Inorganica Chimica Acta, 98 (1985) 43–46

Complex Formation between Lead(II) and Noncyclic, Monocyclic and Bicyclic Ligands in Methanol

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Received June 12, 1984

Abstract

The complex formation between lead(II) and different noncyclic ligands, crown ethers, aza crown ethers, and cryptands has been studied in methanol by titration calorimetry. Comparing the results for the reaction of glycols, glymes, and crown ethers with Pb^{2+} a macrocyclic effect is found which is caused by a favourable entropic change. By inserting nitrogen atoms into the ligands this effect disappears. A cryptate effect for the complexation of lead(II) is observed in the case of the cryptands (221) and (222), which is due to a drastic increase in ΔH. The cavity of the cryptand (211) is too small to accomodate Pb^{2+} without deformation.

Introduction

Since the complexation behaviour of cyclic ligands was first examined it was observed that the stability of complexes with cyclic ligands was larger than that of open-chain ligands.

This 'macrocyclic effect' was first reported by Cabiness and Margerum [1] for the reaction of cyclic tetraamines with Cu^{2+}. Frensdorf [2] got similar results by comparing the stability constants of the complexing reactions of alkaline ions with 18C6 and the noncyclic PG.

A further enhancement of complex stabilities was found for the bicyclic cryptate complexes [3]. The increase is very large and has received the name 'cryptate effect' [3]. A detailed summary of the published literature concerning these two effects is given by Lamb [4].

However some exceptions have been reported where neither macrocyclic nor cryptate effects were observed. Anderegg [5] studied the binding of the ligands DDO, (22), and (222) with Hg^{2+}, Cd^{2+} and Ag^{+}. In all cases the stability constants of the noncyclic, cyclic, and bicyclic ligands have nearly the same value. Only in the complexation of Ag^{+} with (222) was a slight increase in stability found.

Comparing the stability constants of several linear S-containing ligands with their cyclic analogs towards Ag^{+} and Hg^{2+} no macrocyclic effect is observed [6]. This may be caused by the fact that only part of the ring participates in the coordination [7]. The same reason may be responsible for the absence of a macrocyclic effect in the complexation of Pb^{2+} with N- and S-containing crown ethers and their noncyclic analogs [8]. On the other hand, by comparing the stabilities of $[Pb\text{-}18C6]^{2+}$ to those of $[Pb\text{-}TeG]^{2+}$ and $[Pb\text{-}(TeG)_2]^{2+}$ a macrocyclic effect of about 10^4-fold was estimated [9]. This was entirely accounted for by a favourably entropic contribution.

Though many stability constants of cyclic and bicyclic ligands with Pb^{2+} in water and in anhydrous methanol have been reported, only a few thermodynamic values of these reactions are published. So a discussion about the presence or absence of the macrocyclic and cryptate effect is difficult because it is important to separate the enthalpies and entropic factors. In order to get more information about these two effects the interactions of Pb^{2+} with different ligands in absolute methanol were investigated by calorimetric titrations.

Experimental

The noncyclic ligands, shown in Fig. 1, 2,2′-[1,2-ethanediylbis(oxy)] bisethanol (TEG; Merck); 2,2′-[oxybis(2,2-ethanediyloxy)] bisethanol (TeEG; (Merck); 3,6,9,12-tetraoxatetradecane-1,14-diol (PEG; Columbia); 3,6,9,12,15-pentaoxaheptadecane-1,17-diol (HEG; Columbia); 2,5,8,11,14,17-hexaoxaoctadecane (PG; Riedel-de Haen); 1,8-diamino-3,6-dioxaoctane (DDO; Merck); N-(2-aminoethyl)-1,2-ethanediamine (DETA; Ega); N,N′-bis(2-aminoethyl)-1,2-ethanediamine (TETeA; Ega); 1,8-diaminooctane (DAO; Merck), and 2,2′-iminodiethanol (DEA; (Merck) were distilled under vacuum and dried over molecular sieve. The ligands 2,5,8,11,14-pentaoxapentadecane (TeG; Riedel-de Haen),2,5,8,11,14,17,20-heptaoxaheneicosan (HG; Riedel-de Haen); and 1,13-bis(8-chinolyl)-1,4,7,10,13-pentaoxatridecane (K5, Kryptofix-5; Merck), the monocyclic ligands 15-Crown-5 (15C5), 18-Crown-6 (18C6), and the

