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Halide Complexes of Triphenyllead(IV) and Diphenyllead(IV) Ions in Methanol Solution

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The behaviour of triphenyl- and diphenyllead halides $(C_6H_5)_3PbX$ *and* $(C_6H_5)_2PbX_2$ *(X = Cl, Br, J), in methanol solution has been investigated by UV-spectroscopy and by conductometric and potentiometric measurements. The stability constants evaluated from the emf data show that the strength of complexing increases in the order* $Cl^- < Br^- < I^-$ *for both* $(C_6H_5)_3Pb^+$ *and* $(C_6H_5)_2Pb^{2+}$*. The same series was found in this solvent by conductivity measurements, while in the aprotic solvent THF the reverse order was observed. The UV measurements in methanol solution showed a red shift of the Pb–X charge transfer band with increasing atomic weight of X. The emf measurements with the system* $(C_6H_5)_2Pb^{2+}$*–*I^- *also indicate the formation of binuclear complexes, e.g.* $(C_6H_5)_4Pb_2I_2^{2+}$, $(C_6H_5)_4Pb_2I_3^{+}$, *or* $(C_6H_5)_4Pb_2I_4$, *in addition to the usual mononuclear complexes. These results are compared with those of earlier kinetic studies.*

Introduction

Methanol has good solvent properties for organolead compounds, but little is known about its function in the solute–solvent interaction. In contrast to this lack of information about the solvent methanol (and other non-aqueous solvents), various aspects of the behaviour of organolead compounds in water have been dealt with in different papers. Most of these papers were of a qualitative nature however, and – for reasons of solubility – nearly exclusively alkyllead compounds have been studied.

Barbieri[1] and other Italian groups[2] have shown by different methods that anionic alkyllead complexes exist in aqueous solution. Recently alkyllead moieties were quantitatively studied by potentiometric titration with different ligands[3,4,5] and hydrated alkyllead species have been characterized by Raman spectroscopy.[6] The rate of decomposition of $(CH_3)_2PbX_2$, which we studied in aqueous solution by UV and NMR methods,[7,8] proved to be highly dependent on the concentration and on the type of anion X^- present. These effects could be explained by assuming complexed organolead species as the real reacting agents, and also by supposing the formation of bridged intermediates in the rate determining step.

We became interested in studying the solvent function of methanol, when we observed qualitatively, in the course of investigations on the coordination chemistry of organolead compounds, that methanol apparently can interact with these compounds in ways, comparable to, but distinctly different from those of water. In those studies we observed dissociation of organolead compounds as well as coordination of methanol together with other donor ligands to the lead central atom, *e.g.* in $ph_2PbX_2 \cdot n$ pyridine (ph = C_6H_5; X = Cl, Br, J)[7]; but we were never able to isolate solid complexes with methanol as ligand.

This paper reports more detailed studies on the behaviour of phenyllead compounds in methanol.

The following symbols are used:[9]

A = total halide concentration
a = equilibrium concentration of halide ion
B = total organolead(IV) concentration
b = equilibrium concentration of organolead(IV) ion
$\bar{n}$ = average number of ligands bound to each organolead ion = (A–a)/B
β_n = stoichiometric overall stability constant for $BA_n = [BA_n]/ba^n$
K_n = stoichiometric stepwise stability constant for $BA_n = \beta_n/\beta_{n-1}$
β_{qp} = stoichiometric overall stability constant for polymeric complex $B_qA_p = [B_qA_p]/b^qa^p$

Experimental

Potentiometric Measurements

Procedure and apparatus

The complexes were studied by the method of potentiometric titration in a constant ionic medium,[9] varying the ligand concentration at constant organolead concentration while measuring the free halide ion concentration a(A,B). The experiments were done in methanol solutions at 25 °C and $1M$ ionic strength with the cell

Ag–AgX | B M $ph_{4-n}Pb^{n+}$, A M X^-, (1–nB)M Li^+, (1–A)M ClO_4^-, 5 mM $HClO_4$ | RE or GE

(GE = glass electrode; RE = $1M$ $LiClO_4$, 5 mM $HClO_4$ | $1M$LiCl, 5 mM $HClO_4$ | AgCl–Ag; X = Cl, Br, I [in titrations with X = I, Na^+ replaces some of the Li^+]).

The overall solvent composition was calculated as 93 wt% methanol. Water content was mainly due to $LiClO_4 \cdot 3\ H_2O$, with smaller contributions from the $ph_{4-n}Pb(ClO_4)_n$ solutions. Slight variations between experiments, such as would result from a concentration difference in the organolead solutions, had no effect on the results.

The solutions were made acidic to prevent hydrolysis of organolead ions[3,6], also allowing the use of the glass reference electrode for measurements without liquid junction.

The titrations were carried out in a water-jacketed, five-necked cell, with the temperature maintained at 25.00±0.05 °C. Purified nitrogen was continually bubbled through the solutions, after first passing through a thermostated $1M$ $LiClO_4$ solution to attain the proper vapor pressure. Experiments with the light-sensitive iodide complexes were done under red light only.

Aliquots of titrant solution (also at 25 °C) were added with calibrated 0.1–2 ml pipettes. In the experiments reported for ph_2Pb^{2+} with Cl^-, only LiCl titrant solution was added, so that B decreased slightly during the titrations. In all the others, B was maintained constant throughout by also adding equal aliquots of a 2B M organolead perchlorate solution. Some of the titrations were continued to precipitation of the organolead halides.

