueous solution was studied by calorimetric titration. In the case of noncyclic polyethers the contribution of reaction enthalpy to complex stability is much smaller when compared with macrocyclic polyethers. Complex stabilities increase if oxygen donor atoms are substituted by nitrogen. A further increase in complex stability is observed for the macrobicyclic ligands (cryptands), mainly caused by a further increase in reaction enthalpies.

Keywords: Cryptands; Crown ethers; Complexes; Lead

INTRODUCTION

During the last decades, complex formation between crown ethers and cryptands with different cations has been studied in some detail [1–3]. The most frequently examined cations are alkali and alkaline earth ions. Most reactions have been carried out in methanol.

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Surprisingly little is known about complex formation of heavy metal cations in aqueous solution with different macrocyclic or macrobicyclic ligands. However, a knowledge of these stability constants may be important for industrial applications. Purification or recovery of these metals from aqueous solution may be possible by complex formation with immobilized ligands [4], by transport through membranes [5] or by extraction into organic solvents [6].

For a better understanding of the factors influencing complex formation of heavy metal cations the complexation of lead(II) by noncyclic, macrocyclic and macrobicyclic ligands was studied in aqueous solution. For these reactions, only very few results are known in the literature, to date.

EXPERIMENTAL

The noncyclic ligands 2,5,8,11,14,17-hexaoxaoctadecane (PG; Riedel de Haen), 3,6,9,12,15-pentaoxaheptadecane-1,17-diol (HEG; Columbia) and 2,5,8,11,14,17,20-heptaoxaheneicosan (HG; Riedel de Haen) were used as purchased. The macrocyclic ligands 15-crown-5 (15C5; Merck), 18-crown-6 (18C6, Merck), benzo-18-crown-6 (B18C6, Merck), dibenzo-18-crown-6 (DB18C6, Fluka), dicyclohexyl-18-crown-6 (DC18C6, Merck), 4,10-diaza-15-crown-5 (21, Merck), 4,10-diaza-18-crown-6 (22, Merck), the cryptands (211), (221) and (222) (all Merck) and $Pb(NO_3)_2$ (Merck) were used without

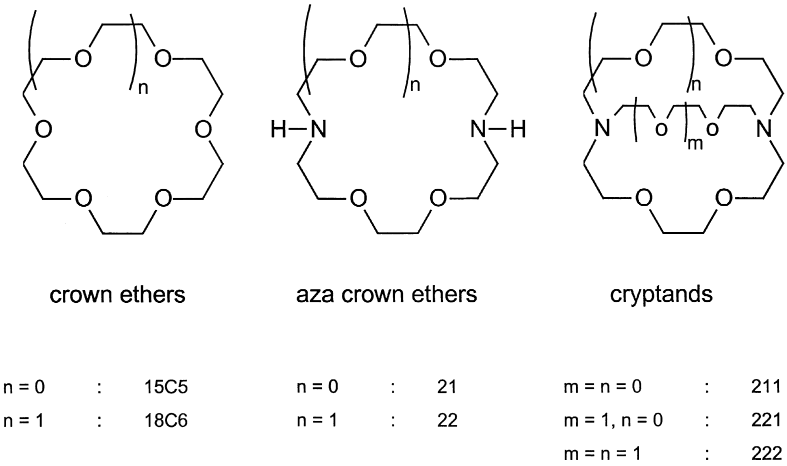

FIGURE 1 Chemical structures of unsubstituted macrocyclic and macrobicyclic ligands used in this study.

further purification. The chemical structures of some of the crown ethers and cryptands are given in Figure 1. Doubly distilled water was used as solvent.

Calorimetric titrations were performed using a titration calorimeter (Tronac Model 458). During the calorimetric titration a solution of the ligand ($0.04-0.08\,\mathrm{mol\,dm^{-3}}$) was added continuously to the salt solution ($2.5-5\cdot 10^{-3}\,\mathrm{mol\,dm^{-3}}$). The heat, Q, produced during the titration is related to the reaction enthalpy after correction for all non-chemical effects by the equation $Q = \Delta n \cdot \Delta H$ where Δn is the number of complexes formed at any time during the titration. Δn depends on the stability of the complex formed in solution. The mathematical treatment of the experimental data has already been described in detail [7–9]. The realibility of the stability constants measured by calorimetric titrations compared with other experimental methods has been proven [10].

RESULTS AND DISCUSSION

The results for the complexation of Pb^{2+} by noncyclic, macrocyclic and macrobicyclic ligands in aqueous solution are given in Table I. In the case of the noncyclic polyethers only very small values of reaction enthalpy are observed, compared with all macrocyclic and macrobicyclic ligands. Thus it is obvious that not all oxygen donor atoms of the noncyclic ligands are involved in complex formation.

The reaction enthalpies for complex formation with macrocyclic polyethers are much higher, as compared with noncyclic polyethers. Surprisingly, the number of oxygen atoms and changes of the basicity of the donor atoms through attached benzo groups has little influence upon reaction enthalpies. Obviously, not all donor atoms of the crown ethers are involved in complex formation. The substitution of two donor atoms in the crown ethers by nitrogen results in a further strong increase of values of reaction enthalpies.

The stability constant and reaction enthalpy of the smallest cryptand (211) is comparable with results for the diazacrown ether (22). This cryptand is not able to encapsulate the lead(II) ion. The larger cryptands form much more stable complexes and values of reaction enthalpies are the highest for all ligands examined. The complex formation with lead(II) is strongly influenced by the nature of the ligand. The stability constants increase from noncyclic polyethers to macrocyclic crown ethers and further to macrobicyclic cryptands.

TABLE I Stability constants, log K, (K in $dm^3 mol^{-1}$) and reaction enthalpies ΔH and entropies TΔS ($kJ mol^{-1}$) for the complexation of Pb^{2+} by different ligands in aqueous solution at 25°C

Ligand	*Log K*	*– ΔH*	*TΔS*
PG		< 1	
HEG	2.02	3.3	8.2
HG	2.08	3.0	8.8
15C5	1.81	10.1	0.2
	1.85[a]	13.6[a]	– 3.1[a]
21	5.6[b]	42.8	– 11.0
18C6	4.16	20.2	3.4
	4.27[a]	21.6[a]	2.7[a]
	4.04 ± 0.03[c]		
B18C6	3.27	20.9	– 2.3
	3.19[d]	17.0[d]	1.1[d]
DB18C6	1.89 ± 0.09[e]		
DC18C6	4.15	25.0	– 1.3
	4.82 ± 0.02[c]		
22	6.6[b]	47.3	– 9.8
211	7.4[b]	42.0	0.1
221	12.1[b]	61.9	6.9
222	12.5[b]	58.8	12.2
	12.36[f]	57.7[f]	12.5[f]

[a] Reference [11]; [b] Reference [12]; [c] Reference [13]; [d] Reference [14]; [e] Reference [15]; [f] Reference [16].

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