that the alcoholic protons of the ligand are being displaced by the bismuth ion. Assuming this occurs and that the stoichiometry of the number of hydroxide ions added per chelate molecule does not change significantly, a reasonable structure for the 1:1 bismuth tartrate complex at pH 14.5 would involve coordination by the two carboxylate groups and the two alcoholic oxygens with an additional two hydroxy groups attached to the bismuth ion to maintain it as a six-coordinate metal ion.

Reference to Figures 1 and 2 indicates that the chemical shifts due to chelation are approximately half as great for the 1:2 complexes as for the 1:1 complexes of lead ion and bismuth ion. This would imply for the 1:2 complexes either that the interaction between metal ion and the alcoholic oxygens is much weaker than for the 1:1 complex or that on the average only one alcoholic oxygen per tartrate is coordinated to the metal ion. The latter seems more reasonable and is consistent with the expected coordination for the two metal ions under alkaline conditions.

The significant increase in chemical shift for the ligand protons of the lead complex and the bismuth complex at pH 14.5 gives strong support to the conclusion that the alcoholic groups are involved in direct coordination of the metal ions. This conclusion is in agreement with an earlier proposal for such coordination for the thorium(IV) tartrate complex.[8]

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF
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Chloro Complexes of Lead(II)

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The finding that $BiCl_4^-$ and $BiCl_6^{-3}$ are prominent in solutions of Bi(III) in hydrochloric acid[1] prompted us to investigate halide complexes of lead of high ligand number. Kivalo[2] deduces from polarographic measurements at $\mu = 1.0$ that no higher complex than $PbCl_3^-$ is observed, but his calculations involved no measurements in which the average ligand number ($\bar{n}$) exceeded 2.2. We had hoped to measure the solubility of $[(CH_3)_4N^+][PbCl_3^-]$ as a function of $[Cl^-]$ but were unable to prepare it owing to the great insolubility of $PbCl_2$. Therefore, the solubility of the latter salt has been determined at ionic strength 4.0 as a function of $[Cl^-]$, and the results have been interpreted with the help of spectrophotometric observations on solutions of Pb(II) in the same media.

Experimental

Reagent grade HCl and $HClO_4$ were diluted with de-ionized distilled water. The dilute acids were standardized using anhydrous sodium carbonate. Lead chloride was recrystallized from hot dilute hydrochloric acid.

Solutions were saturated with $PbCl_2$ by means of a Brønsted saturator[3] thermostated at 25.0 ± 0.1°. Usually one pass was found sufficient for saturation, but more than one pass was used in practice. At least two determinations of the solubility were made at each chloride ion concentration.

Analysis of Pb(II) was done spectrophotometrically by measuring the absorbance of Pb(II) in 6 M HCl at 271 mμ, according to the method of Merritt, Hershenson, and Rogers.[4] All spectrophotometric measurements were made using a Beckman DU spectrophotometer with the cell compartment thermostated at 25 ± 0.5°. $PbCl_2$ was the only solid phase present at all times.

Theoretical

No test for polynuclear complexes could be made since no ions not involved in the equilibrium are present in the salt. None was found[1] in the study of $BiCl_n^{3-n}$ at Bi(III) concentrations higher than Pb(II) concentrations encountered in this study. It is assumed therefore that none is present here, although this has by no means been proved. The working equations for deriving equilibrium constants are

$$S = \frac{[\mathrm{PbCl_2}]}{\beta_2[\mathrm{Cl^-}]^2}\sum_{1}^{N} \beta_n[\mathrm{Cl^-}]^n \tag{1}$$

$$[\mathrm{Cl^-}] = \frac{[\mathrm{Cl^-}]_0}{1 + \mathrm{d}S/\mathrm{d}[\mathrm{Cl^-}]} \tag{2}$$

$$\frac{\mathrm{d}\ln S}{\mathrm{d}\ln [\mathrm{Cl^-}]} = \bar{n} - 2 \tag{3}$$

where S is the solubility (M) of $PbCl_2$, $\beta_n = [PbCl_n^{2-n}]/[Pb^{+2}][Cl^-]^n$, $\bar{n}$ is the average ligand number, and $[Cl^-]_0$ is the concentration of Cl^- in the solvent before saturation. Chemical reactions assumed are

$$\mathrm{PbCl_2(s)} \rightleftharpoons \mathrm{PbCl_2(aq)}$$

$$\mathrm{PbCl_2} + (n-2)\mathrm{Cl^-} \rightleftharpoons \mathrm{PbCl}_n^{2-n}$$

