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Complexes of Organolead (IV) with Fluoride Ions

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The complexity of solutions of some organolead(IV) and fluoride ions has been investigated in a constant ionic medium (1 M *ClO_4) at 25°C by means of potentiometric methods. Only mononuclear complexes have been found and their stability constants have been determined. In addition the Authors have considered the effect of the nature of the organo groups on the formation constants.*

Introduction

Information concerning the possibility of organolead(IV) complexes existence and their stability is very scarce.

Barbieri[1-5] and Tobias,[6] respectively, have published the most significant papers dealing with the chloride complexes of organolead(IV) ions and the hydrolysis of dimethyllead(IV). In a recent work the stability constants of some organolead(IV) acetates have been determined in aqueous solutions.[7] With regard to the fluoride complexes of the organometals of the IV B group, only the tin compounds have been studied thoroughly, in works by Cassol and collaborators.[8-11]

In the case of the organogermanium compounds only the anionic complex $CF_3GeF_5^{2-}$ is known,[12] while only the preparation and physical constants are reported for the organolead(IV) fluorides.[13]

The subject of the present work is the behaviour of dimethyl, diethyl, di-n-propyl, trimethyl, triethyllead ions in aqueous solutions of sodium fluoride.

Experimental Section

Method. The reaction between

$$R_{4-n}Pb^{n+} \quad \text{and} \quad F^- \qquad (n = 1, 2)$$

has been studied at 25°C by measuring with a quinhydrone half cell the competition between hydrogen and organolead(IV) ions for fluoride ion. Hydrogen ion concentration in the organolead(IV) perchlorate solutions of known acid and fluoride analytical concentration was measured by the cell

—R.E./test solution, quinhydrone (s)/Au+

where

$$\text{R.E.} = \text{Ag, AgCl}/0.01\,M\ Cl^-,\ 0.99\,M\ ClO_4^-,\ 1\,M\ Na^+/1\,M\ NaClO_4$$

and the test solution had the general composition

$$B\,M\ R_{4-n}Pb^{n+},\ H\,M\ H^+,\ (1-n\,.\,B-H)\,M\ Na^+,\ A\,M\ F^-,\ (1-A)\,M\ ClO_4^-$$

To check that no error would be introduced by complex formation between organolead(IV) ions and quinhydrone, the cell

—R.E./B M $R_{4-n}Pb^{n+}$, H M H^+, (1—nB—H) M Na^+, 1 M ClO_4^- quinhydrone (s)/Glass Electrode+

was used in preliminary tests.

The experiments were carried out by adding known amounts of standard NaF solution to a known B and H solution till solid organolead(IV) fluorides were formed. The emf (in mV) of cell was given by

$$E = E_o' + 59.15 \log h + E_j \qquad (1)$$

where h was the hydrogen ion cencentrations (expressed in mmole), E_o' a constant for our experimental conditions, and E_j the liquid junction potential between the test solution and the salt bridge. It has been demonstrated by Biedermann and Sillen[14] that $E_j = Jh$. E_o' and J were determined from measurements in the absence of organolead(IV) and fluoride ions. The J value was found to be —0.071 mV mmole^{-1}, in good agreement with the literature.[15] Measurements carried out by substituting organolead(IV) ion for Na^+ at h constant and A = O showed a steady increase of the potential with respect to B, about 20 B mV. This was taken into account when h was calculated by means of the equation (1).

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Chemicals and reagents. Sodium fluoride Merck (p.a.) was purified by crystallization in a « Moplen »* vessel by a water bath. The salt thus obtained was heated at 700°C in a platinum crucible to eliminate traces of SiF_4. Iron(III) and chloride ions were not present in the purified salt. Standard NaF solution, equilibrated at 1 *M* Na^+ with $NaClO_4$, was prepared by weighing the salts according to their formula weights.

The sodium perchlorate, the perchloric acid, the organolead(IV) perchlorates standard solutions were prepared as described in a previous paper.[7]

The quinhydrone, Merck (p.a.) was crystallized from water at 70°C.

To prevent the decomposition of organolead(IV) perchlorates, the solutions were stored in dark bottles at low temperature. These solutions were submitted to the sulphide test to ascertain where lead(II) ions were present, and discarded in the event of a positive result.

