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Studies on the Hydrolysis and Structure of the Aquodimethyllead(IV) Ion by Electromotive Force Measurements and by Raman and Proton Nuclear Magnetic Resonance Spectroscopy[1]

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The equilibrium constants for the hydrolysis of $(CH_3)_2Pb^{2+}$ have been determined by emf measurements of the solution pH as a function of composition at 25° in a 3 *M* (Na)ClO_4 ionic medium. Trial values of the equilibrium constants were estimated by graphical procedures and refined by least squares. The species produced, the refined hydrolysis constants, and the estimated standard deviations are: $(CH_3)_2Pb(OH)_2$, $\log {}^*\beta_{21} = -15.543 \pm 0.004$; $[(CH_3)_2Pb(OH)_3^-]$, $\log {}^*\beta_{31} = -28.52 \pm 0.01$; $[(CH_3)_2Pb(OH)_2Pb(CH_3)_2^{2+}]$, $\log {}^*\beta_{22} = -10.827 \pm 0.003$; and $[((CH_3)_2Sn)_3(OH)_4^{2+}]$, $\log {}^*\beta_{43} = -24.31 \pm 0.01$. The estimated standard deviation in $\bar{n}$ for the set of 503 data items is ± 0.016. The results of Raman and proton nmr studies of nonhydrolyzed solutions indicate that the aquodimethyllead(IV) cation has a linear skeleton and that there are weak covalent interactions between $(CH_3)_2Pb^{2+}$ and water molecules and nitrate ions in the first coordination sphere.

The dimethyllead dihalides, in contrast to the analogous germanium and tin compounds, are only slightly soluble in water. Little information is available on the nature of the species present in solution. Also, in marked contrast to the dimethylgermanium and tin dihalides which give typical molecular liquids and solids containing tetrahedral molecules,[2,3] the lead compounds have been described as ionic on the basis of their physical properties.[4]

In studies of dimethyltin(IV) compounds, it has been observed that the coordination number of tin increases readily from four to six when highly electronegative donors are coordinated to the R_2Sn^{IV} moiety as, for example, in the aquo $(CH_3)_2Sn^{2+}$ ion,[5] the anion $[(CH_3)_2Sn(OH)_4^{2-}]$,[6] and in complexes with chelating ligands like β-diketones.[7-9] The structures and properties of these ions and molecules are most easily interpreted by treating them as complexes of discrete, linear R_2Sn^{2+} ions.[10] By analogy with the tin compounds, it is to be expected that compounds containing the $(CH_3)_2Pb^{IV}$ moiety will have similar structures and that the high melting points of the dimethyllead dihalides are a result of the lead(IV) having a coordination number greater than four with bridging halide ions as is found in the essentially ionic lattice of dimethylthallium iodide.[11] Indeed, a *trans* octahedrally coordinated structure has been suggested for bis(acetylacetonato)dimethyllead(IV),[9] and the Raman spectra of aqueous solutions of $(CH_3)_2Pb(NO_3)_2$, $(CH_3)_2Pb(ClO_4)_2$, and $(CH_3)_2Pb(OH)_2$ have been assigned on the basis of a linear structure for the discrete $(CH_3)_2Pb^{2+}$ cations[12] as also has been found for $(CH_3)_2Sn^{+}$.[5]

In the study of complexes of these organometallic ions with ligands containing electronegative donor atoms, water serves as a particularly simple ligand. Raman spectroscopy provides a very convenient method for studying the structure of the species in aqueous solution since water gives only very weak scattering within about 3100 cm^{-1} of the exciting line. The first step, however, in the study of species in solution is a determination of their stoichiometry, and so measurements have been made on the hydrolysis of $(CH_3)_2Pb^{2+}$. Earlier measurements on $(CH_3)_2Sn^{2+}$ have indicated that the water molecules in the first coordination sphere are quite acidic and that several hydrolysis products, both mono- and polynuclear, are formed.[13-15] After the conditions under which the aquo ion is the only species present in significant concentration were defined, Raman and pmr spectra were used to study the structure of the aquodimethyllead(IV) ion.

Experimental Section

Synthesis.—$(CH_3)_2PbO$ was prepared from $(CH_3)_4Pb$ obtained from the Ethyl Corp. A 68% solution of $(CH_3)_4Pb$ in toluene was titrated with a solution of chlorine in ethyl acetate in the presence of a large excess of Dry Ice and with constant stirring. When the color of chlorine persists, the conversion to $(CH_3)_3PbCl$ is essentially complete. The solution was allowed to warm up to *ca.* −20°, and a second equivalent of chlorine was added in ethyl acetate. The $(CH_3)_2PbCl_2$ produced precipitates as a fine white powder.[16] When the chlorine color again persisted, the solution was allowed to warm up to 5°, and the $(CH_3)_2PbCl_2$ was collected on a glass frit, washed with ethyl acetate and ether, and dried. The product was either recrystallized from water or from dimethylformamide followed by washing with ether and dilute HCl which gave the larger yields. At no time during the recrystallization was the temperature allowed to rise above 40° in order to prevent decomposition. *Anal.* Calcd for $(CH_3)_2PbCl_2$: C, 7.79; H, 1.95; Pb, 67.23; Cl, 23.03. Found for a typical

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preparation: C, 7.65; H, 1.95; Pb, 67.35; Cl, 23.0. Reaction of the $(CH_3)_2PbCl_2$ in water with excess Ag_2O gave a solution of $(CH_3)_2Pb(OH)_2$ from which the AgCl and remaining Ag_2O were removed by filtration. The hydroxide was precipitated from the solution by adding acetone, collected on a frit, washed with acetone and ether, and vacuum dried to constant weight over P_4O_{10}. The hydroxide was handled and stored under nitrogen to prevent carbonate formation. The final analysis corresponded to $(CH_3)_2PbO$. Calcd: C, 9.49; H, 2.39. Found for a typical preparation: C, 9.63; H, 2.40. No strong absorption in the region 3100 to 3800 cm^{-1} was observed in infrared spectra of the product, indicating virtually complete dehydration to the oxide. All of the dimethyllead(IV) compounds prepared were stored in a refrigerator.

Preparation of Solutions.—Standard solutions of $(CH_3)_2Pb(ClO_4)_2$ were prepared by dissolving weighed amounts of $(CH_3)_2PbO$ in standard perchloric acid. Each solution was prepared from a fresh lot of $(CH_3)_2PbO$ which had been analyzed for C and H to test for decomposition. Since the $(CH_3)_2PbO$ was not an especially easily characterized substance and the infrared spectra sometimes showed some weak absorption due to water, there was a possibility for small errors in the concentration of $(CH_3)_2Pb^{IV}$ and in the analytical hydrogen ion concentration of the solutions. Since complete hydration of the oxide to $(CH_3)_2Pb(OH)_2$ would only cause an error of *ca.* 6.6% in the calculated $(CH_3)_2Pb^{2+}$ concentration, this was mainly troublesome in its effect on the analytical hydrogen concentration. To check the concentrations, the solutions were analyzed for $(CH_3)_2Pb^{IV}$. Initially, attempts were made to precipitate the ion as $(CH_3)_2Pb(CrO_4)_2$; however, the product exploded readily when dry. The concentration of $(CH_3)_2Pb^{2+}$ was then determined by adding nitric acid, evaporating the solutions to dryness to cleave the lead–carbon bonds, and repeating the process twice more. The Pb^{2+} produced was determined as the chromate.[17] In addition, the analytical hydrogen ion concentration and, hence, the concentration of $(CH_3)_2Pb^{2+}$ were measured independently with the electrochemical cell described below. The solution was discarded if the average deviation from the mean of these values exceeded 1.5%, in most cases it was only a few parts per thousand.