Equation 2 is used to estimate free $[Cl^-]$ and then eq. 1 is applied to the data using the graphical method of Leden as follows. The slope of the solubility curve in Figure 1 gives $\bar{n} \approx 4$ in 4.0 M $[Cl^-]$. An initial plot of S *vs.* $[Cl^-]^2$ for the points at higher $[Cl^-]$ gives a straight line. The slope and intercept give $[PbCl_2]$ and β_4/β_2 to a first approximation. Similarly, approximate values of β_3/β_2, β_1/β_2, and $1/\beta_2$ are obtained. The approximate values are used to obtain improved values until plots of $S - F_n$ *vs.* $[Cl^-]^{n-2}$ give straight lines all with the same intercept, $[PbCl_2]$. (F_n includes all terms on the right-hand side of eq. 1 except that used in the plot and $[PbCl_2]$.)

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[1] G. P. Haight, Jr., C. H. Spring, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964).

[2] P. Kivalo, *Suomen Kemistilehti*, **28**, 155 (1956).

[3] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 190.

[4] C. Merritt, H. M. Hershenson, and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).

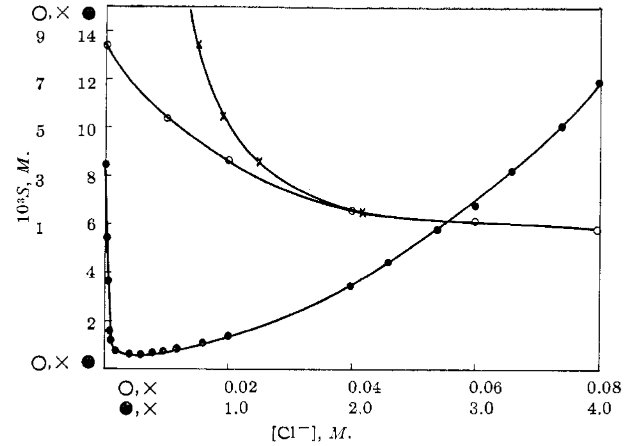

Figure 1.—Solubility of lead chloride *vs.* concentration of chloride ion; $[\overline{\mathrm{H}}^+] = 4.0\ M$, 25°. Upper two curves show points to the left of the minimum on an expanded scale. Circles show $[\mathrm{Cl}^-]_0$, crosses show $[\mathrm{Cl}^-]$ found using eq. 2 and successive approximations. Corrections are less than 1% for $[\mathrm{Cl}^-]_0 > 0.06\ M$.

Results

Figure 1 shows the solubility curve of $PbCl_2$ *vs.* $[\mathrm{Cl}^-]$ together with the corrections required for $[\mathrm{Cl}^-]$ when $[\mathrm{Cl}^-]_0 < 0.1\ M$. The intercepts of all final plots of $S - F_n$ *vs.* $[\mathrm{Cl}^-]^{n-2} = 4.7 \times 10^{-4}\ M = [\mathrm{PbCl_2}]$.