99.99% Nitrogen, further purified following Arthur,[16] was passed through 1 *M* $NaClO_4$ to obtain the correct vapour preassure.

Procedure. The emfs were read at ±0.01 mV by using a Leeds-Northrup K-3 potentiometer with a NLS X-3 digital electrometer as the null point indicator. The cell potentials were stable and reproducible within ±0.05 mV. The cell arrangement, similar to that described by Forsling *et al.*[17] was positioned in a water thermostat at 25.00±0.05 C. All the parts of the apparatus which might come into contact with fluoride solutions were lined with paraffin or constructed in plexiglass.

The bright gold foils, used for the quinhydrone electrodes, were always cleaned before use: initially with hot chromic acid, then with water, subsequently with ethanol, and finally ignited in an alcohol flame.

Ag, AgCl electrodes were prepared following Brown's instructions.[18]

NaF solution was added to the cell from a Radiometer Auto-Burette type ABU 1b equipped with a burette type B 150 unit with a total volume of 2.500 ml. The volumes were read to ±0.001 ml.

Results

Assuming no hydrolysis of organolead(IV) ions at pH<5, the analytical concentration of fluoride, A, and the total concentration of acid, H, in our solutions could be expressed by the equations

$$H = h + HF + HF_2^- \qquad (2)$$

$$A = a + HF + 2HF_2^- + n_B B \qquad (3)$$

where « a » represents the equilibrium concentration of fluoride ion and n_B the average number of fluoride ions bound to an organolead(IV) ion. Equation (2) relied on the assumption that H^+ associated with F^- to form only HF and HF_2^- and that in the investigated concentration range mixed complexes were not present. Taking into account the equilibria

$$H^+ + F^- \rightleftarrows HF \qquad K_1 = [HF]h^{-1}a^{-1} \qquad (4)$$

$$HF + F^- \rightleftarrows HF_2^- \qquad K_2 = [HF_2^-][HF]^{-1}a^{-1} \qquad (5)$$

the insertion of (4) and (5) into (3) yields

$$H = h + K_1ha + K_1K_2ha^2 \qquad (6)$$

$$A = a + K_1ha + 2K_1K_2ha^2 + n_BB \qquad (7)$$

Since H, A, B, K_1, K_2, were known, and h was measured, the function $n_B(\log a)$ could be calculated. The values of the formation constants for the H^+–F^- system were determined in the same experimental conditions. We assumed that the values remained valid in the presence of organolead(IV) ions. For the calculations of n_B and « a » we used the numerical values

$$K_1 = 9.25 \pm 0.05 \times 10^2 \text{ l/mole}^{-1}$$

$$K_2 = 3.9 \pm 0.2 \text{ l/mole}^{-1}$$

Typical titration data are summarized in Table I. Figures 1 and 2 show the formation curves for the systems Et_2Pb^{2+} and Me_3Pb^+ respectively. We can see that the functions $n_B(\log a)$ form a single curve within the limits of experimental errors. We can conclude not only that the previously stated assumptions were correct but also that polynuclear complexes were not formed in detectable amounts.

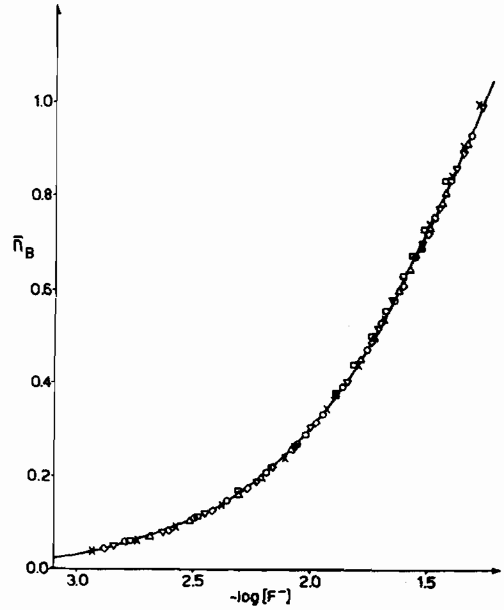

Figure 1. Average number of fluoride ions bound for diethyllead(IV) ion as a function of $-\log[F^-]$ at 25°C in a 1 *M* perchlorate medium: ◇ 44.00 m*M*; × 35.99 m*M*; △ 25.20 m*M*; ○ 22.00 m*M*; ▽ 14.40 m*M*; □ 7.20 m*M* stoichiometric Et_2Pb^{2+} concentration. Curve calculated with $\beta_1 = 35.0$ l/mole^{-1} and $\beta_2 = 350$ l^2/mole^{-2}.