The sulfide test[18] was used to demonstrate the absence of Pb^{2+}, and proton nmr spectra were run on the solutions to test for $(CH_3)_3Pb^+$. No traces of either species were found.

Apparatus and Procedure for Solution Measurements.—The electrochemical cell and the vibrating-reed electrometer circuit used to measure the cell potentials were similar to those described earlier.[13] The titration vessel contained both Beckman General Purpose and E-2 glass electrodes. Runs were discontinued if both electrodes failed to indicate substantially the same pH values. Only the E-2 lithium glass electrode was used at pH values above 8. Calibration of the cells was effected by $HClO_4$–NaOH titration in the 3 *M* $NaClO_4$ medium in the absence of $(CH_3)_2Pb^{2+}$. Back titrations carried out to $\bar{n} \simeq 0$ indicated that the hydrolysis was reversible and that no stripping of methyl groups had occurred.

Raman Spectra.—The Raman displacements from the 4358-A line were recorded photoelectrically with a Cary Model 81 spectrophotometer, and the general procedure for the measurements has been described earlier.[5] All spectra were recorded within a few hours after the preparation of a given solution. The dimethyllead(IV) solutions were maintained at 0° in the light furnace by pumping water through the 7-mm diameter cell which was provided with a 48-cm long water jacket. Dry nitrogen was blown over the cell window to prevent condensation of moisture. Depolarization ratios were determined using large Polaroid cylinders which surrounded the water jacket.

Pmr Spectra.—Proton resonance measurements were made with a Varian A-60 spectrometer at *ca.* 35°. The coupling constants are believed to be accurate to ±1 cps.

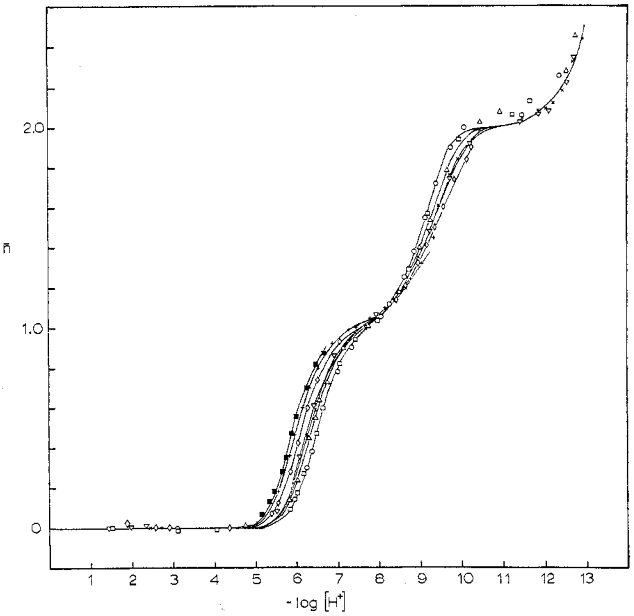

Figure 1.—Average number of protons transferred per $(CH_3)_2Pb^{IV}$ as a function of pH at 25° in a 3 *M* perchlorate medium: ■, 99.16 m*M*; +, 69.35 m*M*; ◇, 33.10 m*M*; ▽, 18.68 m*M*; ×, 16.88 m*M*; △, 12.24 m*M*; □, 6.59 m*M*; ○, 6.07 m*M* stoichiometric $(CH_3)_2Pb^{IV}$ concentration. Only a fraction of the data points is shown for clarity.

Results

Calculation of Equilibrium Constants for the Hydrolysis of $(CH_3)_2Pb(ClO_4)_2$.

—The data in the form of $\bar{n}$, the average number of protons transferred per $(CH_3)_2Pb^{2+}$, as a function of $-\log[H^+]$ are illustrated in Figure 1. The dependence of $\bar{n}$ on the total stoichiometric $(CH_3)_2Pb^{IV}$ concentration indicates that at least one polynuclear complex is formed. The system also exhibits a crossover or "isohydric" point at $\bar{n}$ slightly greater than 1, pH 8.3, indicating that the degree of polymerization is a maximum under these conditions. This behavior is unusual for an aquometal ion although it has also been observed with the hydrolysis of $(CH_3)_2Sn^{2+}$.

The data were used to construct a projection map $\log B(-\log [H^+])_{\bar{n}}$,[19a] where B is the total stoichiometric concentration of $(CH_3)_2Pb^{IV}$. At $\bar{n}$ values less than 0.9, the data give straight lines with slopes $(\partial \log B/\partial -\log [H^+])_n = -2.0$. This indicates that the hydrolyzed species up to $\bar{n} = 0.9$ are all of the generalized type $\{[(CH_3)_2Pb][(CH_3)_2Pb(OH)_2]_n{}^{2+}\}$[19b] where n may be any integer. The degree of polymerization of the system is observed to be a maximum at an $\bar{n}$ value of only slightly greater than 1. The value $\bar{n} = 1$ corresponds to the complete formation of only the first polynuclear complex in the series, that is $[(CH_3)_2Pb(OH)_2Pb(CH_3)_2{}^{2+}]$. Since depolymerization of the polynuclear species occurs for $\bar{n}$ values above about 1.1, the dimer must be the main polynuclear complex formed.

Assuming that $[(CH_3)_2Pb(OH)_2Pb(CH_3)_2{}^{2+}]$ was

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[17] A. I. Vogel, "Quantitative Inorganic Analysis," 2nd ed, Longmans, Green and Co., London, 1955, p 421.

[18] R. Heap, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 658 (1951).

[19] (a) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 374; (b) *ibid.*, p 358.

the only species formed by hydrolysis up to $\bar{n} \simeq 0.9$, the value for the log of the formation constant $^*\beta_{22}$[20] was estimated to be -10.6. A-least squares refinement of this single parameter was carried out for the 313 data points with $\bar{n} < 0.9$ using the Fortran-60 program GAUSS Z[21] and the University of Minnesota's CDC-1604 computer. Equal weights were employed in all of the calculations. In general, it seems best to set up weights as the reciprocals of the variance. For this work, the estimated errors in $\bar{n}_{obsd} - \bar{n}_{calcd}$ up to *ca.* pH 10 are relatively constant. That this is likely to be the case is borne out by an examination of the residuals from a least-squares fit to the $\bar{n}$(log [H^+]) curve for $(C_2H_5)_3Sn^+$, a monoprotic acid,[15] where the correct shape of the curve is known *a priori.* No particular trend in the residuals is evident as $\bar{n}$ increases from 0 to 1. Thus, equal weights are adopted for the data in this work up to pH 10. In more alkaline solutions the errors are undoubtedly larger, and smaller weights would be indicated for fitting with a set of data where there was a uniform distribution of points throughout the entire pH range. In this case experimental difficulties limit the number of points at high pH, so the fit is biased in favor of the data at the lower pH values. Rather than make the fit even less sensitive to these high pH points by giving them small weights, it seemed better to give them the same weight as for the bulk of the points. The refined value was log $^*\beta_{22} = -10.822 \pm 0.003$ with an estimated standard deviation (esd) in $\bar{n}$, $\sigma_{\bar{n}} = \pm 0.0127$. The refinement converged rapidly to this value when other trial values of $^*\beta_{22}$ were used. A normalized projection map[13,19b] was computed for only the two complexes [$(CH_3)_2PbOH^+$] and the dimer [$(CH_3)_2Pb(OH)_2Pb(CH_3)_2{}^{2+}$] and compared with the experimental map log $B(-\log [H^+])_{\bar{n}}$ in order to estimate an upper limit to $^*\beta_{11}$. Using the trial value log $^*\beta_{11} = -7.9$, the two constants were subjected to least-squares refinement using the points with $\bar{n} < 0.9$. The constant for the dimer converges to essentially the same value as in the single-parameter refinement log $^*\beta_{22} = -10.825 \pm 0.005$. Convergence is not obtained for the value of log $^*\beta_{11}$ which is reduced to more and more negative values with very large esd values. The esd in $\bar{n}$ is unchanged by inclusion of the constant for the second species, [$(CH_3)_2PbOH^+$], and remains at ± 0.0127. The same result is obtained when much larger trial values, for example, log $^*\beta_{11} = -6.0$, are used. An upper limit of log $^*\beta_{11} \leqslant -7.4$ can be set since the esd in $\bar{n}$ increases very rapidly when calculations are made using values larger than this. Thus, there is no evidence from these data for measurable concentrations of the simple mononuclear monohydroxo complex in the solutions.

