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Complexation of Pb^{2+} by Cryptands in Propylene Carbonate

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Introduction

As an ongoing part of our study on the complexing properties of cryptands in various solvents, we present here the results concerning the complexation of Pb^{2+} by five diazapolyoxamacrocycles: 21, 22, 211, 221 and 222 (see Fig. 1), in propylene carbonate (PC). This study has been performed by spectrophotometry at 25 °C, with Et_4NClO_4 10^{-2} *M* as supporting-electrolyte. The number and nature of the different complexes in solution and the values of their stability constants β_{xoz}, defined as usually by the following equilibria:

$$xPb^{2+} + yH^+ + zL \rightleftharpoons Pb_xH_yL_z^{(2x+y)+}$$

with here y = 0, have been determined. These are compared with our previous results in water and methanol [1–3].

Experimental

Solvent and Reagents

Propylene carbonate was purified by the method already reported by B. Gosse and A. Denat [4]. Solutins of ligands were prepared by dissolving weighed quantities of ligand in the solvent to obtain a concentration C_L about 10^{-2} *M*.

Lead solutions were prepared just before each experiment from anhydrous $Pb(NO_3)_2$, previously dried at 100 °C for 48 h. Because of its low solubility, a slight excess of this salt was stirred vigorously for 12 h in PC containing 10^{-2} *M* Et_4NClO_4. The saturated solution thus obtained was then filtered and kept at 25 °C in a bath before being titrated.

Tetraethylammonium perchlorate used as supporting electrolyte was recrystallized twice from water and then dried under vacuum at 60 °C for 24 h.

Pb^{2+} Solutions Titrations

As Pb^{2+} solutions exhibit an absorption peak at 270 nm, a spectrophotometric titration could be carried out in a mixed water-PC medium. The saturated Pb^{2+} solution in PC was diluted with an aqueous 10^{-2} *M* $HClO_4$ solution in order to avoid hydrolysis. The solution X thus obtained was analyzed by comparing its spectrum to those of two other solutions, A and B, prepared from two aqueous stock solutions 10^{-2} *M* and 2 × 10^{-2} *M* in $Pb(NO_3)_2$ respectively, each containing the same concentration of $HClO_4$ and Et_4NClO_4 and the same percentage of PC as solution X. If C_X, C_A and C_B are respectively the Pb^{2+} concentrations of solutions X, A and B, and D_X, D_A and D_B the corresponding optical densities for λ's chosen so that $D_B = 2D_A$ exactly, then we have:

$$C_X = \frac{D_X \cdot C_A}{D_A}$$

The mean value for 5 different saturated Pb^{2+} solutions was $C_{Pb} = (4.26 \pm 0.17)\ 10^{-5}$ *M*.

Results thus obtained were first checked by differential pulse polarographic titrations of the Pb^{2+} solutions in PC: two determinations on the same saturated $Pb(NO_3)_2PC$ solutions gave $C_{Pb} = (4.26 \pm 0.35)\ 10^{-5}$ *M*, in excellent agreement with the spectrophotometric results. These results also are a measurement of the $Pb(NO_3)_2$ solubility in PC, in presence of 10^{-2} *M* Et_4NClO_4.

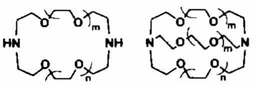
21 m=0,n=1
22 m=n=1
211 : m=0, n=1
221 m=1, n=0
222 m=n=1

Fig. 1. The diazapolyoxamacrocycles.

Experimental procedure

Complexation was studied with a CARY 17D spectrophotometer equipped with an interfacing accessory coupled to a teletypewriter which recorded the optical densities every 5 nm. Temperature was maintained at 25 °C in the cells compartment. 5 ml of the saturated solution of $Pb(NO_3)_2$ in PC were placed in 2 cm cuvettes. The spectra were recorded between 220 nm and 350 nm after each addition of the ligand solution. The reference was a solution of Et_4NClO_4 10^{-2} *M* in PC. Neither the ligand nor the solvent absorb in this region. Data were first treated by the method of optical densities matrix rank analysis, as previously described [5, 6, 2], providing the minimum number of absorbing species necessary to interpret the set of recorded spectra. The measurements were then interpreted by the program LETAGROP-SPEFO [7] which calcu-

TABLE I. Log β_{xoz} of Pb^{2+} Complexes with Some Diazapolyoxamacrocycles in PC, at 25 °C, I = 10^{-2} *M* (Et_4NClO_4).

Complexes	Ligands				
	21	22	211	221	222
PbL^{2+}	8.64 ± 0.27	11.64 ± 0.21	7.01 ± 0.24	16.34 ± 0.33	16.00 ± 0.60
Pb_2L^{4+}	12.30 ± 0.27	15.30 ± 0.31	11.30 ± 0.33	20.07 ± 0.21	21.20 ± 0.80

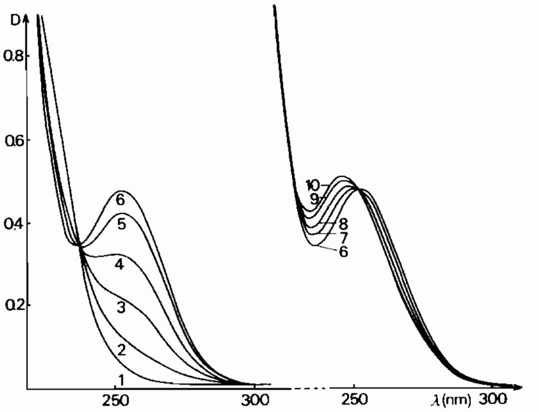

Fig. 2. UV spectra of $Pb(NO_3)_2$ with increasing concentrations of 22. C_{Pb} = 4.27 × 10^{-5} *M*; No spectrum: 10^5 C_L; 1: 0; 2: 1.04; 3: 2.0; 4: 3.0; 5: 4.13; 6: 5.16; 7: 5.67; 8: 6.19; 9: 7.72; 10: 9.25.

lates the stability constants of the different complexes.