The data can be fit nearly equally well with the equations

$$S = \frac{1.6 \times 10^{-6}}{[\mathrm{Cl}^-]^2} + \frac{1.5 \times 10^{-5}}{[\mathrm{Cl}^-]} + 4.7 \times 10^{-4} + 1.9 \times 10^{-4}[\mathrm{Cl}^-] + 6.6 \times 10^{-4}[\mathrm{Cl}^-]^2 \quad (4)$$

$$S = \frac{1.7 \times 10^{-6}}{[\mathrm{Cl}^-]^2} + \frac{1.6 \times 10^{-5}}{[\mathrm{Cl}^-]} + 5.0 \times 10^{-4} + 7.3 \times 10^{-4}[\mathrm{Cl}^-]^2 \quad (5)$$

Table I shows the fit of solubility data to eq. 4. The data do not clearly determine the presence or absence of $PbCl_3^-$. However, spectrophotometric observations of Pb(II) in 2–4 *M* $[\mathrm{Cl}^-]$ show no isosbestic points, indicating the presence of more than two species in rhe region of $[\mathrm{Cl}^-]$ in which $2 < \bar{n} < 4$. β_1 is likewise difficult to resolve from the solubility data. However, β_1 can be estimated spectrophotometrically. As Cl^- is added to $10^{-4}\ M$ Pb^{+2} in 4 *M* $HClO_4$ an isosbestic point at 218.5 mμ is observed up to ≈ 0.01 *M* $[\mathrm{Cl}^-]$. At this $[\mathrm{Cl}^-]$, Pb(II) is about 90% Pb^{+2} and 10% $PbCl^+$. At higher $[\mathrm{Cl}^-]$, $PbCl_2$ becomes important and the isosbestic point disappears. If one assumes that $PbCl^+$ does not absorb at 208.5 mμ where Pb^{+2} has an absorption maximum, one can calculate a minimum value for $\beta_1 = 10.0$. If $PbCl^+$ absorbs, β_1 will be higher. If one uses the absorbance for $PbCl^+$ at 226 mμ given by Hume and Spiro,[5] $\beta_1 = 13$. The solubility data give a value of $\beta_1 \leq 9.4$. Since this corresponds closely to the minimum value obtained spectrophotometrically, we estimate 10 as the value of β_1. Hume and Spiro[5] give $10 \leq \beta_1 \leq 24$. Kivalo[2] gives $\beta_1 = 9.1$ at $\mu = 1.0$.

TABLE I

SOLUBILITY DATA, *M*, at 25°

$[\mathrm{Cl}^-]_0$, *M*	$[\mathrm{Cl}^-]$, *M*	10^3S_{obsd}, *M*	10^3S_{calcd},[a] *M*
0.000	0.0148	8.40	8.41
0.010	0.019	5.40	5.46
0.020	0.025	3.67	3.58
0.040	0.042	1.57	1.81
0.060	0.061	1.20	1.21
0.080	0.080	0.91	1.08
0.100	0.100	0.77	0.82
0.200	0.200	0.61	0.65
0.300	0.300	0.58	0.63
0.400	0.400	0.69	0.70
0.600	0.600	0.89	0.85
0.800	0.800	1.11	1.04
1.00	1.00	1.36	1.32
2.00	1.99	3.48	3.49
3.00	2.98	6.85	6.99
3.30	3.28	8.27	8.35
3.70	3.68	10.20	10.38
4.00	3.97	12.00	11.80

[a] Equation 4 used.

The value of β_2 is not so clearly resolved. The solubility data give $\beta_2 = 293$. Kivalo[2] reports $\beta_2 = 7.4$ at $\mu = 1.0$ (a value as high as 20 is still compatible with his data). The authors' opinion is that 293 is not only the best, but the maximum possible value for β_2 obtainable from the solubility data at $\mu = 4.0$. In 0.136 *M* $[\mathrm{Cl}^-]$ the absorbance of 1.23×10^{-4} *M* Pb(II) is lowered from 0.450 (for Pb^{+2}) to 0.243 at 218.5 mμ where Pb^{+2} and $PbCl^+$ have the same molar absorbance. If $PbCl_2$ is nonabsorbing at this wave length, this leads to a value of $\beta_2 \geq 106$. The more $PbCl_2$ absorbs at 218.5 mμ the higher β_2 will be. Table II shows values of step constants, $K_n = [\mathrm{PbCl}_n{}^{2-n}][\mathrm{PbCl}_{n-1}{}^{3-n}]^{-1} \cdot [\mathrm{Cl}^-]^{-1}$, for various metal ions with electronic structures similar to Pb^{+2}. The values given for this work are derived from eq. 4.