Since depolymerization of the dimer occurs for $\bar{n}$ values much above 1, $(CH_3)_2Pb(OH)_2$ must be the principal new species formed in the solutions at $\bar{n}$ values up to 2. An estimate of log $^*K_{21}$ of -9.2 was made from the pH value corresponding to $\bar{n} = 1.5$, and this was combined with the upper limit to $^*\beta_{11}$ to give the trial value log $^*\beta_{21} = -16.6$. Refinement of the values of $^*\beta_{22}$ and $^*\beta_{21}$ was then carried out using the 479 data points for which $\bar{n} \leqslant 2.0$. The values refine to log $^*\beta_{22} = -10.819 \pm 0.008$ and log $^*\beta_{21} = -15.518 \pm 0.008$ with an esd in $\bar{n}$ of ± 0.036.

Since the experimental $\bar{n}(-\log [H^+])$ curves have a distinct inflection point at $\bar{n} = 2$, there is virtually no overlap in the formation of $(CH_3)_2Pb(OH)_2$ and the anionic species which must exist at $\bar{n} > 2$. The data are considerably less precise at the high pH values necessary to form anionic species; however, there was no evidence for polynuclear anionic complexes. The value for log $^*K_{31}$, -13.0, was estimated from the pH for $\bar{n} = 2.5$, and this was combined with the trial value for $^*\beta_{21}$ to give an estimated value log $^*\beta_{31} = -29.6$. A least-squares refinement was carried out with the entire set of 503 points for the three parameters. This gave the values log $^*\beta_{22} = -10.825 \pm 0.008$, log $^*\beta_{21} = 15.511 \pm 0.008$, log $^*\beta_{31} = -28.49 \pm 0.02$, an esd in $\bar{n}$ of ± 0.036, and an R value $\Sigma|(\bar{n}_{obsd} - \bar{n}_{calcd})|/\Sigma|\bar{n}_{obsd}| = 3.18\%$. Even when vastly different starting values for the constants were used, the least-squares refinement converged on the same set of constants listed above.

The calculated points reproduce the experimental ones quite well except in the vicinity of the isohydric point at $\bar{n} \simeq 1.1$ and at slightly larger $\bar{n}$ values. Since this point occurs slightly above $\bar{n} = 1$, there must be small amounts of one or more polynuclear complexes present which have more than one proton transferred per dimethyllead(IV). Since this is a minor perturbation, it did not seem realistic to attempt to improve the fit by the addition of more than one additional equilibrium constant. Values were estimated for the equilibrium constants for the formation of [$((CH_3)_2Pb)_2(OH)_3{}^{2+}$], [$((CH_3)_2Pb)_3(OH)_4{}^{2+}$], and [$((CH_3)_2Pb)_4(OH)_6{}^{2+}$], $^*\beta_{32}$, $^*\beta_{43}$, and $^*\beta_{64}$, respectively. The following R values, which may be compared to the value of 3.18% obtained from the best three-parameter fit, were obtained: with $^*\beta_{32}$, 2.03%; with $^*\beta_{43}$, 1.60%; with $^*\beta_{64}$, 2.12%. The fit with the constant for the formation of [$((CH_3)_2Pb)_3(OH)_4{}^{2+}$] seemed decidedly better than the other two, and so this was the only polynuclear species other than $((CH_3)_2Pb)_2(OH)_2{}^{2+}$ considered. In the calculations, trial values of the constants $^*\beta_{32}$, $^*\beta_{43}$, and $^*\beta_{64}$ differing by several orders of magnitude were employed, but the refinement converged to the same set of refined values in each case. The final values of the equilibrium constants from the best four-parameter fit, the esd's in the values, and the esd in $\bar{n}$ are given in Table I. In Table II, the observed and calculated $\bar{n}$ values are listed from the last least-squares cycle. The smooth curves in Figure 1 were drawn using this set of constants. Figure 2 shows the distribution of the $(CH_3)_2Pb^{IV}$ species as a function of pH for the most concentrated and the most dilute solutions studied where the quantity $\alpha_{pq} = q[(CH_3)_2Pb)_q(OH)_p]/[(CH_3)_2Pb^{IV}]_{total}$.

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(20) The nomenclature used for equilibrium constants is that of L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

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TABLE I

FINAL EQUILIBRIUM CONSTANTS WITH STANDARD DEVIATIONS FROM LEAST-SQUARES REFINEMENT OF $(CH_3)_2Pb^{IV}$ HYDROLYSIS IN A 3 M (Na)ClO_4 MEDIUM AT 25°

Equilibrium constant	Log value
$^*\beta_{21}$	-15.543 ± 0.004
$^*\beta_{31}$	-28.52 ± 0.01
$^*\beta_{22}$	-10.827 ± 0.003
$^*\beta_{43}$	-24.31 ± 0.01
$\sigma_{\bar{n}}$	± 0.016

Raman Spectra of $(CH_3)_2Pb(NO_3)_2$ and $(CH_3)_2Pb(ClO_4)_2$ Solutions.—Since the emf measurements indicated no appreciable hydrolysis below *ca.* pH 5, spectroscopic studies were made on solutions containing only 0.01 to 0.05 M oxonium ion. The Raman frequencies, integrated intensities, and depolarization ratios are given in Table III. Assignments and approximate descriptions of the normal modes are also given. Because of the rather large diameter of the water-jacketed Raman cell, it was not possible to employ baffles, and the depolarizations are the uncorrected, observed values. The survey spectrum of $(CH_3)_2Pb(NO_3)_2$ solution is illustrated in Figure 3, while Figure 4 shows details of the spectrum recorded at high sensitivity. The values found for the perchlorate frequencies are those of the free ion and are very similar to those observed for aqueous solutions of $(CH_3)_2Sn(ClO_4)_2$.[5] There is some indication of splitting of the doubly degenerate nitrate modes, ν_3 and ν_4.

