Acetato Complexes of Organolead (IV) in Aqueous Solution

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*The complexity of solutions of organolead(IV) and
acetate ions has been investigated in a constant ionic
medium (1 M ClO_4^-) by means of emf measurements
of [H^+]. Only a mononuclear complex formation oc-
cours. The order of the determined stability constants
is correlated with the nature of the organo groups
bound to the lead.*

Introduction

In the last few years research has been carried
out in this Institute on the effect of the nature and
the number of the organo groups attached to the
metal in organometallic compounds on its properties
as an acceptor.[1-3] By studying the formation of coor-
dination compounds between different organometallic
ions and ligands we can make a valid contribution
to this work.

Although the complexes of organometallic ions
have been the subject of extensive study, very little
is known about their stability. In particular, for
organolead ions, only qualitative investigations of
halide complexes[4-9] and a thorough study of dimethyl-
lead(IV) hydrolysis[10] are reported. Only the prepa-
ration and some physical constants are reported for
the organolead acetates.[11] Little information is avai-
lable on the nature of the species present in solution.

This paper refers to the formation and the stability
in the ionic medium 1.0 M (Na^+)ClO_4^- of some or-
ganolead complexes with acetate as ligand.

Experimental Section

Method. Since no reversible electrodes are avai-
lable to measure the free concentrations of acetate

or organolead ions, the reaction between either R_2Pb^{2+}-
($R = Me$, Et, n–Pr, Ph) or $R_3'Pb^+$($R' = Me$, Et) and
OAc^- has been studied by measuring the free hydro-
gen concentration, h, of organolead(IV) perchlorate
solutions of known acid and acetate concentration
by the cell

$$- R.E./test\ solution/Glass\ Electrode +$$

where

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

and the test solution had the general composition

$$B\ M\ R_{4-n}Pb^{n+},\ H\ M\ H^+,\ (1-nB-H)\ M\ Na^+$$
$$A\ M\ OAC^-,\ (1-A)\ M\ ClO_4^-$$
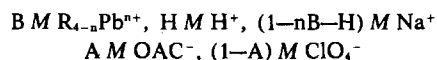
The measured emf E (mV) was related to h (mM) by

$$E = E_o' + 59.15 \log h - 0.060\ h \qquad (1)$$

where E_o' was a constant for our experimental con-
ditions and 0.060 h represents, according to Bieder-
mann *et. al.*,[12] the liquid junction potential between
the test solution and the salt bridge. From the B,
A, H, h, data and the value of the complex formation
costant for the H^+–OAc^- system, which was deter-
mined separately in the same experimental conditions,
the function $\bar{n}_B$ (log a) could be calculated: $\bar{n}_B$ repre-
sents the average number of acetate ions bound for
organolead ion and « a » the equilibrium concentra-
tion of acetate ion. In fact, when known amounts of
standard $HClO_4$ are added to a solution containing
B and A, for the material balance we can, neglecting
hydrolytic equilibria, write

$$H = h + [HOAc] \qquad (2)$$

Taking into account the equilibrium

$$H^+ + OAc^- \rightleftarrows HOAc \qquad K = [HOAc]h^{-1}a^{-1} \qquad (3)$$

insertion of 3) in 2) yields

$$H = h + Kha \qquad (4)$$

Since H and K were known and h was measured
the equation 4) could be solved for «a». The forma-
tion function was calculated from the expression

$$\bar{n}_B = (A - a - Kha)/B \qquad (5)$$

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The formation constant of the H^+–OAc^- system in $1\,M\,(Na^+)ClO_4^-$ was found to be $K = 3.93 \times 10^4\,l.\,mole^{-1}$.

Chemicals and Reagents. Sodium perchlorate was prepared by neutralizing Na_2CO_3 (Merck p.a.) with $HClO_4$ (Merck p.a.). The stock solution was analyzed by evaporating a known volume of solution and weighing the residue as $NaClO_4$.

Perchloric acid solution (about $1\,M$) was prepared from $HClO_4$ 70% (Merck p.a.) and standardized against Borax and Na_2CO_3. The results agreed to within 0.2%.