TABLE II

STEP FORMATION CONSTANTS OF CHLORO COMPLEXES

Complex	K_1	K_2	K_3K_4	K_5K_6	Medium	Ref. and technique
$TlCl_n{}^{1-n}$	0.79	0.2	(K_3 = 0.1)	. . .	4.0 *M* $NaClO_4$	6 sol.
$PbCl_n{}^{2-n}$	10	29	1.4[a]	≤0.02	4 *M* H^+	sol. sp.[b]
$PbCl_n{}^{2-n}$	9.5	0.8	1.4?[c]		1 *M* Na^+	2 pol.
$BiCl_n{}^{3-n}$	229	14			2 *M* Na^+, 1 *M* H^+	7 sol.
$BiCl_n{}^{3-n}$			380	6.0	4 *M* H^+	1 sol.
$SnCl_n{}^{2-n}$	28	8	0.9	. . .	. . .	8 sol.

[a] $K_3 \leq 0.4$. [b] This work; solubility = sol., polarographic = pol., spectrophotometry = sp. [c] Recalculated assuming no $PbCl_3^-$.

Species of $PbCl_n{}^{2-n}$ with *n* Higher than 4.—The

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(5) T. G. Spiro and D. N. Hume, *Inorg. Chem.*, **2**, 863 (1963).

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(7) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

(8) G. P. Haight, Jr., W. Evans, and J. Zoltewicz, *ibid.*, **16**, 311 (1962).

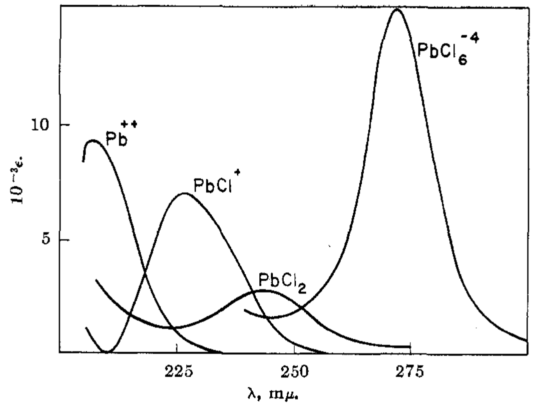

Figure 2.—Absorption spectra deduced for various $PbCl_n^{2-n}$ species. Pb^{+2} and $PbCl_6^{-4}$ spectra were measured directly. Spectra of $PbCl^+$ and $PbCl_2$ were calculated using K_1 and K_2 values obtained in this study.

spectrum of Pb(II) continues to change as [HCl] is increased above 4 *M*. An isosbestic point for the two species of highest *n* is observed only after reaching 6 *M* HCl. A limiting spectrum is observed between 10 and 11 *M* HCl which we attribute to $PbCl_6^{-4}$ by analogy with observations on $BiCl_n^{3-n}$ spectra.[1] This species is formed in significant concentrations only when $[Cl^-] > 4.0$ so only an upper limit can be given to its formation constant. The measured spectra for Pb^{+2} and $PbCl_6^{-4}$ are shown in Figure 2 together with those calculated for $PbCl^+$ and $PbCl_2$ using the constants given above. Knowledge concerning equilibria involving $PbCl_3^-$ is too scanty to permit calculation of $PbCl_4^{-2}$ and $PbCl_3^-$ spectra.

In summary, Pb^{+2} forms weaker complexes with Cl^- than Bi^{+3} while showing a similar preference for even numbers of ligands. Ultraviolet absorption bands are shifted to shorter wave lengths for the +2 central ion consistent with their characterization as ligand-to-metal charge-transfer bands. Although $SnCl_n^{2-n}$ and $PbCl_2^{2-n}$ complexes are of comparable strength up to $n = 4$, Sn(II) complexes do not exhibit the sharp charge-transfer band in the ultraviolet and give no evidence of forming a complex with $n > 4$.