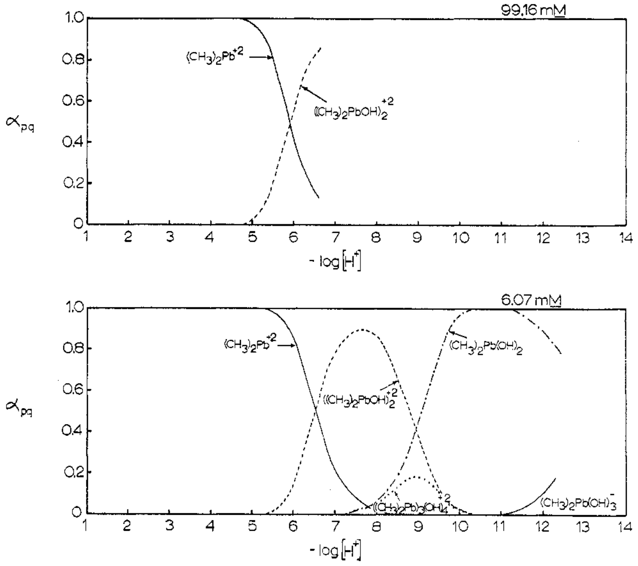

Figure 2.—Distribution of $(CH_3)_2Pb^{IV}$ among the different species as a function of pH for solutions with 99.16 and 6.07 mM $(CH_3)_2Pb^{IV}$.

There was no indication in any of the spectra of a line at *ca.* 504 cm^{-1} which has been attributed to $(CH_3)_3Pb^{IV}$ impurities.[12]

Pmr Spectra of $(CH_3)_2Pb(ClO_4)_2$ Solutions.—The indirect lead–proton spin–spin coupling constant $J(^{207}Pb–CH_3)$ of the aquo ion was determined to be 135.1 cps

TABLE II

LISTING OF OBSERVED AND CALCULATED $\bar{n}$ VALUES FROM THE LAST LEAST-SQUARES CYCLE USING THE CONSTANTS IN TABLE I (M = TOTAL $[(CH_3)_2Pb^{IV}]$; L = $[H^+]^{-1}$)