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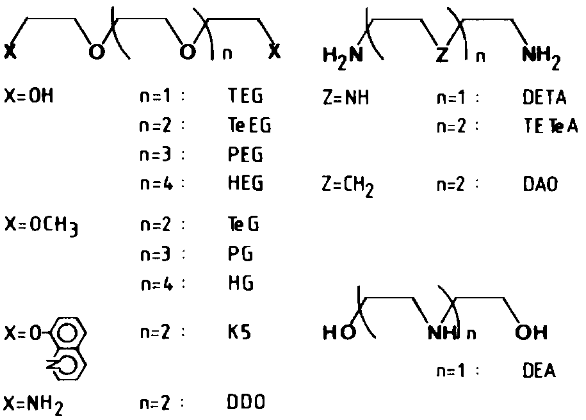

Fig. 1. The oligoethylenglycols and related compounds studied in this work.

cryptands (21), (22), (211), (221) and (222) (all Merck), see Fig. 2, were used without further purification.

All solutions of $Pb(NO_3)_2$ (Merck) were prepared by dissolving the dried salt in anhydrous methanol (H_2O contents less than 0.01%; Merck).

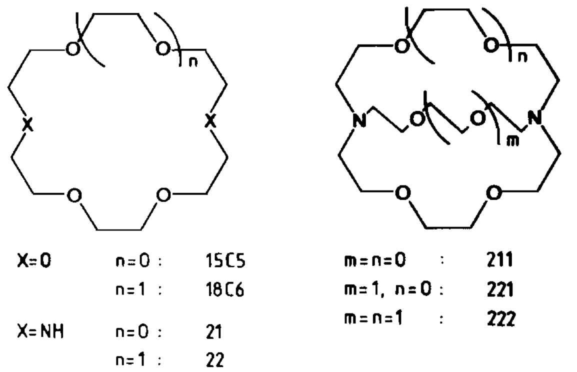

Fig. 2. Crowns, monocyclic azacrowns, and cryptands studied in this work.

With one exception all stability constants and reaction enthalpies were determined by titration calorimetry using a Tronac Model 450 calorimeter. The ligand solutions (0.04–0.08 M) were titrated into the $Pb(NO_3)_2$ solutions (3×10^{-3}–6×10^{-3} M). A typical thermogram for the titration of Pb^{2+} with 15C5 is given in Fig. 3.

The heat Q produced during the reaction and corrected for all non-chemical heat effects, is related to the reaction enthalpy

$$Q_t = \Delta H \times \Delta n_t$$

where Δn_t is the number of moles of complex formed at the time t. Δn_t itself is a function of the stability constant of the measured reaction. Because the temperature increase during the titration is small, the stability constant is practically unchanged.

In all cases the reaction could be described by the following equation

$$Pb^{2+} + L \rightleftharpoons PbL^{2+} \quad K = \frac{[PbL^{2+}]}{[Pb^{2+}]\,[L]}$$

Log K and ΔH values were calculated from the thermogram by known techniques [10].

Log K values for the reaction with nitrogen containing ligands and 18C6 were found to be greater than 5 and could not be calculated from the thermogram. Only in one case was it possible to determine the stability constant by potentiometric titration; in all other cases insoluble precipitations were formed under the experimental conditions.