(*) Moplen = polypropylene (Montecatini).

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

H m*M*	B m*M*	A m*M*	h m*M*	a m*M*	n
9.11_1	14.31	4.97	5.32_1	0.76	0.02_6
9.08_4	14.27	7.43	3.86_3	1.44	0.04_9
9.05_7	14.23	9.88	2.80_4	2.37	0.08_1
9.03_0	14.18	12.32	2.07_6	3.55	0.11_8
9.00_4	14.14	14.74	1.59_4	4.90	0.15_9
8.98_6	14.12	16.34	1.36_5	5.87	0.18_7
8.96_0	14.07	18.74	1.11_1	7.39	0.23_1
8.94_2	14.05	20.33	0.984	8.43	0.26_0
8.91_6	14.00	22.70	0.834	10.04	0.30_3
8.90_0	13.98	24.28	0.753	11.14	0.33_0
8.87_3	13.94	26.63	0.658	12.80	0.37_2
8.84_7	13.90	28.96	0.581	14.51	0.41_1
8.81_3	13.84	32.06	0.500	16.79	0.46_3
8.77_1	13.78	35.89	0.424	19.69	0.52_5
8.73_0	13.71	39.69	0.365	22.62	0.58_2
8.68_8	13.65	43.45	0.320	25.58	0.63_8
8.64_7	13.58	47.18	0.283	28.60	0.68_7
8.60_6	13.52	50.87	0.252	31.66	0.73_2
8.56_6	13.46	54.53	0.227	34.71	0.77_6
8.52_6	13.39	58.19	0.206	37.77	0.82_0
8.48_7	13.33	61.74	0.188	40.79	0.86_0
8.44_8	13.27	65.30	0.173	43.92	0.89_3
8.40_9	13.21	68.82	0.159	47.02	0.92_6
8.33_3	13.09	75.77	0.137	53.15	0.99_1

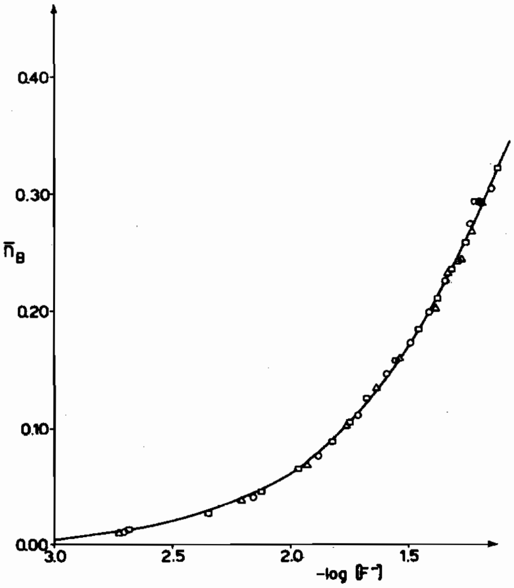

Figure 2. Average number of fluoride ions bound for trimethyllead(IV) ion as a function of $-\log[F^-]$ at 25°C in a 1 *M* perchlorate medium: Δ 62.87 m*M*; ○ 35.93 m*M*; ☐ 17.96 m*M* stoichiometric Me_3Pb^+ concentration. Curve calculated with $\beta_1 = 6.5$ l/mole^{-1}.

For the dialkyllead(IV) ions the formation curves reach the maximum at $n_B \simeq 1$. Therefore, considering that only R_2PbF^+ and R_2PbF_2 species were formed according to the equilibria:

$$[R_2PbF^+][R_2Pb^{2+}]^{-1}[F^-]^{-1} = \beta_1 \qquad R_2Pb^{2+} + F^- \rightleftarrows R_2PbF^+$$

$$[R_2PbF_2][F^-]^{-2}[R_2Pb^{2+}]^{-1} = \beta_2 \qquad R_2Pb^{2+} + 2F^- \rightleftarrows R_2PbF_2$$

we had for n the relation

$$n = \frac{\beta_1 a + 2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} \qquad (8)$$

From the equation (8) rearranged as

$$\beta_2 a^2(2-n) + \beta_1 a(1-n) = n \qquad (9)$$

β_1 and β_2 were determined by using the least squares method.