LOG L	NOBS	NCAL
*** M = 0.01868 ***		
1.420	.003	.000
1.543	-.002	.000
1.611	.002	.000
1.701	.000	.000
1.980	.007	.000
2.365	.012	.000
5.532	.089	.057
6.080	.358	.346
6.427	.615	.611
6.916	.862	.856
7.944	1.066	1.047
8.739	1.262	1.250
9.240	1.481	1.476
9.731	1.749	1.745
10.833	1.927	1.943
11.441	2.033	2.028
11.884	2.059	2.075
12.108	2.081	2.120
12.530	2.216	2.264
12.704	2.351	2.349
*** M = 0.03310 ***		
1.544	-.003	.000
1.611	.002	.000
1.702	-.002	.000
1.982	.005	.000
2.369	.010	.000
5.540	.089	.059
6.088	.358	.352
6.437	.615	.617
6.927	.862	.860
7.947	1.066	1.047
8.724	1.262	1.244
1.891	.026	.000
2.022	.021	.000
2.180	.012	.000
2.295	.012	.000
2.421	.007	.000
2.599	.002	.000
2.915	.002	.000
4.337	.000	.000
5.170	.032	.021
5.393	.071	.054
5.551	.120	.101
5.640	.161	.139
5.727	.208	.186
5.837	.278	.257
5.945	.355	.337
6.036	.423	.408
6.098	.470	.458
6.176	.528	.518
6.268	.596	.586
6.512	.739	.737
6.629	.795	.793
6.720	.830	.830
6.840	.872	.870
7.098	.932	.933
7.326	.971	.971
7.460	.988	.988
7.698	1.014	1.018
7.841	1.033	1.036
8.055	1.063	1.068
8.296	1.110	1.114
8.441	1.145	1.147
8.533	1.170	1.171
8.670	1.212	1.210
8.778	1.249	1.244
8.874	1.285	1.276
8.947	1.317	1.302
9.046	1.356	1.338
9.176	1.411	1.390
9.250	1.443	1.421
9.384	1.503	1.480
9.428	1.525	1.500
9.498	1.559	1.533
9.592	1.604	1.578
9.696	1.650	1.631
9.781	1.694	1.674
9.877	1.739	1.722
10.029	1.802	1.796
10.132	1.843	1.842
10.241	1.881	1.885
1.895	.022	.000
2.027	.018	.000
2.186	.009	.000
2.301	.010	.000
2.427	.005	.000
2.605	.001	.000
2.922	.001	.000
4.431	.000	.001
5.176	.032	.021
5.399	.071	.055
5.557	.120	.103
5.646	.161	.142
5.733	.208	.189
5.842	.278	.261
5.950	.355	.341
6.041	.423	.412
6.103	.470	.461
6.180	.528	.521
6.271	.596	.588
6.514	.739	.738
6.632	.795	.794
6.722	.830	.830
6.841	.872	.871
7.098	.932	.933
7.326	.971	.971
7.459	.988	.988
7.694	1.014	1.017
7.837	1.033	1.036
8.047	1.063	1.067
8.283	1.110	1.111
8.425	1.145	1.143
8.517	1.170	1.167
8.651	1.212	1.204
8.756	1.249	1.237
8.919	1.317	1.292
8.848	1.285	1.267
*** M = 0.01688 ***		
1.383	.006	.000
1.566	-.002	.000
1.796	-.004	.000
1.930	-.009	.000
2.084	-.006	.000
2.431	-.000	.000
4.842	.007	.002
5.786	.150	.139
5.929	.224	.220
6.062	.312	.315
6.262	.456	.472
6.260	.455	.470
6.364	.536	.550
6.447	.592	.609
6.580	.674	.694
6.637	.715	.726
6.798	.788	.804
6.963	.845	.865
7.155	.901	.917
7.465	.966	.975
7.739	1.010	1.015
8.102	1.066	1.074
8.406	1.129	1.144
8.646	1.203	1.220
8.803	1.268	1.280
8.981	1.352	1.358
9.272	1.525	1.506
9.483	1.610	1.624
9.589	1.669	1.684
9.756	1.764	1.775
9.936	1.844	1.859
10.257	1.938	1.955
10.495	1.992	1.986
11.519	2.054	2.034
11.862	2.078	2.072
12.047	2.095	2.106
12.211	2.119	2.147
12.368	2.150	2.198
12.447	2.178	2.229
12.513	2.201	2.257
12.589	2.317	2.291
12.986	2.442	2.506
1.383	.009	.000
1.563	.009	.000
1.794	.001	.000
1.927	-.005	.000
2.083	-.004	.000
2.430	.000	.000
4.842	.007	.002
5.783	.150	.138
5.925	.224	.218
6.058	.312	.312
6.259	.456	.469
6.256	.455	.467
6.359	.536	.546
6.442	.592	.606
6.574	.674	.691
6.630	.715	.723
6.791	.788	.801
6.956	.845	.863
7.146	.901	.915
7.453	.966	.973
7.726	1.010	1.013
8.086	1.066	1.071
8.383	1.129	1.138
8.619	1.203	1.211
8.773	1.268	1.268
*** M = 0.01224 ***		
1.772	-.020	.000
1.901	-.015	.000
2.006	-.010	.000
2.189	-.008	.000
2.441	-.000	.000
2.882	.006	.000
4.771	.015	.001
5.813	.142	.120
6.019	.244	.234
6.185	.357	.356
6.309	.449	.454
6.445	.554	.558
6.569	.636	.645
6.726	.732	.738
6.905	.817	.820
7.159	.904	.903
7.453	.968	.965
7.721	1.015	1.009
7.992	1.058	1.054
8.265	1.116	1.112
8.497	1.179	1.180
8.656	1.237	1.238
8.791	1.296	1.295
8.883	1.341	1.338
8.996	1.397	1.395
9.126	1.470	1.466
9.239	1.538	1.531
9.429	1.654	1.645
9.681	1.795	1.788
9.966	1.914	1.910
10.452	2.030	1.990
12.526	2.279	2.262
12.730	2.448	2.363
10.924	2.082	2.007
1.766	.000	.000
1.895	-.001	.000
2.001	-.001	.000
2.182	.013	.000
2.435	.004	.000
2.874	.008	.000
4.768	.015	.001
5.805	.142	.116
6.011	.244	.229
6.177	.357	.350
6.300	.449	.447
6.435	.554	.551
6.560	.636	.639
6.717	.732	.732
6.894	.817	.816
7.147	.904	.900
7.441	.968	.963
7.701	1.015	1.006
7.974	1.058	1.051
8.244	1.116	1.107
8.473	1.179	1.172
8.627	1.237	1.226
8.756	1.296	1.280
*** M = 0.00659 ***		
1.523	.008	.000
1.637	-.006	.000
1.806	-.011	.000
1.906	-.003	.000
1.959	-.014	.000
2.106	-.021	.000
2.258	-.027	.000
2.497	-.028	.000
2.671	-.016	.000
3.123	-.023	.000
4.079	-.016	.000
5.859	.090	.086
6.044	.169	.167
6.196	.267	.264
6.338	.365	.371
6.497	.471	.497
6.672	.604	.625
6.856	.714	.737
7.064	.818	.833
7.476	.939	.953
7.974	1.035	1.053
8.378	1.142	1.163
8.732	1.292	1.316
9.207	1.571	1.606
9.985	1.941	1.961
11.286	2.065	2.020
11.657	2.135	2.046
1.523	.006	.000
1.635	.008	.000
1.805	-.003	.000
1.906	-.001	.000
1.969	-.050	.000
2.119	-.029	.000
2.268	-.046	.000
2.508	-.040	.000
2.683	-.024	.000
3.136	-.027	.000
4.099	-.016	.000
5.863	.090	.087
6.047	.169	.169
6.202	.267	.268
6.344	.365	.376
6.502	.471	.501
6.678	.604	.627
6.859	.714	.739
7.066	.818	.834
7.476	.939	.953
7.969	1.035	1.052
8.364	1.142	1.158
8.711	1.292	1.305
*** M = 0.00607 ***		
1.912	-.015	.000
2.242	-.021	.000
2.342	-.019	.000
2.599	-.016	.000
3.109	-.014	.000
5.962	.139	.118
6.123	.214	.203
6.267	.308	.303
6.377	.383	.388
6.895	.733	.749
7.001	.783	.800
7.125	.834	.850
7.349	.905	.920
7.638	.972	.985
8.029	1.049	1.066
8.282	1.117	1.134
8.482	1.184	1.206
8.638	1.252	1.275
8.750	1.309	1.333
8.866	1.378	1.399
8.992	1.456	1.477
9.145	1.551	1.578
9.258	1.628	1.653
9.397	1.717	1.742
9.547	1.801	1.826
9.770	1.905	1.917
10.070	2.002	1.976
2.162	-.019	.000
4.649	.004	.000
6.346	.392	.363
6.461	.473	.455
6.570	.549	.540
6.678	.625	.617
6.801	.700	.696
6.946	.775	.774
7.112	.849	.845
7.354	.922	.921
9.479	1.756	1.790
9.623	1.830	1.862
10.147	1.974	1.983
11.442	2.062	2.028
12.341	2.255	2.189
1.917	-.035	.000
2.245	-.025	.000
2.342	-.019	.000
2.598	-.015	.000
3.108	-.013	.000
5.954	.139	.115
6.119	.214	.201
6.262	.308	.299
6.373	.383	.385
6.891	.733	.747
6.997	.783	.798
7.121	.834	.849
7.346	.905	.919
7.632	.972	.984
8.011	1.049	1.062
8.260	1.117	1.128
8.459	1.184	1.197
8.614	1.252	1.264
8.724	1.309	1.319
8.840	1.378	1.384
8.961	1.456	1.457
9.108	1.551	1.553
9.218	1.628	1.626
9.351	1.717	1.713
9.481	1.802	1.791
9.684	1.906	1.887
9.953	2.005	1.960
2.171	-.042	.000
4.762	.003	.001
5.588	.263	.249
6.360	.392	.375
6.470	.473	.462
6.578	.549	.545
6.683	.625	.621
6.805	.700	.699
6.950	.775	.776
7.118	.849	.848
7.355	.922	.921
*** M = 0.09916 ***		
5.139	.074	.050
5.337	.129	.110
5.387	.150	.132
5.449	.178	.164
5.506	.207	.196
5.546	.230	.221
5.585	.254	.248
5.631	.284	.280
5.694	.327	.327
5.730	.355	.355
5.762	.378	.380
5.803	.408	.413
5.850	.443	.450
5.885	.469	.477
5.927	.501	.510
5.962	.526	.536
6.004	.557	.567
6.054	.592	.602
6.113	.631	.642
6.171	.668	.679
6.226	.702	.710
6.300	.742	.750
6.388	.784	.791
6.484	.826	.830
6.585	.870	.864
5.589	.263	.250
5.140	.074	.051
5.332	.129	.108
5.382	.150	.130
5.444	.178	.161
5.500	.207	.192
5.539	.230	.217
5.578	.254	.243
5.624	.284	.275
5.686	.327	.321
5.723	.355	.349
5.755	.378	.374
5.795	.408	.406
5.841	.443	.443
5.876	.469	.470
5.918	.501	.503
5.952	.526	.529
5.994	.557	.560
6.045	.592	.596
6.103	.631	.635
6.162	.668	.673
6.217	.702	.705
6.291	.742	.745
6.379	.784	.787
6.473	.826	.826
6.575	.870	.861
*** M = 0.06935 ***		
1.472	.003	.000
1.608	.006	.000
1.804	.002	.000
2.048	.003	.000
2.351	.000	.000
2.741	.000	.000
5.022	.019	.022
5.229	.061	.053
5.369	.099	.093
5.471	.139	.135
5.546	.176	.174
5.610	.212	.213
5.674	.254	.256
5.740	.298	.303
5.828	.363	.371
5.902	.420	.429
5.967	.471	.481
6.062	.540	.553
6.145	.600	.612
6.239	.662	.673
6.306	.701	.712
6.411	.757	.766
6.519	.806	.814
6.616	.845	.849
6.737	.885	.886
6.883	.922	.920
7.057	.956	.952
7.289	.988	.983
7.463	1.008	1.003
7.640	1.028	1.022
7.795	1.047	1.041
7.994	1.072	1.068
8.153	1.097	1.094
8.286	1.120	1.119
8.392	1.143	1.140
8.511	1.170	1.166
8.653	1.205	1.200
8.779	1.240	1.232
8.914	1.281	1.268
9.027	1.317	1.300
9.153	1.359	1.337
9.267	1.399	1.372
9.357	1.446	1.402
1.473	.002	.000
1.610	.005	.000
1.805	.002	.000
2.050	.003	.000
2.352	-.000	.000
2.743	-.000	.000
5.026	.019	.022
5.237	.031	.055
5.376	.099	.095
5.480	.139	.139
5.554	.176	.179
5.618	.212	.218
5.682	.254	.261
5.747	.298	.309
5.834	.363	.375
5.908	.420	.434
5.974	.471	.486
6.067	.540	.556
6.150	.600	.615
6.242	.662	.675
6.310	.701	.714
6.413	.757	.767
6.521	.806	.814
6.617	.845	.850
6.739	.885	.886
6.885	.922	.921
7.058	.956	.952
7.289	.988	.983
7.463	1.008	1.003
7.638	1.028	1.022
7.792	1.047	1.040
7.989	1.072	1.067
8.146	1.097	1.093
8.277	1.120	1.117
8.381	1.143	1.138
8.499	1.170	1.164
8.638	1.205	1.197
8.760	1.240	1.227
8.891	1.281	1.262