The Ag–AgCl electrodes were prepared from Ingold micro-silver electrodes (type Ag-800-NS-M8), by electrolysis of $0.1M$ HCl, KBr, or KI solutions.[10]

The Ag–AgCl reference electrode was prepared from a modified Schott Ag–AgCl double junction reference electrode (type 9860/9), consisting of an inner electrode compartment and removable outer salt bridge compartment, with ceramic diaphragm junctions. To avoid difficulties with an aqueous-nonaqueous liquid junction, the saturated KCl solution and salts were removed from the inner compartment, and replaced with a solution of $1M$ LiCl in the same 93% methanol used throughout the cell.

Ingold standard glass electrodes (type 201-NS) were used. These, and the Ag–AgX electrodes, were stored in water and allowed to equilibrate in the alcoholic titration solutions for at least several hours before each experiment.

Emf values were read to 0.1 mV using a Knick model 350/34 pH meter. Readings were made at each point for the Ag–AgX measuring electrode against each of the two reference electrodes. In addition, the potential between the two reference electrodes could be checked, and in some cases small corrections made for apparent drift with time in the potential of GE. After each addition, readings were generally stable within several minutes, and remained so for at least several hours.

Preparation of solutions

The $ph_{4-n}Pb(ClO_4)_n$ solutions were prepared freshly for each set of experiments by dissolving weighed samples of ph_2PbO or ph_3PbOH in a slight excess of standard $0.2M$ $HClO_4$ (calculated to neutralize the sample and leave a final concentration of 5 mM $HClO_4$) and diluting to volume with methanol. The absence of Pb^{2+} was determined by a sulfide test. The concentrations were checked by potentiometric titration of the residual acid with NaOH, using Gran's method for calculating the endpoint in the presence of the hydrolyzable organolead ions.[9,11] Halide titrant solutions were prepared with the composition, x M LiX (or NaX), (1–x)M $LiClO_4$, 5 mM $HClO_4$ (x = 0.1–1.0), and analyzed by potentiometric titration with standard $AgNO_3$. It was found necessary to prepare the NaI solutions in the dark, using solvent previously degassed with nitrogen, in order to avoid a rapid discoloration apparently caused by air oxidation of iodide. These solutions were prepared just before an experiment, to analyze and use immediately.

Conductometric and Spectrophotometric Measurements

Conductivities were measured at 20.0±0.1 °C in a water-jacketed cell, using a Philips cell, Metrohm E 605 Konduktoskop, and Haake-Ultrathermostat. Measurements were made after the solutions had been standing for one hour, except for the ph_2PbI_2 solutions which were measured immediately after preparation. Merck pa CH_3OH was used as solvent in these measurements.

UV spectra were recorded using a Perkin–Elmer EPS-3T spectrophotometer and 1 mm path length quartz cells. The ph_3PbClO_4 and $ph_2Pb(ClO_4)_2$ solutions were prepared similarly to those for the emf measurements. Since however no $LiClO_4 \cdot 3\ H_2O$ was added, only a very small amount of water was introduced. The final methanol content in the solvent was calculated to be ~99.6 wt%. Blank solutions containing no organolead compound but equivalent concentrations of water, acid, and alkali halide were used as reference. Measurements were made over the range 210–360 nm, except at the higher concentrations of LiBr and NaI, where strong absorption by the halides interfered, at wavelengths shorter than 212(LiBr) and 234 (NaI)nm.

Materials

ph_2PbO was prepared by the reaction of $ph_2Pb(OAc)_2$ with aqueous NaOH in ethanol. The acetate was prepared from ph_4Pb and acetic acid. ph_3PbOH was prepared from commercial ph_3PbOAc (DAP GmbH) by reaction with aqueous KOH in ethanol.[12] ph_3PbCl was prepared from ph_4Pb and HCl. For conductivity measurements ph_2PbCl_2 and ph_2PbBr_2 were prepared according to ref. 13 and ref. 14; ph_2PbI_2 was prepared by iodination of ph_4Pb in the dark,[7] and the products were recrystallized from a CH_3COCH_3/CH_3OH mixture. The purity of the compounds was checked by C, H, and Pb analysis, and by their IR spectra, and all were stored in the refrigerator. The absence of Pb^{2+} was demonstrated by testing with Na_2S.

Lithium perchlorate was prepared from reagent grade $HClO_4$ and Li_2CO_3, twice recrystallized as the trihydrate from doubly-distilled water, and air-dried at room temperature. Stock solutions were prepared by weight and analyzed for Li^+ by ion exchange. Reagent grade LiCl, and Merck Suprapur LiBr and NaI were used. Doubly-distilled deionized water was used for the aqueous solutions.

Methanol (pa) was further purified by passing through columns of dried 3A molecular sieves, anion exchange resin (Merck Lewatit M5080), and cation exchange resin (Merck Lewatit S1080G1), followed by fractional distillation.[15] Tetrahydrofuran (pa) was dried by refluxing with $[(CH_3)_2CH_2]_2Mg$, followed by fractional distillation.

Results

Conductometric and Spectrophotometric Measurements

The UV spectra are shown in Figures 1–3 for methanol solutions of ph_3PbClO_4 and $ph_2Pb(ClO_4)_2$, alone