Sodium acetate, $NaCH_3COO\,.\,3H_2O$, (Merck p.a.) was used without purification. To standardize the stock solution the sodium was determined as $NaCl$ by evaporating a known amount with HCl.

Organolead perchlorate solutions were prepared by treating R_2PbO or R_3PbOH with a slight excess of dilute standard $HClO_4$. The dialkyllead content of the solutions was determined by spectrophotometric titration with PAR.[13] The trialkyllead content of the solutions was determined by amperometric titration with $NaBPh_4$.[14] Thus the analytical excess of hydrogen ions in the stock solutions was known:

$$[H^+] = [ClO_4^-]-n[R_{4-n}Pb^{n+}] \qquad (6)$$

In addition, the analytical hydrogen ion concentration and, hence, the concentration of organolead ions were measured independently with the electrochemical cell described above. The results agreed to within 0.2%. The EDTA test[14] was used to demonstrate the absence of Pb^{2+}. $R_2Pb(OH)_2$ and R_3PbOH compounds were prepared by hydrolyzing the organolead halides with wet silver oxide. Diorganolead oxides were obtained by dehydrating the intermediate hydroxides. Ph_2PbO was prepared by treating Ph_2PbCl_2 in absolute alcohol with alcoholic solution of KOH.[15] The precipitate was washed with water until no chloride ion could be detected.

Dimethyllead dibromide was prepared from Me_4Pb and Br_2 in ethyl acetate.[16]

Diethyllead dichloride was prepared from Et_4Pb and dry HCl in toluene.[17]

Dipropyllead dichloride was prepared by using Saunders and Stacey's method.[18]

Diphenyllead dichloride was prepared as reccomended by Setzer et. al.[19]

Trimethyl and triethyllead chlorides were prepared by treating the corresponding tetraorganolead compounds with dry HCl in Et_2O.[20]

All of the organolead compounds prepared were stored in a refrigerator.

Procedure. The emf measurements were performed in a paraffin oil thermostat at $25.00\pm0.05°C$ using the electrode vessels and salt bridge designed

by Forsling *et. al.*[21] Cell potentials were read at 0.01 mV by a Leeds and Northrup K–3 potentiometer with a Keithley 610 B electrometer as the null point indicator. They remained constant for several hours within ±0.1 mV.

A Beckmann G.P. glass electrode was used.

99.99% Nitrogen, further purified, following Arthur,[22] was bubbled through $1\,M\,NaClO_4$ to obtain the correct water vapour pressure.

Ag, AgCl electrodes were prepared according to Brown.[23]

Perchloric acid was added to the cell from a Radiometer Auto-burette type ABU 1b equipped with Burrette unit type B 150. The volumes were read at 0.001 ml.

Results and Discussion

The results of a typical run through are given in Table I. For each experimental point «a» was calculated by means of equation (4). As mentioned above the equation presupposes that the hydrolysis of organolead ions is negligible. Our preliminary experiments have shown that, as exhaustively demonstrated by Tobias *et. al.*[10] for dimethyllead(IV), hydrolytic equilibria in solutions of $[R_{4-n}Pb^{n+}]<0.1\,M$ and $pH<5$ may be neglected. Only in the case of diphenyllead(IV) is the limiting pH value about 4.

Table I. Typical Titration Data For Diethyllead (IV) Acetato Complexes

H mM	h mM	A mM	B mM	n_B	$-\log a$
12.93	0.0125	58.23	18.36	1.03	1.578
14.53	0.0148	58.17	18.35	1.02	1.602
19.33	0.0240	58.00	18.29	0.99₄	1.688
22.51	0.0323	57.89	18.26	0.96₈	1.751
25.67	0.0438	57.77	18.22	0.94₇	1.827
28.83	0.0596	57.66	18.18	0.91₃	1.910
31.97	0.0839	57.54	18.15	0.88₀	2.014
35.10	0.121	57.43	18.11	0.83₃	2.133
38.22	0.184	57.32	18.08	0.77₅	2.278
41.33	0.289	57.21	18.04	0.69₆	2.441
44.42	0.470	57.10	18.01	0.59₈	2.623
47.51	0.776	56.99	17.97	0.48₅	2.814
50.58	1.28	56.88	17.94	0.36₈	3.008
53.63	2.19	56.77	17.90	0.26₄	3.223
56.68	3.63	56.66	17.87	0.18₁	3.429
59.72	5.67	56.55	17.83	0.12₇	3.615
62.74	8.12	56.44	17.80	0.093	3.766