The validity of these assumptions is shown by the good agreement between the $n_B(\log a)$ points and the curves calculated by using β_1, β_2 values.

For the trialkyllead(IV) ions the maximum values of n_B were about 0.3. So we only considered the formation of R_3PbF.

Figure 3 shows the distribution of the formed complexes as a function of the free ligand concentration.

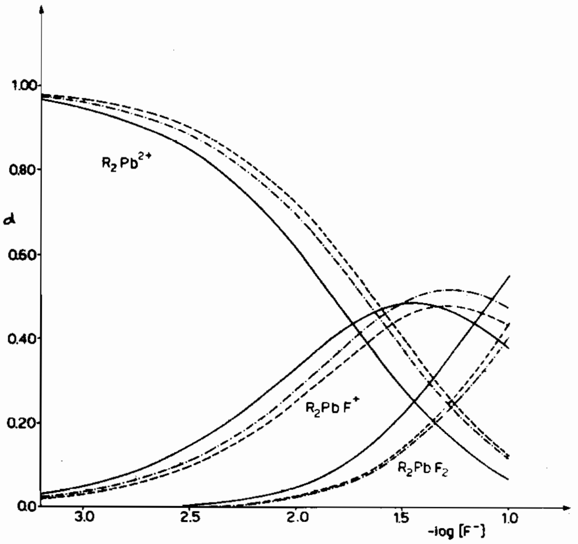

Figure 3. Distribution curves of complexes of diorganolead(IV) ions and fluoride as a function of the free ligand concentration: Me_2Pb^{2+} ————; Et_2Pb^{2+} — — — —; n—Pr_2 Pb^{2+} —·—·—·—,

Discussion

In Table II are reported the stability constants β_1, β_2. In order to correlate the order of stability with the nature of the R-groups we consider, according to Cook *et al.*,[19] three main factors: steric (S), inductive (I) and solvent (W) effects.

Table II. Stability Constants of Organolead(IV) Fluoride Complexes

Species	β_1(l/mole^{-1})	β_2(l^2/mole^{-2})	$\beta_2/\beta_1 = K_2'$(l/mole^{-1})
Me_2Pb^{2+}	54.0±1.1	783±32	14.5
Et_2Pb^{2+}	35.0±0.8	351±36	10.0
n—Pr_2Pb^{2+}	40.5±1.0	345±29	8.5
Me_3Pb^+	6.5±0.3	—	—
Et_3Pb^+	3.5±0.3	—	—

For the studied compounds steric factors do not play an important role. On the other hand, these

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(19) G. R. Cook and D. F. Martin, *J. Inorg. Nucl. Chem.*, *26*, 1249 (1964).

factors, if present, would give this order:

$$Me > Et > n\text{—}Pr$$

The same order should be found by considering only coulombic attraction. This is true if we take into consideration the inductive effect, the only, or rather the most significant, factor.

The opposite order:

$$n\text{—}Pr > Et > Me$$

could be correlated with the solvent effect, *i.e.* with the hydrophobic character of the organometallic ions. In this case the ease of displacement of bound water to organometallic ions by the ligand should follow the increase of hydrophobic character.

It appears that the observed order for β_1 values of R_2Pb^{2+} ions can be explained by assuming a balance of inductive and solvent effects. The observed variations of K_2' values can be best correlated with a continuous prevalence of (I) on (W) effect. The last consideration can be again made for the trialkyllead ions.

A comparison between the values of the formation constants shows that the fluoride complexation is much less extensive with organolead(IV) than with analogous organotin(IV) systems (about 100 times). In spite of the well known behaviour of organotin(IV) as typical Leden-Chatt « A » groups ions, nothing definite can yet be said about the nature of organolead ions. To sum up, we can only state that available data concerning the stability with the OH^-, CH_3COO^-, F^- ligands, do not allow any valid conclusions to be reached. Further work is obviously needed, and additional studies on Cl^- and CN^- ligands are being made in this Institute.