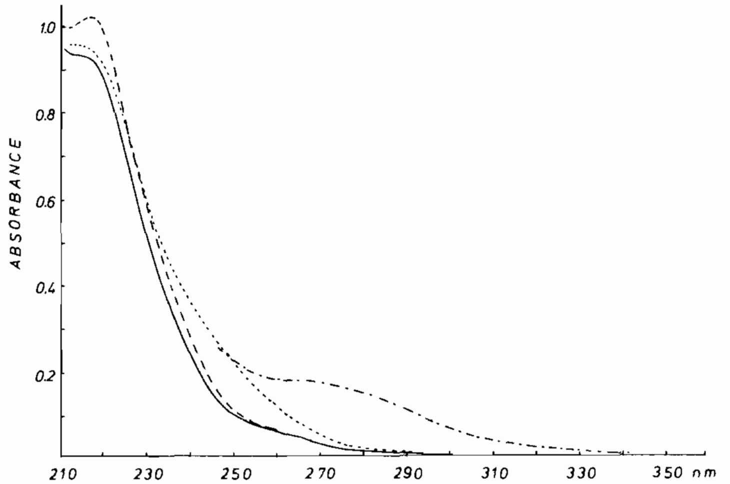

Figure 1. Ultraviolet spectra for $ph_3Pb(ClO_4)$ in methanol, alone (——), and in the presence of 10 m*M* LiCl (– – –), LiBr (· · · · ·), or NaI (–·–·–). $[ph_3Pb^+]$ = 0.1 m*M*, $[HClO_4]$ = 0.5 m*M*, path length = 1 mm.

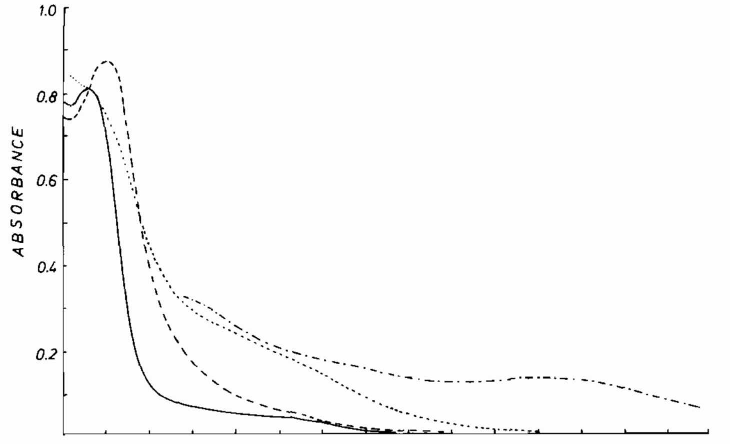

Figure 2. Ultraviolet spectra for $ph_2Pb(ClO_4)_2$ in methanol, alone (——), and in the presence of 1–10 m*M* LiCl (– – –), LiBr (· · · · ·), or NaI (–·–·–). $[ph_2Pb^{2+}]$ = 0.1 m*M*, $[HClO_4]$ = 0.5 m*M*, path length = 1 mm.

TABLE I. Molar Conductivities Λ_m ($ohm^{-1}\ cm^2\ mol^{-1}$) of ph_2PbX_2 Solutions in Methanol and Tetrahydrofuran (THF) [Cell constant: 1.39 cm, temperature: 20.0 ± 0.1 °C].

X	in Methanol					in THF
Cl	mM	0.2313	0.4626	0.7779	3.579	0.6250
	Λ_m	33.59	25.14	20.45	10.51	6.27×10^{-3}
Br	mM	0.1883	0.3818	1.8830	7.568	0.6250
	Λ_m	30.91	23.18	12.06	7.14	19.04×10^{-3}
I	mM	0.1625	0.5201	1.7790	4.9110	0.6250
	Λ_m	23.92	13.13	7.33	4.46	1.76

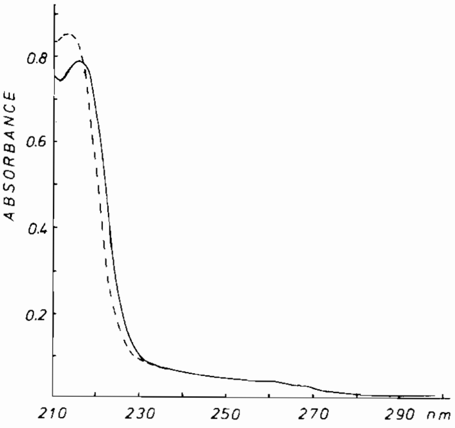

Figure 3. Ultraviolet spectra for $ph_2Pb(ClO_4)_2$ in methanol (~99.6%, ——), and in methanol–water mixtures (34–76 wt% MeOH, ---). [ph_2Pb^{2+}] = 0.1 mM, [$HClO_4$] = 0.5 mM, path length = 1 mm.

and in the presence of a large excess of halide ligand. In the latter case, Pb–X CT bands are observed in addition to the known phenyl group absorptions (K-bands), and are seen to become broader and extend to longer wavelengths as the ligand changes in the series X = Cl, Br, I.

The spectrum for $ph_2Pb(ClO_4)_2$ in CH_3OH/H_2O mixed solvents as well is shown in Figure 3. There is a blue shift of about 3 nm in the peak and a slight increase in absorbance in the spectrum for the mixed $CH_3OH–H_2O$ system compared to the spectrum for the CH_3OH solution. The results of the conductivity measurements are given in Table I, with Λ values decreasing in the order

$$ph_2PbCl_2 > ph_2PbBr_2 > ph_2PbI_2$$

in methanol, and in the reverse order in THF solution.

