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Complexes of the Dimethyltin(IV) Ion in Aqueous Solution. II. Bidentate Ligands with Nitrogen and Oxygen Donors[1]

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The stability constants of the 1,10-phenanthroline, acetylacetonato, and picolinato complexes of the dimethyltin(IV) ion have been determined for solutions with $[NO_3^-] = 0.1$ *M* by e.m.f. measurements of $[H^+]$. Since an appreciable fraction of the total $(CH_3)_2Sn^{+2}$ was distributed in the hydroxo complexes $(CH_3)_2SnOH^+$ and $((CH_3)_2Sn)_2(OH)_2^{+2}$, the hydrolysis constants for the formation of these species were redetermined to be $\log {}^*\beta_{11} = -3.2 \pm 0.2$ and $\log {}^*\beta_{22} = -4.6 \pm 0.3$ for the nitrate medium. The values for the first stepwise formation constants as $\log K_1$ are: phenanthroline, 4.2; acetylacetonato, 6.6; picolinato, 5.1. These values are compared with those determined for other divalent ions. The dimethyltin(IV) ion behaves as a typical Leden–Chatt "A" group ion and is similar to the lead(II) and presumably the tin(II) ion.

Introduction

Although the complexes of the tin(IV) halides have been the subject of extensive study, very little is known about the stability of complexes of the alkyltin(IV) ions. In this paper, the discussion will be restricted to the complexes of the dialkyltin(IV) ions, R_2Sn^{+2}, which probably occur in aqueous solution as $R_2Sn(OH_2)_2^{+2}$. It has long been known that the dialkyltin(IV) dihalides form rather unstable, readily hydrolyzed coördination compounds with unidentate nitrogen donors. These complexes usually have the composition $R_2SnX_2 \cdot 2B$ and are presumed to be similar to the addition compounds formed with SnX_4. Many of these complexes have been tabulated in a recent review.[3] It has been reported that simple oxygen donors do not form isolable complexes with the dialkyltin(IV) halides.[4] The complexes $(n\text{-}C_4H_9)_2SnCl_2 \cdot$dipy (2,2′-dipyridyl = dipy) and $(n\text{-}C_4H_9)_2$Sn(oxinate)$_2$ (8-hydroxyquinoline = Hoxinate) also have been prepared.[5] Recently Alleston and Davies, in an effort to synthesize stable addition compounds of the dialkyltin dihalides with nitrogen donors, prepared a variety of complexes with 2,2′-dipyridyl and 1,10-phenanthroline. These all were quite stable and had sharp melting points.[6] Irving and Cox also have observed that certain organometallic cations like the dialkyltin(IV) and the alkylmercury(II) ions form very stable complexes with sulfur donors such as the conjugate base of 3-mercapto-1,5-diphenylformazan.[7] The rather great stability of the latter complexes was attributed to d_π–p_π back donation from the tin atom. There is thus some evidence indicating that the dialkyltin(IV) ions might form a new class of "B" type ions according to the Leden–Chatt classification,[8,9] similar in their properties to the cadmium(II) ion. Recently the methylmercury(II) ion has been observed to have "B" character.[10]

Although the study of coördination compounds of tin(IV) under other than anhydrous conditions is difficult because of the extensive hydrolysis and polymerization which results from the great stability of tin(IV) oxygen bonds,[11] it is possible to study some complex formation equilibria of the dialkyltin(IV) ions in aqueous solution.[12] The two methide ligands of $(CH_3)_2Sn^{+2}$ reduce the extensive hydrolysis and polymerization observed with Sn^{+4}. It was decided to study the equilibria in aqueous solution of complexes of the dimethyltin(IV) cation in order to obtain information on the stability of complexes of these ions with nitrogen and oxygen donors. Bidentate ligands were chosen, since the studies on the stability of the hydroxo complexes have indicated that tin tends to adopt a coördination number of four with the two methide ligands already occupying two of these coördination sites.[12] These bidentate ligands should minimize the tendency toward the formation of mixed hydroxo complexes, and the only complex formation reaction to be anticipated with the bidentate ligand L is $(CH_3)_2Sn^{+2} + L^{-n} = (CH_3)_2SnL^{+(2-n)}$. Even if additional water molecules are loosely coördinated by $(CH_3)_2SnL$, these would not be expected to transfer protons in the acidic solutions studied.[13] Since the aquo dimethyltin(IV) ion is still a rather strong aquo acid, it is necessary to have accurate data on the hydrolytic equilibria, and these have been published recently.[12] It also is desir-

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[2] Research Fellow in Chemistry.

[3] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[4] G. E. Coates, "Organometallic Compounds," Second Edition, Methuen and Co., London, 1960, p. 184.

[5] Reference 4, p. 190; D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 756 (1961).

[6] D. L. Alleston and A. G. Davies, *ibid.*, 2050 (1962).

[7] H. Irving and J. J. Cox, *ibid.*, 1470 (1961).

[8] I. Leden and J. Chatt, *ibid.*, 2936 (1955).