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CONTRIBUTION FROM THE THIOKOL CHEMICAL CORPORATION,
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The Chemistry of Alane. VII.[1] Trialkylamine Phenylalanes

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The extensive literature on organoaluminum compounds contains no methods for the preparation of aryl-substituted alanes of the type $ArAlH_2 \cdot NR_3$.[2] Recently, Peters and co-workers[3] have prepared trimethylamine complexes of ethyl- and methylalanes ($RAlH_2 \cdot N(CH_3)_3$, where R is CH_3 or C_2H_5).

We wish to report the synthesis of the trimethylamine and triethylamine complexes of phenylalane by an additional method (eq. 1), suitable for the preparation of any substituted alane and originally reported by Wittig[4] for the preparation of triphenylaluminum.

$$n\mathrm{RLi} + \mathrm{Cl}_n\mathrm{AlH}_{3-n}\cdot\mathrm{NR'}_3 \longrightarrow n\mathrm{LiCl} + \mathrm{R}_n\mathrm{AlH}_{3-n}\cdot\mathrm{NR'}_3;\quad n = 1, 2, 3 \qquad (1)$$

Reaction in benzene of triethylamine chloroalane with an equimolar quantity of phenyllithium resulted in the nearly quantitative precipitation of LiCl. Freeze drying the benzene filtrate yielded $C_6H_5AlH_2 \cdot N(C_2H_5)_3$ (I) as a pale yellow liquid. Similarly, the reaction of triethylamine dichloroalane with two equivalents of C_6H_5Li gave a pale yellow liquid, $(C_6H_5)_2AlH \cdot N(C_2H_5)_3$ (II). The synthesis was repeated with $ClAlH_2 \cdot N(CH_3)_3$ to give $C_6H_5AlH_2 \cdot N(CH_3)_3$ (III), also a yellow, viscous liquid, which decomposed rapidly above 50°. Also prepared by this method were $CH_3AlH_2 \cdot N(CH_3)_3$, identical in physical properties and infrared spectrum with the compound reported by Peters,[3] and $n\text{-}C_4H_9AlH_2 \cdot N(CH_3)_3$, the infrared spectrum of which resembled that of $C_2H_5AlH_2 \cdot N(CH_3)_3$[3] (Al–H absorption at 1750 $cm.^{-1}$).

The infrared spectra of I, II, and III were remarkably similar with the exception of the Al–H absorption, which occurred at 1770 $cm.^{-1}$ for I, 1780 $cm.^{-1}$ for II, and 1772 $cm.^{-1}$ for III, and they showed the characteristic absorptions of the tertiary amine as well as those of a monosubstituted aromatic ring in the 840–720 $cm.^{-1}$ region.

The molecular weight determinations in benzene showed degrees of association of 1.16 and 1.31 for I and II, respectively. The determinations were performed at concentrations of 0.05 *M*, and the effect of concentration on apparent molecular weight was not examined. It is interesting to note that the degree of association of the series $(C_2H_5)_3N \cdot AlH_3$, $(C_2H_5)_3N \cdot AlH_2(C_6H_5)$, and $(C_2H_5)_3N \cdot AlH(C_6H_5)_2$ increased as the substitution on aluminum increased (1.05,[5] 1.16, and 1.31, respectively) in spite of the fact that there is an increase in the number of bulky groups surrounding the aluminum. At the same time, the diphenyl derivative is more stable than the monophenylalane. This difference in stability may be related to the inherent tendency for disproportionation in monosubstituted alanes.

Surprisingly enough, the corresponding $(CH_3)_3N$

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[1] Paper VI: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, to be published.

[2] J. R. Surtees, *Chem. Ind.* (London), 1260 (1964), has reported the synthesis of $(C_6H_5)AlH_2$ but he was unable to prepare the trimethylamine complex by the addition of $N(CH_3)_3$ to the alane.

[3] F. M. Peters, B. Bartocha, and A. J. Bilbo, *Can. J. Chem.*, **41**, 1050 (1963).

[4] G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

[5] J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960), found a value of 1.10 for $(C_2H_5)_3N \cdot AlH_3$.