From the disproportionative reaction of $Pb(NO_3)_2$ with the $[Ag\text{-}K5]^+$ complex, using the stability constant of the silver-ion complex with K5 in methanol (log K = 7.02 at 25 °C) the stability of the lead complex could be calculated. The ionic strength was 5×10^{-2} M, and $N(C_2H_5)_4NO_3$ was used as supporting electrolyte. The detailed experimental procedure is given in [11].

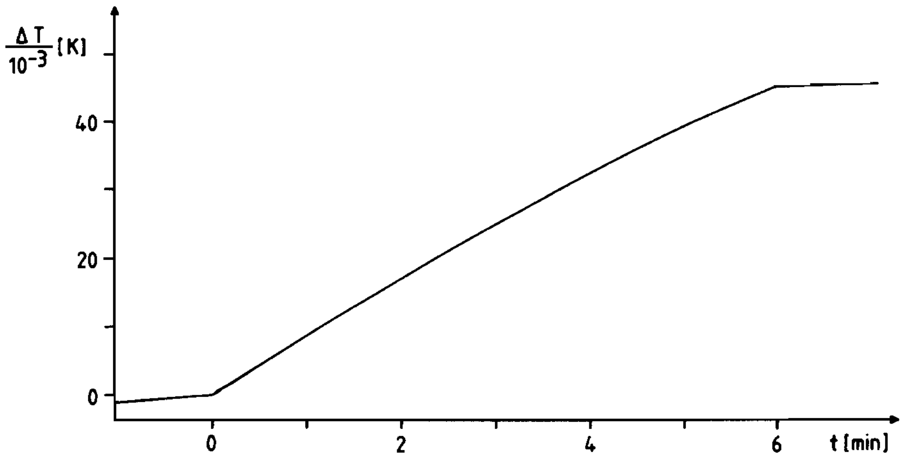

Fig. 3. Thermogram for the titration of lead(II) with 15C5. The titration starts at t = 0 and ends at t = 6 min.

Results and Discussion

The values of log *K*, ΔH, and $T\Delta S$ for the reactions of Pb^{2+} with noncyclic ligands are given in Table I. The stability constants of the glycols are nearly ten times greater when compared with the glymes. Though reaction enthalpies of the corresponding glycols and glymes are nearly the same the differences in stability are mainly caused by less favorable entropic changes in the case of the glymes.

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

Ligand	log K	$-\Delta H$ (kJ mol^{-1})	$T\Delta S$ (kJ mol^{-1})
TEG	4.04	2.9	20.0
TeEG	3.17	13.3	4.8
PEG	3.32	31.4	−12.5
HEG	3.61	37.5	−17.0
TeG	2.06	7.2	4.5
PG	2.22	26.4	−13.7
HG	2.22	38.9	−26.2
K5	5.12	27.6	1.5
DDO	>5	33.8	
DAO	>5	27.0	
DEA	>5	13.9	
DETA	>5 10.25[a]	33.9	
TETeA	>5 11.60[a]	43.5	

[a] In 80% Ethanol, from ref. [15].

With rigid end groups K5, a derivate of TeEG, is not comparable with TeEG and TeG. The increase in stability is only due to the stronger interaction between Pb^{2+} and the nitrogen atoms of the end groups leading to a greater value of ΔH. The entropy change is nearly identical for these three ligands. The complexation of alkaline ions with K5 is also stronger than with the corresponding glycol and glyme. In this case the enhancement results only from more favourable entropy changes. In contrast to the complexation of Pb^{2+} ΔH does not vary with these ligands [12].

It is obvious that all other nitrogen-containing ligands form complexes with Pb^{2+} which are stronger by several orders of magnitude than in the case of glycols and glymes. Even the ligand with one nitrogen atom and two hydroxal groups, DEA, complexes the ion with a stability constant greater than 10^5 M^{-1}. DEA shows a value of ΔH just twice that of the value found for DAO. It may be concluded from this that the two hydroxyl groups of DEA do not take part in complexation, and furthermore that the strength of a Pb–N bond is of the order of 14 kJ mol^{-1}. The Pb–O bond is much weaker. It is not possible to calculate from the experimental data an approximate value for the strength of this bond, although it is somewhere between 3 and 8 kJ mol^{-1}. These results have to be taken into account in discussing whether or not there exists a macrocyclic and cryptate effect for the complexation of Pb^{2+}.