Potentiometric Measurements

Calculation of the halide ion concentration a

Halide ion concentrations were calculated from the emf readings according to the rearranged form of the Nernst equation

$$\log a = c_1 + c_2 D \qquad (1)$$

with the experimental parameters c_1 and c_2 determined from calibration titrations done in the absence of organolead ions (where a = A). A standard linear least squares procedure was used to calculate the best values of the constants,[16] assuming the greatest experimental error to be in E rather than in logA. Sample values of c_1 and c_2 for the Ag–AgBr electrode are shown with the data in Tables II and III. A good linear fit was observed in all cases, and the slopes corresponded well with the theoretical value of 0.01690 (F/2.303RT) calculated from the Nernst equation. The intercepts of the calibration lines for E_{RE}(Ag–AgX *vs.* RE) were found to vary considerably more than those for E_{GE}(Ag–AgX *vs.* GE) between experiments done at different times, probably due to variations in

TABLE II. Sample Titration Data for $ph_3Pb^+ + Br^-$, with B = 8.013 mM, at 25 °C, 1M Ionic Medium.[a]

A, mM	a, mM	$\bar{n}$	a′, mM	$\bar{n}'$
0.4177	0.0565	0.0451	0.0570	0.0450
0.8336	0.1189	0.0892	0.1202	0.0890
1.248	0.1857	0.133	0.1855	0.133
1.661	0.2561	0.175	0.2567	0.175
2.073	0.3346	0.217	0.3361	0.217
2.482	0.4190	0.258	0.4209	0.257
2.891	0.5086	0.297	0.5127	0.297
3.298	0.6102	0.335	0.6162	0.335
3.703	0.7236	0.372	0.7261	0.372
4.106	0.8417	0.407	0.8458	0.407
5.001	1.152	0.480	1.161	0.479
5.889	1.517	0.546	1.532	0.544
6.770	1.944	0.602	1.960	0.600
7.645	2.443	0.649	2.474	0.645
9.358	3.586	0.720	3.650	0.712
11.04	4.908	0.766	5.000	0.754
12.71	6.363	0.792	6.510	0.773
16.76	10.01	0.842	10.25	0.813
20.67	13.76	0.862	13.90	0.844
24.43	17.43	0.874	17.51	0.864
31.57	24.61	0.870	24.70	0.858
38.24	31.41	0.853	31.59	0.830

[a] The values a and $\bar{n}$ are calculated from E_{GE} ($\log a = -8.962 + 0.01683\ E_{GE}$ and a′ and $\bar{n}'$ from E_{RE} ($\log a' = -1.930 + 0.01698\ E_{RE}$). The data up to A = 12.71 mM was included in the calculation of β_1.

TABLE III. Sample Titration Data for $ph_2Pb^{2+} + Br^-$, with B = 6.054 m*M*, at 25° C, 1*M* Ionic Medium.[a]

A, m*M*	a, m*M*	$\bar{n}$	a′, m*M*	$\bar{n}'$
0.9404	0.00615	0.154	0.00600	0.154
1.877	0.02056	0.307	0.01350	0.308
2.811	0.02638	0.460	0.02464	0.460
3.740	0.04456	0.611	0.04222	0.611
4.666	0.07411	0.759	0.07065	0.759
5.589	0.1259	0.902	0.1189	0.904
6.508	0.2094	1.040	0.2034	1.041
7.425	0.3429	1.170	0.3324	1.172
8.337	0.5268	1.290	0.5142	1.292
9.320	0.7696	1.412	0.7529	1.403
10.15	1.063	1.501	1.056	1.502
11.05	1.440	1.588	1.434	1.589
11.95	1.888	1.662	1.874	1.664
12.85	2.381	1.729	2.382	1.729
14.83	3.745	1.831	3.743	1.832
16.81	5.325	1.897	5.320	1.897
18.76	6.994	1.943	7.006	1.942
20.71	8.669	1.988	8.645	1.992
22.63	10.44	2.013	10.44	2.013
26.40	14.06	2.038	14.02	2.045
30.12	17.70	2.052	17.61	2.067
33.78	21.27	2.067	21.27	2.067
37.38	25.02	2.042	24.98	2.048
46.19	33.83	2.041	34.08	2.000
54.68	42.50	2.010	42.98	1.933

[a] The values a and $\bar{n}$ are calculated from E_{GE} (loga = −8.945 + 0.01680 E_{GE}) and a′ and $\bar{n}'$ from E_{RE} (loga′ = −2.152 + 0.01707 E_{RE}). The data up to A = 20.71 m*M* was included in the calculation of the stability constants.

the junction potentials. Since the constants were determined for each experiment, however, this was no problem.

Calculation of Stability Constants

The stability constants β_n were calculated from the sets of experimentally measured values (A,B,a) using a weighted least squares technique described by Sullivan *et al.*[17] For the formation of N monomeric complexes BA_n, the expression for $\bar{n}$ is rearranged to the form

$$U(A,B,a) = \sum_{n=0}^{N} (A-a-nB)\beta_n a^n = 0 \qquad (2)$$

and the best set of β's to fulfill this condition is determined by minimizing the sum S (over all the data points)

$$S = \sum_{i=1}^{I} w_i U^2 (A,B,a)_i \qquad (3)$$

with respect to the β's. The weights are calculated as,

$$w_i = 1/(\delta U)^2, \delta U \sim \frac{\delta U}{\delta a}\sigma_a \qquad (4)$$

starting with an approximate set of β's, and using an iterative procedure to obtain a constant solution. The final set of β's is then used to calculate S_{min}, for the standard deviations and to check the internal consistancy of the fit.

A program was written to carry out the calculations for N = 1–3, using a Hewlett–Packard model 9820A calculator. Constant values of the β's were generally obtained within a few iterations. Values of σ_a corresponding to about 1.5–3.5% uncertainty in the free ligand concentrations (comparable to that estimated from the uncertainty of the measurements) were found to give $S_{min}/(I-N) = 1$, and variations in this range did not affect the final β's. Some calculations were also made using a graphical extrapolation technique, plotting the function

$$F_t = \sum_{0}^{t-1} (\bar{n}-n)\beta_n a^{n-t}/(t-\bar{n}) \qquad (5)$$

against $(t+1-\bar{n})a/(t-\bar{n})$ for t = 1, 2, 3..., to obtain a succession of β's as the limiting slopes and intercepts.[9] Results obtained in this way were consistent with those from the least squares calculations. This procedure was used to evaluate β_3 for $ph_2Pb^{2+} + Br^-$, where only a small range of data was involved, and β_1 and β_2 were already known. Additional calculations were necessary for the $ph_2Pb^{2+} + I^-$ system, where the formation of dimers was suspected. These are described below.