TABLE III

RAMAN SPECTRA OF AQUEOUS SOLUTIONS OF DIMETHYLLEAD(IV) COMPOUNDS AT 0°

0.8 *M* $(CH_3)_2Pb(ClO_4)_2$ + 0.01 *M* $HClO_4$

$\bar{\nu}$ ClO_4^-, cm^{-1}	Assignment	$\bar{\nu}$ $(CH_3)_2Pb^{2+}$, cm^{-1}	A^a	Assignment
		150	. . .	ν_{14} PbC_2 deform $(E_u)^c$
		425	. . .	PbO stretch
460	ν_2 (E)			
		480	1170	ν_3 PbC_2 stretch (sym) (A_{1g})
630	ν_4 (F_2)			
933	ν_1 (A_1)			
1125	ν_3 (F_2)	1208	150	ν_2 CH_3 deform (sym) (A_{1g})
		2952	150	ν_1 CH_3 stretch (sym) (A_{1g})
		3055	50	ν_8 CH_3 stretch (antisym) (E_g)

0.9 *M* $(CH_3)_2Pb(NO_3)_2$ + 0.05 *M* HNO_3

$\bar{\nu}$ NO_3^-, cm^{-1}	Assignment	$\bar{\nu}$ $(CH_3)_2Pb^{2+}$, cm^{-1}	A^a	ρ^b	Assignment
		150	. . .	1.15	ν_{14} PbC_2 deform $(E_u)^c$
		425	. . .		PbO stretch
		480	1560	0.53	ν_3 PbC_2 stretch (sym) (A_{1g})
710	ν_4 (E′)				
730	ν_3 $(A_1)^d$				
1045	ν_1 (A_1)				
		1208	248	0.72	ν_2 CH_3 deform (sym) (A_{1g})
1350	ν_1 $(A_1)^d$				
1415	ν_3 (E′)				
1460	ν_4 $(B_1)^d$				
		2950	230	0.43	ν_1 CH_3 stretch (sym) (A_{1g})
		3055	85	1.4	ν_8 CH_3 stretch (antisym) (E_g)

[a] Integrated intensity (cm^{-1} × % deflection). [b] Uncorrected. [c] Weakly active in most $(CH_3)_2M$ ions and molecules. [d] Frequencies of coordinated nitrate ion; numbering scheme is that of J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

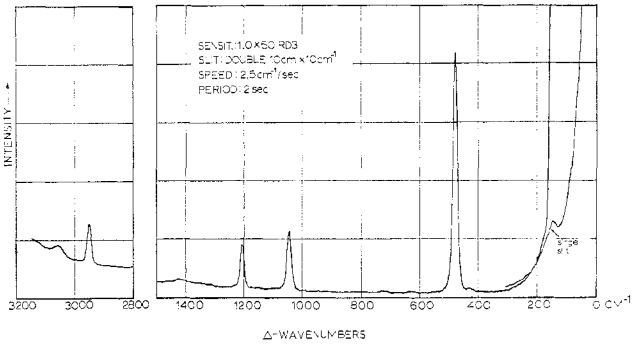

Figure 3.—Raman spectrum of aqueous 0.9 *M* $(CH_3)_2Pb(NO_3)_2$ at 0°.

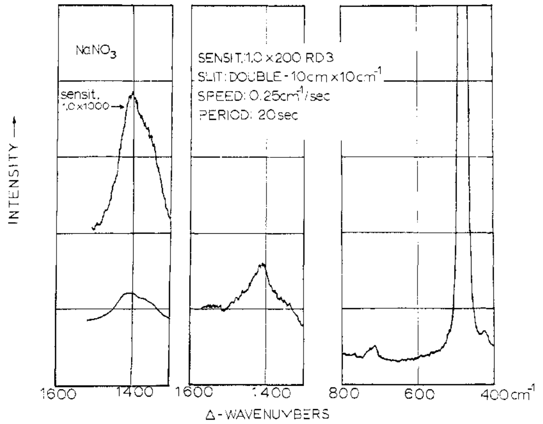

Figure 4.—Raman spectra of 0.9 *M* $(CH_3)_2Pb(NO_3)_2$ and of 2.0 *M* $NaNO_3$ at high sensitivity.

from measurements on solutions containing 0.13 *M* $(CH_3)_2Pb(ClO_4)_2$ + 0.74 *M* $HClO_4$. The value for a 0.15 *M* solution of $(CH_3)_2Pb(OH)_2$ in water was 128.3 cps. Both of these solutions showed only a single methyl proton signal, indicating that there was no appreciable contamination by $(CH_3)_2Pb^{IV}$. The *ca.* 0.1 *M* stock solution used in the emf measurements where the final stoichiometric dimethyllead(IV) concentration was 18.68 m*M* was examined 1 week after preparation, and there was still no signal due to $(CH_3)_3$-Pb^{IV} species. Aged solutions of $(CH_3)_2Pb(OH)_2$ did show a weak signal upfield from the main proton resonance caused by the formation of small amounts of trimethyllead(IV) species.

Discussion

The hydrolysis of $(CH_3)_2Pb^{2+}$ proved to be rapid and reversible. As expected, hydrolysis is much less extensive with dimethyllead(IV) than with the analogous dimethyltin(IV) system although the products formed in the two systems are very similar. In contrast to most simple aquo ions, hydrolysis does not lead to a large number of species in solution, owing, at least in part, to the blocking effect of the two methyl groups. Because of the tendency of $(CH_3)_2PbOH^+$ to condense, only an upper limit could be estimated for the magnitude of the first hydrolysis constant, log $^*\beta_{11} < -7.4$. Comparison with the value for the formation of $(CH_2)_2$-$SnOH^+$, log $^*\beta_{11} = 3.55 \pm 0.01$,[15] shows that the lead species, as expected, has a smaller polarizing effect on water molecules in the first coordination sphere. In both the dimethyllead(IV) and dimethyltin(IV) systems, the simple mononuclear conjugate base has a pronounced tendency to dimerize. In the dimethyllead(IV) solutions studied in this work where the stoichiometric concentrations were greater than 5 m*M*, $[(CH_3)_2Pb(OH)_2Pb(CH_3)_2{}^{2+}]$ is the only hydrolyzed species present in significant concentrations at $\bar{n}$ values up to nearly 1.

As the pH is raised increasing $\bar{n}$ above 1, depolymerization occurs in both the $(CH_3)_2Sn^{2+}$ and the $(CH_3)_2$-Pb^{2+} systems with the formation of the simple uncharged dihydroxides. This behavior is very unusual in the hydrolysis of metal ions where simple associated hydroxides are rarely found in solution at finite concentrations. In strongly alkaline solutions, the anionic complex $[(CH_3)_2Pb(OH)_3^-]$ is formed, and again the dimethyllead(IV) system resembles the dimethyltin(IV) one where an analogous species is found. The most surprising difference between the two systems is that no precipitation was observed with any of the dimethyllead(IV) solutions, while stannoxanes precipitate from the dimethyltin(IV) solutions at $\bar{n}$ = 1.5 or less if the stoichiometric concentration is about

TABLE IV

HYDROLYSIS CONSTANTS OF DIMETHYL COMPLEXES OF d^{10} METAL IONS AND OF THE REDUCED $d^{10}s^2$ IONS[a]

Ion	Log $*K_{11}$	Log $*K_{21}$	Log $*K_{31}$	Log K_d[b]	Medium
$(CH_3)_2Tl^+$[22]	-13.0	...	...	0.6	Variable
Tl^+	-13.6	...	...	...	0 corrected
$(CH_3)_2Sn^{2+}$	-3.55[15]	-5.45[15]	-11.5[6,c]	2.6[15]	3 M (Na)ClO_4
Sn^{2+}	-3.9	...	...	3.4	3 M (Na)ClO_4
$(CH_3)_2Pb^{2+}$	<-7.4	>-8.1	-13.0	>4.0	3 M (Na)ClO_4
Pb^{2+}	-7.9	-9.6	-11.5	...	3 M (Na)ClO_4

[a] Data taken from ref 20 except where noted. [b] Equilibrium constant for $[2M(OH)] = [M(OH)_2M]$. [c] 0.1 M chloride medium.