Results and Discussion

Three kinds of spectra can be observed corresponding to the following systems:

i) Pb^{2+}/22 and Pb^{2+}/222
ii) Pb^{2+}/21 and Pb^{2+}/221
iii) Pb/211

Figures 2–4 show examples of each case, *i.e.* the spectra of $Pb(NO_3)_2$ solutions in presence of increasing quantities of 22, 221 and 211 respectively.

In the case of 22, an apparent maximum is observed at 255 nm for the lower ligand concentrations (1.04 × 10^{-5} < C_L < 4.13 × 10^{-5} *M*). This peak then moves towards the lower wavelengths with raising C_L and is stabilized at 240 nm. Two isobestic points at 252 and 237 nm are noted.

For the 211 system, the absorption peak at 250 nm becomes more intense until $C_L \cong 5 \times 10^{-5}$ *M*, *i.e.* about the 1:1 stoechiometry. Then it decreases and moves towards the lower λ's as C_L raises.

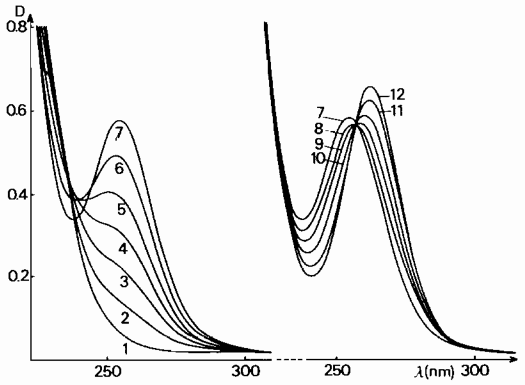

Fig. 3. UV spectra of $Pb(NO_3)_2$ with increasing concentrations of 221. C_{Pb} = 4.43 × 10^{-5} *M*; No spectrum: 10^5 C_L; 1: 0; 2: 0;86; 3: 1.71; 4: 2.56; 5: 3.42; 6: 4.27; 7: 5.12; 8: 5.96; 9: 681; 10: 7.66; 11: 8.50; 12: 9.34.

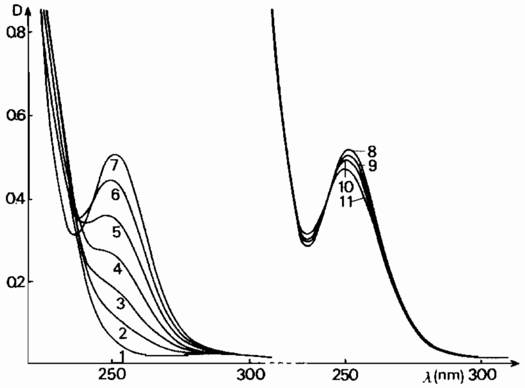

Fig. 4. UV spectra of $Pb(NO_3)_2$ with increasing concentrations of 211. C_{Pb} = 4.43 × 10^{-5} *M*; n) spectrum: 10^5 C_L; 1: 0; 2: 1.04; 3: 2.0; 4: 3.10; 5: 4.13; 6: 5.16; 7: 5.67; 8: 8: 5.24; 9: 6.84; 10: 7.63; 11: 8.43.

For the 221 system, an absorption maximum is found again at 255 nm. A second peak forms at 262 nm with increasing ligand concentration, as the first disappears.

In all cases, except the 211 system, treatment of the data by the matrix rank method shows that they can be interpreted with a minimum of three independent absorbing species, one of them being necessarily the free Pb^{2+} cation. For 211, two species are enough to interpret the full set of data. Treatment by program LEGRAGROP-SPEFO shows, in all cases, the formation of the mononuclear PbL^{2+} and binuclear Pb_2L^{4+} complexes. The corresponding logarithms of the stability constants are given in Table I. The confidence intervals correspond to $\pm 2\sigma$.

The 1:1 complexes are more stable in PC than in water or methanol as expected for a less solvating medium.

The most stable complex is formed with 221 whose cavity radius (1.1 Å) is the nearest to the lead cation radius (1.18 Å) [8].

This *size effect* and the large *macrocyclic effect* observed for 222 and 221 1:1 bicyclic complexes, compared to their homologues monocyclic complexes with 22 and 21 respectively, are good arguments for a *cryptate structure* of $Pb222^{2+}$ and $Pb221^{2+}$.

On the contrary $Pb211^{2+}$ is less stable in PC than in methanol and even than in water. This fact could be related to the non-inclusive nature of this species, the cavity of the 211 certainly being too small to encage the lead cation. The transfer from water to a less solvating solvent may also lead to structural or conformational changes and to a destabilization of the complex.

In PC as in methanol [2, 3] binuclear species are found in addition to the 1:1 complexes. In these complexes the metallic cations cannot be both in the macrocyclic cavity due to size considerations. In Pb_2211^{4+} both Pb^{2+} cations must necessarily be outside the cavity. For Pb_2221^{4+} and Pb_2222^{4+} we could consider the two structures already proposed for copper binuclear complexes in methanol [3], *i.e.* the first Pb^{2+} inside the cavity, the second outside, or both outside the cavity. But up to now we have no means to distinguish between these two possibilities.

These results will be discussed in more detail later, and used to test the new extrathermodynamic assumption involving cryptates, recently proposed in the literature.

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