Results for the Triphenyllead(IV) Halide Complexes

Sample data for one titration are given in Table II, and a summary of the calculations for the ph_3Pb^+ complexes is given in Table IV. All the data could be treated assuming monomeric complexes with N = 1 either by linear extrapolation or by the weighted least squares calculations. The reported values were calculated by the latter procedure.

The formation curves are shown in Figure 4 (with only part of the data points included for clarity). As expected for monomeric complexes, the plots of $\bar{n}$ (loga) do not depend on B. It can be seen that the experimental curves for Cl^- and Br^- begin to level off well below $\bar{n}$ = 1, as the excess of halide ion becomes quite large, and eventually even begin to drop. These last points were not included in the calculations (the maximum A/B ratio used is indicated in the Tables II and III), and the titrations were continued in this region mainly to check for the formation of higher complexes (this effect is also found in the data shown later for ph_2Pb^{2+} with Cl^- and Br^-). The reason for this drop is not clear (thermodynamic non-ideality of the solutions at higher concentrations?), but it seems more likely the result of some experimental factor, compounded by the increasing sensitivity of $\bar{n}$ to error in this range, than of a genuine property of the complex system. The possibility of decomposition was considered, but generally no Pb^{2+} was detected in the solutions at the end of the titrations.

TABLE IV. Experiments to Determine the Stability Constants for $ph_3Pb^+ + X^-$, at 25 °C, 1*M* Ionic Medium.

X	B, m*M*	A, m*M*	Maximum A/B used in calcs.	Number of data pts. in calcs.	β_1, M^{-1}
Cl	8.03	0.497–52.9	1.6	60	458 ± 3
	3.21	0.497–29.1	2.8		
Br	8.01	0.418–38.2	1.6	58	813 ± 6
	2.40	0.418–31.6	2.8		
	8.01[a]	0.453–13.8	0.9		
I	3.20[a]	0.453–41.5	1.7	52	2710 ± 9
	1.60[a]	0.453–34.3	0.6		

[a] Experiments done under red light only.

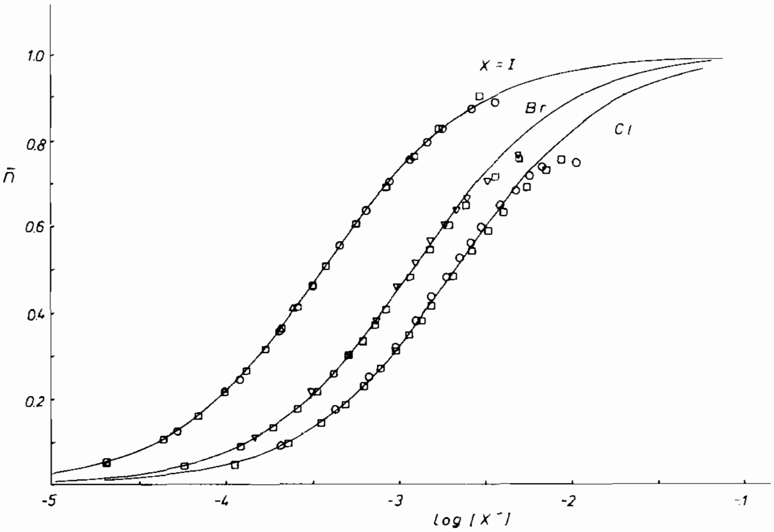

Figure 4. Average number of halide ions X^- bound per triphenyllead(IV) ion, n̄, as a function of log $[X^-]$, for the following total organolead concentrations; □ 8.0, ○ 3.2, ▽ 2.4, △ 1.6 m*M*. The solid curves are calculated using the β_1 values given in Table IV.

Results for the Diphenyllead(IV) Chloride and Bromide Complexes

Data for one titration is given in Table III, and a summary of the calculations is given in Table V. The formation curves are shown in Figure 5 (again with only part of the data included for clarity).

The data for the chloride complexes could be treated assuming mononuclear complexes with N = 2, although here again the data points begin to fall away from the calculated curve at higher chloride concentrations. The data curve for the bromide complexes could similarly be fit for N = 2 at the lower ligand concentrations, but then is seen to rise more steeply. Although the maximum n̄ reached is only slightly greater than 2, the data at the higher ligand concentrations is decidedly better fit by the curve calculated for N = 3, indicating that some of the complex $ph_2PbBr_3^-$ could be formed in this region. After it was found that small amounts of Pb^{2+} could be detected in complex solutions left standing overnight after a titration, sulfide tests were made during a subsequent one, but only very small amounts of Pb^{2+} (estimated <1%) could be detected after several hours in the light. In addition, an experiment with Br^- was carried out in the dark, to test for a possible decomposition effect. These points are plotted along with the others in Figure 2, and can be seen to differ only in rising slightly higher before leveling off at the end.

Results for Diphenyllead(IV) Iodide Complexes

As seen from the data in Figure 5, the behaviour of the diphenyllead iodide complexes is quite different from that of any of the others, indicating both stronger complexing and a more complicated system. These were also the only colored solutions, all showing a light yellow color depending on organolead concentration,

TABLE V. Experiments to Determine the Stability Constants for $ph_2Pb^{2+} + X^-$, at 25° C, 1 *M* Ionic Medium.

