

Chloride Complexes of Organolead(IV) Ions

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The complexity of solutions of some organolead (IV) and chloride ions has been investigated in a constant ionic medium (1 M ClO₄) at 25°C by means of potentiometric methods. Only mononuclear complexes have been found and the stability constants have been determined.

A comparison among fluoride, acetato, chloride complexes has been done in order to gain some knowledge about the nature of the ligand-metal bond.

Introduction

The chloride complexes of organolead (IV) ions in aqueous solutions have previously been the subject of a great number of investigations¹⁻⁶ in which polarographic, ion exchange and solubility methods have been applied. The papers¹⁻⁴ were of qualitative nature, in the remaining ones the stability constants of only some R₃PbCl complexes are reported.⁵⁻⁶

Recently precise measurements with electrochemical cells have been made to determine the extent of association of acetate and fluoride ions with organolead (IV) ions.⁷⁻⁸ Therefore, for the same organolead (IV) ions (Me₂Pb²⁺, Et₂Pb²⁺, n-Pr₂Pb²⁺, Me₃Pb⁺, Et₃Pb⁺) the emf investigations have been extended to the Cl⁻ ligand in order to obtain quantitative informations regarding the nature and the stability of the species present in aqueous solutions of sodium chloride.

Symbols:

B = total organolead (IV) concentration

A = total chloride concentration

b = equilibrium concentration of organolead (IV) ion

a = equilibrium concentration of chloride ion

\bar{n}_B = average number of chloride ions bound to each organolead (IV) ion

$$= (A - a) / B$$

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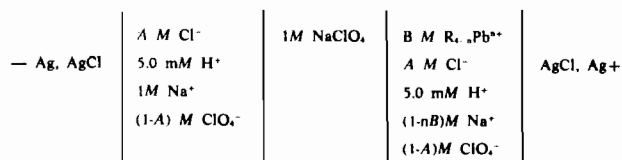
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Experimental Section

Method. The experiments have been carried out as potentiometric titrations.

The starting solutions of an organolead (IV) ion were titrated with a NaCl standard solution till solid organolead (IV) chlorides were formed.

In order to minimize activity coefficients changes the total ionic concentration was adjusted to 1 M by adding NaClO₄. Concentration cells of the type



were set up and the potentials measured as function of the chloride concentration. The presence of 5.0 mM HClO₄ was sufficient to prevent any significant hydrolysis of the aquo-organolead (IV) ions.⁹

Chemicals and Reagents. 1.0058 M NaCl (Merck suprapurum) solution was prepared by weighing the salt according to its formula weight. The sodium perchlorate, the perchloric acid, the organolead perchlorates standard solutions were prepared, stored and checked as reported in a previous paper.⁷ The distilled water used in the preparations of all of the solutions was obtained by distillation of demineralized water from an alkaline KMnO₄ solution in an all glass apparatus. 99.99% Nitrogen, further purified according to Arthur, was bubbled through 1 M NaClO₄ to obtain the correct vapor pressure.

Procedure. The emfs were read within ±0.01 mV by using a Leeds and Northrup K-3 potentiometer used in combination with a Sefram type GT 2D galvanometer.

The cell potentials were stable and reproducible within ±0.05 mV.

The cell arrangement was thermostated at 25°C ± 0.05.

NaCl standard solution was added to both half cells from a Radiometer Auto-burette type ABU - 1b equipped with a burette type B 150 unit with a total volume of 2.500 ml.

Ag, AgCl electrodes were prepared according to Brown.¹⁰

(9) C. E. Freidline and R. S. Tobias, *Inorg. Chem.*, 5, 354 (1966).

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Differences between different silver chloride electrodes were always less than 0.05 mV.

Results

As an example, the equilibrium data for the chlorocomplex formation of $\text{Et}_2\text{Pb}^{2+}$ are shown in Figure 1 and Table I: \bar{n}_B is plotted as a function of $-\log[\text{Cl}^-]$.

Table I. Typical Titration Data for Diethyllead (IV) Chloride Complexes.