In Table II stability constants and thermodynamic values for the reaction with cyclic and bicyclic ligands are given. The stability of the complexes with 15C5 and the different glycols have the same order of magnitude. HEG, the noncyclic analog of 15C5, interacts stronger with Pb^{2+} than the cyclic ligand. This is not surprising because the cavity of 15C5 (r = 0.9 Å) is too small for Pb^{2+} (r = 1.2 Å) [13]. Therefore it cannot interact with all donor atoms of the ligand. The noncyclic ligand has no steric difficulties to surround the ion. On the other hand the entropic term favours the cyclic ligand.

TABLE II. Stability Constants (log K; K in M^{-1}) and Thermodynamic Parameters for the Reaction of Pb^{2+} 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	3.92	24.7	−2.4
18C6	>5 7.7[a] 6.5[b]	45	
21	7.87[c]	18.1	26.5
22	9.48[c]	29.1	24.7
211	8.18[c]	24.6	21.8
221	15.11[c]	67.9	17.9
222	10.41[c]	72.7	−13.4

[a] See text for explanation. [b] In 70% MeOH, from ref. [16].
[c] From ref. [17].

This behaviour is even more pronounced with 18C6 as ligand since its cavity (r = 1.4 Å) [13] is big enough to accommodate the lead ion. The ΔH value of this reaction is nearly the same as with HEG and HG. The big increase in complex stability with 18C6 can be traced back to a favourable entropic change. This result is in agreement with that found in water [9].

It is possible to estimate a value of log $K \approx 7{,}7$ for the reaction between 18C6 and Pb^{2+} in methanol under the assumption that only enthalpy changes are responsible for the difference in complex stability of 15C5 and 18C6, while the reaction entropies for both ligands are almost identical. The validity of this hypothesis can be proved by comparison with the other cyclic and bicyclic ligands examined. The difference in log K between the ligands (21) and (22) results only from an enthalpic change. The same effect is observed for the bicyclic ligands (211) and (221). In both cases the entropic term for the complexation of Pb^{2+} is unaltered.

The reaction between the lead ion and nitrogen-containing cyclic ligands is quite different. No variation in complex stability could be observed between monocyclic and noncyclic ligands. Even the reaction enthalpies of DAO and (22) are equal. Both ligands contain two nitrogen atoms and (22) four additional oxygen atoms. Obviously the oxygen atoms do not play an important role in the complexation.

The high stability constant of the bicyclic ligand (221) compared with all other ligands is due to a drastic increase in ΔH. The same is true for (222). However, an entropic change compensates for this effect resulting in a lower stability constant. Although these ligands contain two nitrogen atoms, the reaction enthalpy was found to be 5 times larger than the formation enthalpy of a single Pb–N bond. This enhancement cannot be explained by the participation of the oxygen atoms in the complex formation. No indication is found for this in the case of the monocyclic azacrowns. The low ΔH value for the complexation of the smallest bicyclic ligand (211) (r = 0.8 Å) [14] may be caused by its deformation during the reaction with the lead ion (r = 1.2 Å) [13].

Summarizing the results it is evident that a macrocyclic effect occurs for the complex formation between Pb^{2+} and crown ethers. Favourable entropic contributions are responsible for this effect. Introduction of two nitrogen atoms into the cyclic ligand causes the disappearance of the macrocyclic effect.

The extremely high values of ΔH for the bicyclic ligands can be interpreted as a cryptate effect. Thus both macrocyclic and cryptate effects play a role in the complexation of lead(II).

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