X	B, m*M*	A, m*M*	a	b	β^c
Cl	15.3 -14.8	0.921-30.7	1.8	151	$\beta_1 = 1.830(8) \times 10^4, M^{-1}$
	7.64- 7.50	0.921-19.1	2.3		
	7.33- 7.05	0.921-38.3	1.3		$\beta_2 = 0.821(8) \times 10^7, M^{-2}$
	4.37- 4.23	0.921-38.3	2.6		
	3.82- 3.78	0.460- 5.57	1.5		
	2.22- 2.19	0.921-13.6	1.7		
Br	12.11	0.940-61.2	2.8	115	$\beta_1 = 3.090(18) \times 10^4, M^{-1}$
	9.59^d	0.996-90.7	4.3		
	6.05	0.940-54.7	3.4		$\beta_2 = 3.140(30) \times 10^7, M^{-2}$
	2.42	0.940-30.5	5.4		$\beta_3 = 0.355(10) \times 10^3, M^{-3}$
I	9.59^d	23.8 -173.0	3.5	114	$\beta_{11} = 7.6(2) \times 10^4, M^{-1}$
	8.51^d	1.80 - 58.8	3.2		
	4.25^d	0.903- 49.3	4.7		$\beta_{12} = 36.0(2.0) \times 10^7, M^{-2}$
	2.13^d	0.903- 29.3	6.9		$\beta_{13} = 32.0(2.5) \times 10^9, M^{-3}$

[a] Maximum A/B used in calculations. [b] Number of data points in calculations. [c] ( ) = standard deviations. [d] Experiments done under red light only.

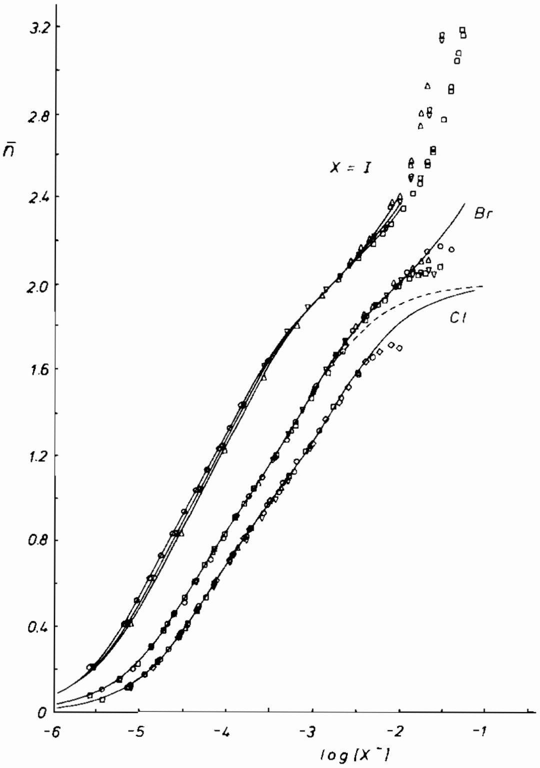

Figure 5. Average number of halide ions X^- bound per diphenyllead(IV) ion, n̄, as a function of log[X^-], for the following total organolead concentrations; for X = Cl, □ 15.3, ○ 7.6 and 7.3, ◊ 4.4, ▽ 3.8, △ 2.2 m*M;* for X = Br, □ 12.1, ○ 9.6, ▽ 6.1, △ 2.4 m*M;* for X = I, □ 9.6, ○ 8.5, ▽ 4.3, △ 2.1 m*M*. The solid curves are calculated using the $\beta_1, \beta_2, \beta_3$, resp. β_{11}, β_{12} and β_{13} values given in Table V. The broken line for Br^- is calculated with $\beta_3 = 0$. The curves for I^- are calculated using the dimeric constants $\beta_{22}, \beta_{23}, \beta_{24}$, and β_{25} as well, as described in the text.

even when kept in the dark and showing no evidence for decomposition.

It seems clear that higher complexes (N>3) of some sort are being formed here. No leveling off of the formation curves was observed, even at n̄ approaching 4, but it is doubtful how much trust should be put in the data in this region, considering the difficulties encountered with the other systems at high ligand concentrations.

In addition, the data seem to indicate some dimer formation. When the formation of polynuclear species B_qA_p is also considered, n̄ can no longer be expressed in terms of a and the β's alone, but becomes a function of b as well. A characteristic of polynuclear system is thus that a set of formation curves, n̄(log $A)_B$, is obtained, which in one general case may exhibit a cross-over point corresponding to a maximum in the degree of condensation.[9] The splitting observed here between the formation curves is not great (and experimental error must always be considered), but the trend is continued over the entire range of measurements, including the cross-over point. Calculations for the measurements with both reference electrodes are also in good agreement throughout, beginning to deviate from each other only above the cross-over. Even if one can claim that some dimers are present, however, a large amount of very accurate data, especially extending to lower B's, would be necessary to attempt a detailed analysis of the system. With the data available here, calculations were carried out to determine the mononuclear formation constants, and to obtain some idea about the nature of the complexes.

Plots were made of n̄(log $B)_a$, using (n̄, a) pairs read from smoothed curves through the data points. Calculating values of $\delta \bar{n}/\delta \log B$ from these, and making a graphical integration, values of the mean degree of condensation $\bar{r}$ were estimated from equation (6).[9]

$$\bar{r} = 1 - \left[\int_0^a (\delta \bar{n}/\delta \log B)_a d\log a\right]_B \qquad (6)$$

Graphical integrations were also made of equation (7) to calculate b(B,a),

$$\log(B/b) = \left[\int_0^a (\bar{n} + (\delta \bar{n}/\delta \ln B)_a) d\log a\right]_B \qquad (7)$$

and these results combined to calculate $\bar{p}$ and $\bar{q}$, the average values for the number of ligands and central groups, respectively, in the complexes B_qA_p,

$$\bar{p} = (B\bar{n})/(B\bar{r}-b) \quad \sim \bar{n}/\bar{r} \quad b \ll B \qquad (8)$$

$$\bar{q} = (B-b)/(B\bar{r}-b) \quad \sim 1/\bar{r} \quad b \ll B \qquad (9)$$

Calculating from the data for B = 2.1 and 4.3m*M*, maxima in $\bar{q}$ of 1.8 and 1.6 in the cross-over region were obtained. These are consistent with the formation of dimeric complexes B_2A_p, although it should be emphasized that this calculation involves many approximations.