B/mM	A/mM	a/mM	\bar{n}_B
39.07	2.00 ₈	1.48 ₅	0.013 ₄
38.99	4.00 ₇	2.95 ₆	0.027 ₆
38.92	5.99 ₆	4.43 ₁	0.040 ₃
38.84	7.98 ₃	5.90 ₁	0.053 ₆
38.76	9.95 ₆	7.35 ₆	0.067 ₁
38.57	14.86	10.97	0.10 ₁
38.38	19.72	14.59	0.13 ₄
38.19	24.53	18.21	0.16 ₅
38.01	29.29	21.72	0.19 ₉
37.83	34.01	25.22	0.23 ₂
37.64	38.68	28.71	0.26 ₅
37.46	43.31	32.17	0.29 ₇
37.29	47.90	35.67	0.32 ₄
36.93	56.93	42.50	0.39 ₁
36.59	65.80	49.31	0.45 ₁
36.25	74.50	56.20	0.50 ₅
35.92	83.05	63.02	0.55 ₈
35.59	91.44	69.81	0.60 ₆
35.27	99.67	76.49	0.65 ₇
34.96	107.76	83.09	0.70 ₆
34.65	115.71	89.74	0.75 ₅
34.34	123.52	96.13	0.79 ₈
34.04	131.19	102.81	0.83 ₄

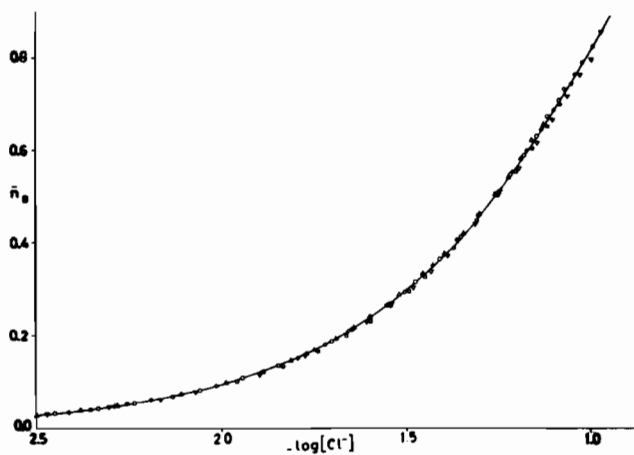


Figure 1. Average number of chloride ions bound for diethyllead (IV) ion as a function of $-\log[\text{Cl}^-]$ at 25°C in a 1M perchlorate medium: Δ 97.67 mM; \circ 78.15 mM; \diamond 58.62 mM; \square 39.07 mM; ∇ 19.54 mM stoichiometric $\text{Et}_2\text{Pb}^{2+}$ concentration. Curve calculated with $\beta_1 = 9.21 \cdot \text{mole}^{-1}$

The equilibrium ligand concentrations were calculated from the equation:

$$\frac{\Delta E/\text{mV}}{59.15} = \log \frac{A}{a}$$

where ΔE is the E.M.F. of concentration cells in which half a cell contained no organolead ion and the same analytical concentration of sodium chloride of the other half a cell. Thus \bar{n}_B was obtained by the equation:

$$\bar{n}_B = (A-a)/B$$

The measurements of the complex formation at different analytical concentrations of organolead (IV) ion give the same formation curve within the experimental errors, so there is no indication of polynuclear complexes. For the dialkylorganolead (IV) ions the experimental data, in the range of concentrations investigated, can be explained by the existence of a 1:1 and a 2:1 complexes according to the following equilibria:



When only two complexes are formed

$$\bar{n}_B = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2}$$

By a graphical method¹¹ the β_1 and β_2 values were obtained as the intercept and the slope of the plot of

$$\frac{\bar{n}_B}{(1-\bar{n}_B)a} \text{ against } \frac{(2-\bar{n}_B)a}{(1-\bar{n}_B)}$$

Figure 1 shows the agreement between the experimental \bar{n}_B ($\log a$) points and the curve calculated by the appropriate β_1 , β_2 values.

For the trialkyl lead ions typical titration data are reported in Table II. It is found that only 1:1 complex is formed, at least in the range of concentration investigated.

A point by point calculation gave the stability constant values of the monochlorocomplexes.

Table II. Chloride Complexing of the Triethyllead (IV) Ion.