In Figure 1 and 2 the formation curves for the Et_2Pb^{2+} and Ph_2Pb^{2+} systems are respectively reported. The experimental points for different organometal and hydrogen ion concentrations fall on the same curve so that we can ignore polynuclear and hydrolytic equilibria.

Because the n_B *vs.* log a curves reach the maximum value at $n \simeq 1$, we may assume that only R_2PbOAc^+

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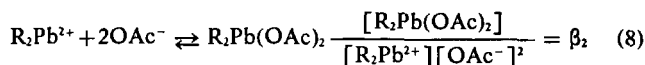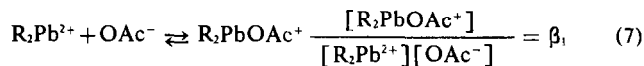(16) G. Gruttner and E. Krause, *Ber.* 49 1425 (1916).
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and $R_2Pb(OAc)_2$ are formed according to the equilibria

$$R_2Pb^{2+}+OAc^- \rightleftarrows R_2PbOAc^+ \quad \frac{[R_2PbOAc^+]}{[R_2Pb^{2+}][OAc^-]} = \beta_1 \quad (7)$$

$$R_2Pb^{2+}+2OAc^- \rightleftarrows R_2Pb(OAc)_2 \quad \frac{[R_2Pb(OAc)_2]}{[R_2Pb^{2+}][OAc^-]^2} = \beta_2 \quad (8)$$

Assuming this we get the following expression of n_B as a function of «a»

$$\bar{n}_B = \frac{\beta_1 a + 2\beta_2 a^2}{1+\beta_1 a+\beta_2 a^2} \quad (9)$$

from which β_1 and β_2 can be determined. To this aim we used the least squares method with the equation (9) rearranged as:

$$(2-\bar{n})a^2\beta_2+(1-\bar{n})a\beta_1 = \bar{n} \quad (10)$$

Figure 1 and 2 show the agreement between the experimental $\bar{n}_B(\log a)$ points and the curves calculated by using the appropriate β_1, β_2 values.
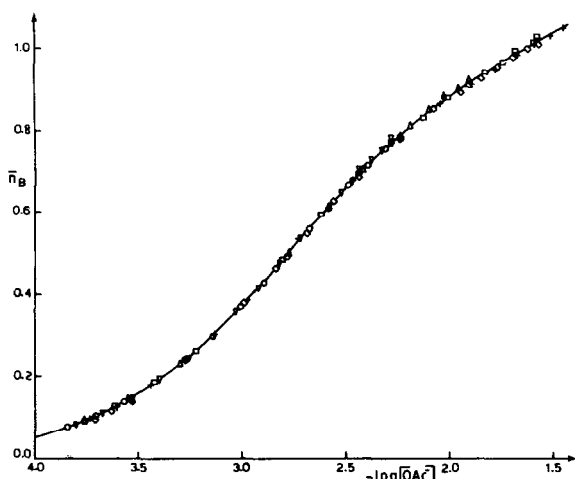

Figure 1. Average number of acetate ions bound per diethyllead(IV) ion as a function of $-\log[OAc^-]$ at 25°C in a $1\,M$ perchlorate medium:

Δ 4.62 mM— 23.26 mM;   ◇ 9.25 mM—58.70 mM;
O 18.51 mM— 23.48 mM;   □ 18.51 mM—58.70 mM;
+ 18.51 mM—117.40 mM;   ▽ 46.28 mM—46.12 mM
stoichiometric Et_2Pb^{2+}—OAc^- concentrations. Curve calculated with $\log \beta_1 = 2.77$ and $\log \beta_2 = 3.28$.

On examining the values of the stability constants (Table II) we observe that the main reaction product is the species R_2PbOAc^+. The higher complex $R_2Pb(OAc)_2$ is present in detectable amounts only in fairly concentrated solutions of ligand.