To separate out the mononuclear terms, the functions $\bar{n}(B)_a$ were extrapolated to B = 0, to obtain $\bar{n}_1(a)$ as the limit. This is a difficult extrapolation to make on the basis of three points, but a second attempt gave results consistent with the data, and the $\bar{n}_1(a)$ values thus obtained were treated by both the linear extrapolation and weighted least squares methods (with N = 3) to give the β_{11}, β_{12}, and β_{13} reported in Table V.

The values of b calculated from equation (7) were also used to attempt another graphical procedure for the separation and evaluation of the stability constants, based on extrapolation to b = 0 of the functions,[9]

$$(B-b)/ba = \sum_1^P \beta_{1p} a^{p-1} + \sum_1^P 2\beta_{2p} b^{q-1} a^{p-1} \qquad (10)$$

This procedure yielded positive values for β_{11}–β_{13} and for β_{22}–β_{25}, but the results did not fit the data well, with β_{1p}'s somewhat too high, and β_{2p}'s somewhat too low (β_{1p} resp. β_{2p} refer to $ph_2PbI_p^{(2-p)+}$ resp. $ph_4Pb_2I_p^{(4-p)+}$).

Approximate values for the dimeric formation constants were finally estimated by comparing various standard curves with the experimental ones. The solid curves drawn in Figure 5 were calculated using the β_{1p}'s from Table V, with

$$\beta_{22}/(\beta_{11})^2 = 50$$

$$\beta_{23}/\beta_{11}\beta_{12} = \beta_{24}/(\beta_{12})^2 = \beta_{25}/\beta_{12}\beta_{13} = 150$$

It can be seen that terms for N = 4 or higher would be necessary to fit the data at the highest ligand concentrations, but the uncertainty in this range was considered too large to continue the calculations. It also seems necessary to include terms for at least three dimeric species to obtain a consistent fit over the entire range, although this certainly cannot be taken as evidence for the existence of any particular complex. Based on the present data one can argue, however, for an equilibrium between a series of monomeric complexes with N>3 and dimeric complexes of some sort.

Results in Aqueous Solution

Some experiments were tried with ph_2Pb^{2+} and Cl^- in aqueous solution, but the combination of low solubility and weak chloride complexing made the measurements difficult. The results indicated weak complex formation similar to that observed for alkyllead chlorides[5] with a β_1 around 10, but not reliable value could be obtained.

Discussion

The appearance of Pb–X charge transfer bands on the addition of halides to solutions of $ph_2Pb(ClO_4)_2$ in methanol (containing 0.4% water) proves that halide ligands coordinate with the organolead ions. According to expectation, the CT bands are found at higher wave lengths with increasing atomic weight of X, and the absorption curve shows a striking increase in structure when Br^- and still more strongly when I^-, is added (Figure 2). Considering the results of the potentiometric measurements over a similar concentration range, one can assume that essentially the following species are responsible for the different Pb–X CT bands: ph_3PbX(solv.); ph_2PbX^+(solv.); ph_2PbX_2 (solv.). In the case of X = I it is possible that anionic and dimeric species are also involved. In solutions of $(CH_3)_2PbCl_2$ in methanol and in water, where no interference by phenyl group absorptions (K-bands) is possible, we also found the Pb–X CT bands at 200–250 nm.[7,8]

The blue shift and increase in absorbance in the range 210–230 nm which are observed in the spectrum of ph_2Pb^{2+} on changing the solvent from methanol (containing 0.4% water) to a water/methanol mixture (Figure 3) can probably be interpreted in terms of CT processes between lead and coordinated solvent molecules, as caused by a change in the inner coordination sphere.

The conductivities of ph_2PbX_2 in methanol, and therefore also the degree of dissociation proved to be substantially lower than the conductivities of solutions of strong electrolytes in this solvent.[18] This corresponds with the UV results, just as does the observation that the conductivity of ph_2PbX_2 in methanol decreases with increasing atomic weight of X, *i.e.* that association increases going from Cl to I.

The stability, constants, derived from the potentiometric measurements (Table VI) also show that for

TABLE VI. Stability Constants[a] for the Diphenyllead(IV) and Triphenyllead(IV) Halides Complexes in 93% Methanol at 25 °C in a 1*M* Lithium Perchlorate Medium.

	X^-	$\beta_1 \times 10^{-4}, M^{-1}$	$\beta_2 \times 10^{-7}, M^{-2}$	$\beta_3 \times 10^{-9}, M^{-3}$	$K_2 \times 10^{-4}, M^{-1}$	$K_3 \times 10^{-4}, M^{-1}$
ph_3Pb^+	Cl^-	0.0458(3)	–	–	–	–
	Br^-	0.0813(6)	–	–	–	–
	I^-	0.2710(9)	–	–	–	–
ph_2Pb^{2+}	Cl^-	1.830(8)	0.821(8)	–	0.0449	–
	Br^-	3.090(18)	3.140(30)	0.355(10)	0.102	0.00113
	I^-	7.6(2)[b]	36.0(2.0)[c]	32.0(2.5)[d]	0.474	0.00889

[a] ( ) = standard deviations. [b] β_{11}. [c] β_{12}. [d] β_{13} of Table V.

both ph_2Pb^{2+} and ph_3Pb^+, the strength of complexing increases in the order

$$Cl^- < Br^- < I^-$$

This would indicate that the phenyllead ions behave as soft acceptors in methanol under the experimental conditions. However the inverted series of conductivities found for ph_2PbX_2 in THF solution, compared with that in methanol (Table I), indicates that this statement may not be generally applied to the behaviour of these acceptor ions in another solvent (especially when the softness or hardness and the protic nature of the solvents differ, and when the soft or hard character of the acid might be influenced rather easily).