B/mM	A/mM	a/mM	b/mM	$\beta_1/(\text{l mole}^{-1})$
41.44	4.00 ₇	3.50 ₃	40.94	3.4 ₉
41.36	5.99 ₆	5.23 ₃	40.59	3.6 ₂
41.28	7.98 ₃	6.97 ₂	40.27	3.6 ₀
41.20	9.95 ₆	8.68 ₇	39.93	3.6 ₆
41.00	14.86	12.98	39.12	3.7 ₀
40.79	19.72	17.26	38.33	3.7 ₂
40.60	24.53	21.61	37.68	3.5 ₉
40.40	29.29	25.77	36.88	3.7 ₀
40.20	34.01	29.96	36.15	3.7 ₄
40.01	38.68	34.14	35.47	3.7 ₅
39.82	43.31	38.28	34.79	3.7 ₈
39.63	47.90	42.45	34.18	3.7 ₆
39.25	56.93	50.58	32.90	3.8 ₁
38.89	65.80	58.66	31.75	3.8 ₃
38.53	74.50	66.78	30.81	3.7 ₅
38.17	83.05	74.79	29.91	3.6 ₉
37.83	91.44	82.63	29.02	3.6 ₇
37.49	99.67	90.19	28.01	3.7 ₅

(11) F. J. C. Rossotti and H. Rossotti, The determination of stability constants. McGraw-Hill-Company, Inc. 1961 New York.

Discussion

In Table III are reported the stability constants β_1 , β_2 . As suggested in previous papers⁷⁻⁸ the dependence of the stability constants upon the nature of the R-groups could be correlated with two main opposite factors: inductive effects of the R-groups and solvation of the organolead (IV) ions. With the typical hard F^- ligand⁸ we found that the inductive effect is predominant. The most likely explanation is that

Table III. Stability Constants of Organolead (IV) Chloride Complexes.

Species	$\beta_1/(l\text{mole}^{-1})$	$\beta_2/(l^2\text{mole}^{-2})$	$\beta_2/\beta_1 = K_2/(l\text{mole}^{-1})$
$\text{Me}_2\text{Pb}^{2+}$	5.8 ± 0.2	20.3 ± 1.0	3.5
$\text{Et}_2\text{Pb}^{2+}$	9.2 ± 0.2	54.9 ± 1.8	6.0
$n\text{-Pr}_2\text{Pb}^{2+}$	9.7 ± 0.3	69.4 ± 2.0	7.2
Me_3Pb^+	2.1 ± 0.2	—	—
Et_3Pb^+	3.7 ± 0.2	—	—

Table IV. Stability Constants, β_1 , of R_2PbX^+ ($\text{X} = \text{OAc}^-$, F^- , Cl^-) Complexes.

Species	OAc^-	F^-	Cl^-
$\text{Me}_2\text{Pb}^{2+}$	420 ± 20	54.0 ± 1.1	5.8 ± 0.2
$\text{Et}_2\text{Pb}^{2+}$	590 ± 30	35.0 ± 0.8	9.2 ± 0.2
$n\text{-Pr}_2\text{Pb}^{2+}$	870 ± 40	40.5 ± 1.0	9.7 ± 0.3

the interaction between acceptor and ligand is of an essentially electrostatic character.

On the contrary, the acetate ion,⁷ a ligand which ought to form markedly covalent bonds, shows the opposite trend (Table IV).

It should be noted that the chloride ligand shows mainly the same behaviour of the acetate ion, therefore Cl^- should form a bond with some covalent character. It has been demonstrated by Tobias⁹ that there are covalent interactions between $\text{Me}_2\text{Pb}^{2+}$, water molecules and nitrate ions in the first coordination sphere.

This view agrees also with the ratios between the values of the stability constants of $\text{Me}_2\text{Pb}^{2+}$ with F^- and Cl^- ions and of $\text{Me}_2\text{Sn}^{2+}$ with the same ligands.¹²⁻¹³ In fact the very large ratio for $\text{Me}_2\text{Sn}^{2+}$ (about 2,000) proves that this acceptor is typically hard.

Consequently the interactions between acceptor and ligand are essentially electrostatic. On the other hand the rather little ratio for $\text{Me}_2\text{Pb}^{2+}$ (about 10) suggests, according to Ahrland,¹⁴ that the bond between $\text{Me}_2\text{Pb}^{2+}$ and Cl^- has some covalent character.

A conclusive prove of this hypothesis could be gained only by calorimetric and Raman measurements.

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