Since the acetate ion behaves as a bidentate ligand, our results are in good agreement with the tendency of lead to adopt a coordination number of four, with two R-groups occupying two of these coordination sites. Coordination numbers of five or six have also, however, been verified by other authors.

It is interesting to compare the constants for R_2Pb^{2+} and Pb^{2+}. The values reported for Pb^{2+} (3 M ClO_4^- medium) are $\log \beta_1 = 2.33$ and $\log \beta_2 = 3.60$.[24] The presence of the unpaired 6s electrons in Pb^{2+} should reduce the strength of the metal ligand bond. So, according to Tobias et. al.[25], diorganolead(IV) ions would be expected to be better electron acceptors than lead (II), as is proved by comparing β_1 values.

For the trialkyllead ions there is evidence of the existence of only one fairly unstable complex.
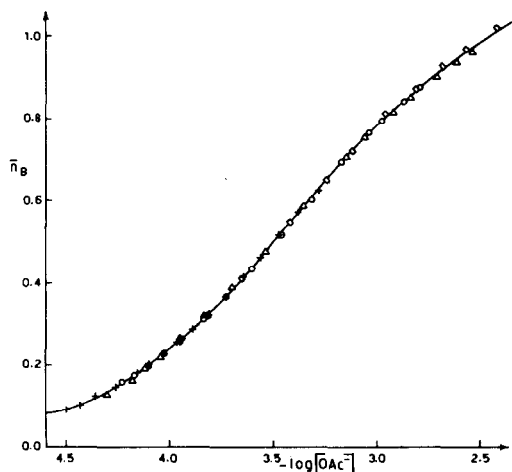

Figure 2. Average number of acetate ions bound per diphenyllead(IV) ion as a function of $-\log[OAc^-]$ at 25°C in a $1\,M$ perchlorate medium:

◇ 2.14 mM—22.41 mM;   Δ 6.42 mM—22.41 mM;
O 10.70 mM—22.41 mM;   + 21.39 mM—22.41 mM
stoichiometric Ph_2Pb^{2+}—OAc^- concentrations. Curve calculated with $\log \beta_1 = 3.50$ and $\log \beta_2 = 4.90$.

Table II. Stability Constants of Organolead Acetato Complexes

Species	$\log \beta_1$	$\log \beta_2$	$\log\beta_2-\log\beta_1=\log K_2$
Me_2Pb^{2+}	2.62 ±0.02	3.62±0.04	1.00
Et_2Pb^{2+}	2.77 ±0.02	3.28±0.05	0.51
$n-Pr_2Pb^{2+}$	2.94 ±0.02	3.95±0.03	1.01
Ph_2Pb^{2+}	3.50 ±0.01	4.90±0.06	1.40
Me_3Pb^+	0.54₃±0.02	—	—
Et_3Pb^+	0.44₅±0.02	—	—

The order of the stability constants (β_1) for the acetate complexes of the organolead ions as a function of the nature of the organo groups is as follows:

$$Ph_2Pb^{2+} > n-Pr_2Pb^{2+} > Et_2Pb^{2+} > Me_2Pb^{2+} \quad (a)$$

$$Me_3Pb^+ > Et_3Pb^+ \quad (b)$$
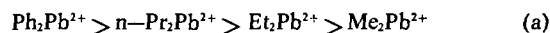
As suggested by Cook et. al.[26] for the diorganothallium(III) complexes, the order of stability a) would be inverted if inductive effects were the most impor-

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tant factor. It appears that the observed variations in the stabilities of the diorganolead complexes can be correlated with solvent effects. This means that the increase in the observed β_1 values follows the increase of the hydrophobic character of the organometal ions. Thus the oxygen donor acetate will be more successful in displacing coordinated water molecules in the aquodiorganolead ions.

On the other hand, the inductive effects cannot be altogether neglected. In fact not only can the increased stability of Me_3Pb^+ over Et_3Pb^+ be ratio-nalized in terms of an inductive effect, but the sequence of the K_2 values may also, in our opinion, be discussed in terms of these concepts.