It is interesting to compare our potentiometric results with those found by Pilloni *et al.*,[4,5] where a preference is seen for the harder F^- ligand over Cl^- in aqueous solution. As pointed out by those authors, however the difference is much smaller than that observed for the typically hard $(CH_3)_2Sn^{2+}$ ion.

It is also seen from our results that the complexing for ph_2Pb^{2+} with Cl^- is much stronger in methanol than in water. This would be expected from the lower dielectric constant, and from the poorer solvation of the Cl^- ions by methanol.[19]

The particular formation of polynuclear species in the system ph_2Pb^{2+}–I^-–methanol can be correlated with the experimental results on the decomposition of ph_2PbX_2 (X = Cl, Br, I) in methanol solution. Under comparable experimental conditions (10^{-6}–10^{-4} molar solutions, room temperature) in the dark and in daylight with prolonged standing (~1 month) decomposition – according to (I) – could be observed only in the system with X = I.[7]

$$2\,(C_6H_5)_2PbI_2 \rightarrow (C_6H_5)_3PbI + C_6H_5I + PbI_2 \qquad (I)$$

We suppose the polynuclear species (observed only in the system with X = I) to have a decisive kinetic function as intermediates in this decomposition reaction, facilitating primarily ligand exchange in ph_2PbI_2 to give ph_3PbI and $phPbI_3$. The latter is unstable decomposing into phI and PbI_2.[20] This would correspond to results of kinetic studies on the decomposition of $(CH_3)_2PbX_2$ in water in the presence of alkali halides (following in principle reaction I as an addition of a redistribution reaction and a consecutive decomposition of $RPbX_3$). The decomposition rate reaches a maximum with X = I.[8] The various influences on the decomposition rate have been explained by assuming bridged polynuclear methyllead intermediates in the rate determining step.[8] It would be interesting to know how the formation of polynuclear complexes is dependent on concerted influences of anion and solvent, and how far rates of redistribution reactions are influenced by such interdependencies.

References

1 R. Barbieri, *Ric. Sci. Rend., A3,* 635 (1963); R. Barbieri, M. Giustiniani, G. Faraglia and G. Tagliavini, *Ric. Sci. Rend., A3,* 975 (1963); R. Barbieri, G. Faraglia and M. Giustiniani, *Ric. sci. Rend., A4,* 109 (1964); R. Barbieri, G. Faraglia, M. Giustiniani and L. Roncucci, *J. Inorg. Nuclear Chem., 26,* 203 (1964); M. Giustiniani, G. Faraglia and R. Barbieri, *J. Chromatogr., 15,* 207 (1964); U. Croatto and R. Barbieri, *Ric. Sci. Rend., 8,* 441 (1965).

2 G. Tagliavini, *Ric. Sci. Rend., A8,* 1533 (1965); V. Peruzzo, S. Faleschini and G. Plazzogna, *Gazz. Chim. Ital., 99,* 993 (1969).

3 G. Pilloni and F. Milani, *Inorg. Chim, Acta, 3,* 689 (1969).

4 G. Pilloni and F. Magno, *Inorg. Chim, Acta, 4,* 105 (1970).

5 G. Pilloni and F. Magno, *Inorg. Chim. Acta, 5,* 30 (1971).

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

7 H.-J. Haupt and F. Huber, not published; H.-J. Haupt, *Dissertation, Aachen 1969.*

8 H.-J. Haupt, F. Huber and J. Gmehling, *Z. anorg. allg. Chem., 390,* 31 (1972).

9 F.J.C. Rosotti and H. Rosotti, "The Determination of Stability Constants", McGraw-Hill, New York, 1961.

10 J.G. Ives and G.J. Janz, "Reference Electrodes, Theory and Practice", Academic Press, New York, 1961.

11 G. Gran, *Analyst, 77,* 661 (1952).

12 R. West, R. H. Baney and D. L. Powell, *J. Am. Chem. Soc., 82,* 5402 (1965).

13 A. Werner and P. Pfeiffer, *Z. anorg. Chem., 17,* 100 (1898).

14 A. Polis, *Ber. dtsch. chem. Ges., 20,* 3331 (1887).

15 C.D. Ritchie and P.D. Heffley, *J. Am. Chem. Soc., 87,* 5402 (1965).

16 J. Beers, "Introduction to the Theory of Error", Addison–Wesley Comp., Reading, Mass., 1957.

17 J.C. Sullivan, J. Rydberg and W.F. Miller, *Acta Chem. Scand., 13,* 2023 (1959).

18 J.A. Davies and A.R. Gordon, *J. Chem. Physics, 60,* 1433 (1956); R.S. Drago and K.F. Purcell, "Coordinating Solvents", in: T.C. Waddington, "Non-Aqueous Solvent Systems", London and New York, 1965, 236, 248.

19 A.J. Parker, *Chem. Rev., 69,* 1 (1969).

20 H. Lindemann and F. Huber, *Z. anorg. allg. Chem., 394,* 101 (1972).