10 mM or greater. Also, appreciable concentrations of higher polynuclear complexes than the dimer exist in solution at pH values just slightly lower than that necessary to cause precipitation of the stannoxanes.

Table IV lists data for three pairs of ions which have about the same polarizing effect on coordinated water molecules: $(CH_3)_2Sn^{2+}$ and Sn^{2+}, $(CH_3)_2Pb^{2+}$ and Pb^{2+}, and $(CH_3)_2Tl^{+}$[22] and Tl^+.

Before discussing possible structures for the dimethyllead(IV) hydrolysis products, it is useful to examine the spectroscopic evidence bearing on the structure of the simple aquodimethyllead(IV) ion. Raman spectra have been recorded photographically for aqueous solutions of dimethyllead(IV) compounds by Goggin and Woodward[12] and assigned on the basis of a linear skeletal structure with effective D_{3d} symmetry as was found for the isoelectronic dimethylthallium(III) ion.[23] Originally we recorded the spectra of our solutions to test for trimethyllead(IV) species which are formed by disproportionation of $(CH_3)_2Pb^{2+}$, for example, by reaction 1[17] since all of Goggin's dimethyllead solutions

$$2(CH_3)_2Pb^{2+} + X^- = (CH_3)_3Pb^+ + Pb^{2+} + CH_3X \qquad (1)$$

contained trimethyllead impurities. No Raman lines attributable to trimethyllead(IV) species could be detected in the spectra. Although our spectra differ in certain respects from those of Goggin, his assignment of the linear structure to the ion is certainly correct. Comparison of our spectrum of $(CH_3)_2Pb(NO_3)_2$ solution, Figure 3, with that published earlier for $(CH_3)_2Sn(NO_3)_2$ solution which contains linear $H_3C{-}Sn{-}CH_3^{2+}$ ions shows that they are virtually identical with only the small expected frequency shifts.

The differences between our photoelectrically recorded spectra and those determined photographically by Goggin and Woodward may be summarized as follows. First the skeletal bending vibration is observed at 150 cm^{-1} in our spectra but not in Goggin's. Although this appears weakly in the spectra of the linear ions and molecules $(CH_3)_2Hg$,[24] $(CH_3)_2Tl^+$,[23] and $(CH_3)_2Sn^{2+}$,[5] it generally has been considered to be symmetry-forbidden taking the ions as having D_{3d} symmetry. A more detailed consideration of the selection rules for free internal rotators of this type indicates that the bending mode should be Raman active.[25] A very weak line at *ca.* 425 cm^{-1} is observed in both our nitrate and perchlorate spectra, and this was not observed by Goggin. This is shown in Figure 4. The 504-cm^{-1} line attributed by Goggin to the antisymmetrical skeletal stretching vibration of $(CH_3)_3Pb^+$ impurities is absent from all of our spectra. A weak line at 562 cm^{-1} which was observed by Goggin and assigned to a methyl rocking mode is absent from our spectra. There is some indication in our spectra for splitting of the doubly degenerate ν_3 and ν_4 nitrate modes, and this is also shown in Figure 4. Finally, the antisymmetrical C–H stretching vibration is observed in our spectra at 3055 cm^{-1}, but apparently it was not of sufficient intensity to be recorded in Goggin's spectra.

The very weak line at 425 cm^{-1} occurs at approximately the frequency which would be expected for Pb–O bond stretching involving the coordinated aquo groups. A line attributed to Hg–O bond stretching in the aquo CH_3Hg^+ ion has been observed by Goggin and Woodward at 463 cm^{-1}.[26] Unfortunately, the intensity in the $(CH_3)_2Pb^{2+}$ spectrum was so low that it was not possible to determine the state of polarization; however, the line is absent from spectra of $NaNO_3$ run under the same conditions so it is not likely that it is the vibrational mode which is observed at 450 cm^{-1} in pure water.[27]

The assignment of the line observed by Goggin at 562 cm^{-1} to a methyl rocking vibration does not seem correct since this vibration would be expected to occur with a frequency some 200 cm^{-1} higher. Determination of the methyl rocking frequency for the aquo ion $(CH_3)_2Sn^{2+}$ from infrared spectra of thin solution films[5] showed that this occurred at about the same frequency as in most other methyltin compounds. In the Raman spectrum of $(CH_3)_4Pb$, the methyl rocking fundamentals are assigned to a line at 769 cm^{-1} and to the shoulder at *ca.* 800 cm^{-1}.[28] These fundamentals are observed at 769 and 796 cm^{-1} in the infrared spectra of $(CH_3)_4Pb$. Thus, the line observed by Goggin at 562 cm^{-1} is probably due to an impurity.

Finally, in addition to the line at 1415 cm^{-1} due to the free nitrate ν_3, lines at 1350 and 1460 cm^{-1} are observed. In addition, the broad line derived from ν_4 of the free nitrate ion appears to consist of two components at *ca.* 710 and 730 cm^{-1}. These frequencies are similar to those reported by Goggin and Woodward for coordi-

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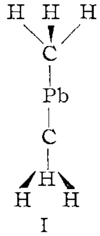
nation of the nitrate ion to $(CH_3)Hg^+$[26] and by Hester and Plane for coordination of nitrate ion to a variety of cations.[29] The numbering of the frequencies of the coordinated nitrate ion in Table III is that of Ferraro.[30] Quite extensive association has been reported for Pb^{2+} and nitrate ion.[31,32] Thus, the spectra tend to indicate some inner-sphere coordination of nitrate ions, but this is certainly not extensive in these approximately 1 M solutions. It should be noted that the ν_3 nitrate line is very broad even in 2 M $NaNO_3$ solution and appears to have a shoulder at about 1350 cm^{-1}; however, the component at 1460 cm^{-1} is absent. There was no evidence in the spectra for splitting of degenerate perchlorate modes.

The ion $(CH_3)_2Pb^{2+}$ resembles $(CH_3)Hg^+$ in that H_2O and probably NO_3^- are attached by bonds having some covalent character in contrast to $(CH_3)_2Sn^{2+}$ where the interactions appear to be essentially of the hard-sphere coulombic type. The frequency assignments are given in Table III on the basis of effective D_{3d} symmetry, and the numbering system is that employed earlier for $(CH_3)_2Sn^{2+}$. Strictly speaking, the symmetry is somewhat lower because of the interaction of the ion with water molecules, but this has no significant effect on the selection rules for the vibrations of the $(CH_3)_2Pb^{2+}$ moiety.

The values of the ^{207}Pb–proton indirect spin–spin coupling constants of the aquodimethyllead(IV) ion also tend to indicate that the ion has a linear skeleton. The Fermi contact term appears to dominate the spin–spin coupling between heavy metal nuclei and protons[33] as, for example, in methylthallium(III)[34–36] and methyltin(IV) compounds.[5,7,37–40] In all of these cases, there seems to be an approximately linear relation between the indirect metal–proton spin–spin coupling constants and the s character in the metal orbitals used to bond to the carbon atoms. Data on trimethyllead(IV) compounds indicate that a similar relation holds for ^{207}Pb–proton coupling.[41] Thus, it would be expected that the coupling constants should approximately double in going from $(CH_3)_4Pb$ where the hybridization is presumed to be predominantly sp^3 to the linear approximately sp-hybridized $(CH_3)_2Pb^{2+}$. Matwiyoff and Drago[41] have reported the value $J(^{207}Pb–CH_3)$ = 62.0 cps for $(CH_3)_4Pb$ in benzene solution. The value observed in this work for aqueous solutions of $(CH_3)_2Pb(ClO_4)_2$, 135.1 cps, is somewhat more than twice the value for tetramethyllead.

Although the structure of the simple aquodimethyllead(IV) ion is most certainly linear, the structures of the associated hydroxo species are not at all certain. Goggin recorded the Raman spectrum of 0.5 M $(CH_3)_2Pb(OH)_2$ and assigned the lines on the basis of a linear structure for the cation and only hard-sphere coulombic interactions with the hydroxide ion. This spectrum, however, contains a weak, depolarized line at 537 cm^{-1} which was assigned as a methyl rocking vibration by analogy with the line at 562 cm^{-1} in the aquo ion spectrum. Since the assignment for the aquo ion is almost certainly incorrect, it is unlikely that this is due to methyl rocking. Kawasaki, Tanaka, and Okawara have assigned the antisymmetrical PbC_2 skeletal vibration to a strong band at 541 cm^{-1} in the infrared spectrum of bis(acetylacetonato)dimethyllead.[42] The line reported at 537 cm^{-1} in the hydroxide spectrum may, therefore, be the antisymmetrical skeletal stretching vibration made Raman active by a decrease in symmetry upon coordination of hydroxo groups, or it may be due to an unknown impurity. The frequency seems rather high for the antisymmetrical stretch since a calculation using a simple valence force field together with effective methyl masses[43] and the symmetrical stretching frequency predicts the value 514 cm^{-1}. The values for $J(^{207}Pb–CH_3)$ are about 7 cps lower for aqueous solutions of $(CH_3)_2Pb(OH)_2$ than for the aquo ion, and a similar decrease has been observed upon coordination of hydroxo groups to $(CH_3)_2Sn^{2+}$.[6] The nature of the associated hydroxo complexes is currently under further study in this laboratory.

It is concluded that the simple aquo ion has the linear structure (I). The very stable dimer presumably has the di-μ-hydroxy-bridged configuration (II). Since the dimer is the only polynuclear complex formed in high concentrations, there apparently is relatively little tendency for the lead atom to coordinate four hydroxo groups. In the dimethyltin(IV) system, structural studies on the stannoxanes that precipitate from solution have indicated that tin atoms coordinate to the bridging oxygen atoms.[44] The fact that no similar compounds precipitate from the dimethyllead(IV) solutions and the low concentration of higher polynuclear species in the solutions seem to indicate that such coordination does not occur in the lead case. There may be some decrease in the C–Pb–C angle in the dimer and in $(CH_3)_2Pb(OH)_2$ due to the coordination of the two hydroxo groups to the lead atoms. Although there seems to be little question about the exist-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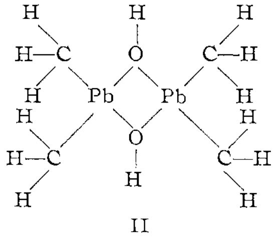
II

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ence of $[(CH_3)_2Pb(OH)_2Pb(CH_3)_2^{2+}]$, $(CH_3)_2Pb(OH)_2$, and $[(CH_3)_2Pb(OH)_3^-]$, the same is not true about the fourth complex assumed in fitting the data. Since this is a small effect and the other assumptions give rather good fits to the data, it is possible that there are very low concentrations of more than one additional species. The addition of more base to the dimethyllead(IV) solution breaks down the dimer and any other polynuclear species, and $(CH_3)_2Pb(OH)_2$ is essentially the only complex in solution at pH ~10.5. Since cleavage of the lead–carbon bond occurs rather rapidly in strongly alkaline solutions, it is difficult to study the anionic species which are formed at high pH.

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A Study of the Complexity and Basicity Constants of the Complexes of Copper(II) with Tetraphosphate Using the Dropping-Amalgam Electrode

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The shapes of anodic and the first portions of the cathodic polarographic waves obtained with the dropping copper amalgam electrode in solutions containing copper(II) and excess tetraphosphates correspond to a reversible electrode reaction. The cathodic diffusion current region is poorly developed in alkaline solutions. The reversible behavior of the electrode in equilibrium with the bulk of the solution permits the determination of formulas, stabilities, and acidities of the complexes formed between copper(II) and tetraphosphate on the basis of the pH measured by a glass electrode and the potential of a dropping copper amalgam electrode. The stepwise formation constants for Cu^{2+} with $P_4O_{13}^{6-}$ are $10^{9.44}$ and $10^{1.16}$. The 1:1 complex is the predominant species in a solution containing tetraphosphate in excess above a pH of 7 owing to the quadridentate bonding capacity of the tetraphosphate ion and the corresponding usual coordination number of copper(II). The successive addition of hydrogen ions to the complex containing two tetraphosphate ligands produces a relatively smaller effect on the complexity constant, presumably because the excess dangling PO_3 tetrahedra can be protonated without greatly affecting the complex bonding. A method of predicting polyphosphate complexity constants is shown from the observation that the mean free energy associated with the complex bond formation in all copper polyphosphate complexes is essentially a linear function of the mean ionic charge of the bonding PO_4 tetrahedra.

Introduction

The present investigation is one of a series concerned with the complexes of copper(II) with linear polyphosphates[1,2] and another concerned with the chemistry of tetraphosphates in aqueous solutions. The tetraphosphate papers are concerned with acidity constants[3] and complexes with mercury(I)[4] as well as the guanidinium ion.[5]

The complex-forming properties of linear polyphosphates are influenced by the presence of several positions in the molecule at which protonation or complexation can occur. Consequently, the possibility of forming polynuclear species exists in ligand-deficient solutions, and protonated complexes are formed in acidic solutions. The reversible behavior of the copper amalgam electrode in equilibrium with the copper polyphosphates permits a complete interpretation of the very complex equilibria which would otherwise be exceedingly difficult, if not impossible. The accuracy of the results is enhanced by the fact that the electrode is also reversible in ligand-free solutions if the pH is of the order of 3.0 or less.

In particular, a series of studies under similar experimental conditions in which only the length of the ligand chain and the number of coordinating positions are changed permits a greater insight concerning the statistical, as well as intrinsic, factors influencing complex bonding. Furthermore, the results can be extrapolated to predict the properties of polyphosphate complexes of other metal ions for which no reversible electrode is available.

Since Thilo and Ratz[6] first prepared tetraphosphate by the alkaline hydrolysis of cyclic tetraphosphate and Quimby[7] crystallized its guanidinium salt, several papers have also been written on its separation by various chromatographic procedures, its crystallization by heavy metal ions, and the irreversible polarography of the Zn, Cd, and Pb salts. Many of these references and the procedure for preparing the tetraphosphate are given in the first paper of this series,

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