[9] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[10] M. Schellenberg and G. Schwarzenbach, "Proceedings of the Seventh International Conference on Coördination Chemistry," Stockholm, Sweden, 1962, p. 157.

[11] R. C. Courtney, R. L. Gustafson, S. Chaberek, and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 2121 (1958).

[12] R. S. Tobias, I. Ogrins, and B. A. Nevett, *Inorg. Chem.*, **1**, 638 (1962).

[13] R. L. Gustafson and A. E. Martell, "Proceedings of the Seventh International Conference on Coördination Chemistry," Stockholm, Sweden, 1962, p. 163.

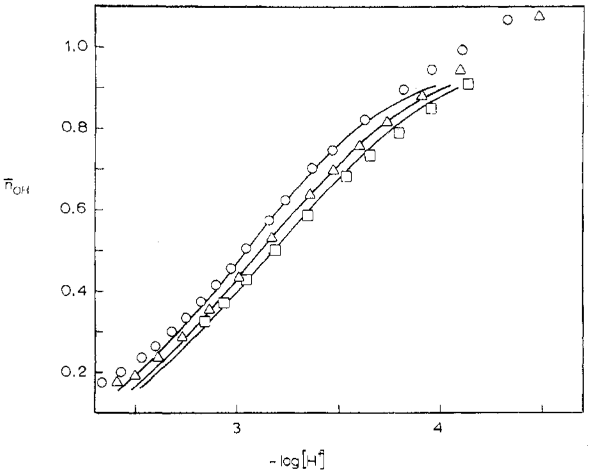

Fig. 1.—Average number of OH^- bound per dimethyltin(IV), $\bar{n}_{OH}$, as a function of $-\log [H^+]$; B = ○ 10 mM, △ 5 mM, and □ 2.5 mM. Curves calculated for $\log {}^*\beta_{11} = -3.2$, $\log {}^*\beta_{22} = -4.6$.

able that the ligand form quite stable complexes and that it be the conjugate base of as strong an acid as possible, so that the ligand can compete favorably with the hydroxide ion in aqueous solution.

Three ligands were selected for this study: 1,10-phenanthroline and the acetylacetonate and picolinate anions. Phenanthroline contains only nitrogen donor atoms, and because of the availability of vacant antibonding π-orbitals it might be expected to form stable complexes with $(CH_3)_2Sn^{+2}$ if d_π–p_π bonding is important. In the absence of π-bonding, phenanthroline generally forms complexes of stability comparable to ethylenediamine. For this study, it also possesses another advantage over ethylenediamine in that the conjugate acid is much stronger. The second ligand, acetylacetonate, with only oxygen donor atoms, was chosen since it tends to form particularly stable complexes with the Leden–Chatt "A" type ions.[8,9] The third ligand, picolinate, was selected to provide an example of a ligand with both nitrogen and oxygen donor atoms. In addition, the conjugate acid is much stronger than acetylacetone.

Because of the low solubility of the conjugate acid of phenanthroline in a perchlorate medium, it was necessary to work in a nitrate medium. Since most of the earlier work with these ligands has been carried out with 0.1 M NO_3^-, this ionic medium was chosen. A re-evaluation of the hydrolysis constants also was made, for the earlier studies of the hydrolysis were for the 3 M ClO_4^- medium.[12]

Experimental

Preparation of Solutions.—The general procedure for the preparation and standardization of the dimethyltin(IV) solutions has been described earlier.[12] In this case $(CH_3)_2SnO$ was dissolved in dilute nitric acid. Nitric acid solutions were standardized against Na_2CO_3, NaOH solutions against potassium acid phthalate and nitric acid, and $NaHCO_3$ solutions *vs.* nitric acid. All solutions were adjusted so that $[NO_3^-] = 0.1$ M by adding KNO_3. The phenanthroline was Eastman and G. F. Smith reagent, and the acetylacetone was Eastman reagent grade. Eastman picolinic acid was purified by sublimation and recrystallized from benzene.

Apparatus and Procedure.—The electrochemical cell used to determine the equilibrium hydrogen ion concentration, Ag/AgCl/10 mM NaCl, 90 mM KNO_3//100 mM KNO_3// solution/glass electrode, was essentially the same as that described earlier.[12] The glass electrode was a Radiometer G-202A. The cell potentials were read to 0.1 mv. using a Radiometer PHM-4 pH meter. The cell was immersed in a water thermostat maintained at 25 ± 0.1°, and all of the apparatus was contained in a room thermostated at 25 ± 2°.

The cell was calibrated as an H^+ concentration probe by titrating $NaHCO_3$ and $NaC_2H_3O_2$ with HNO_3 in the medium with $NO_3^- = 0.1$ M. A potassium hydrogen phthalate solution, 0.05 M, was used as a standard to check the glass electrode before and after a run. If the cell potential in millivolts is written as $E = E^0 + 59.15 \log [H^+] + E_j$, it usually is found that the correction term E_j can be represented as a linear function of the hydrogen ion concentration, $E_j = k[H^+]$. The absolute magnitude of k increases as the concentration of the supporting electrolyte is reduced. In this case with the 0.1 M NO_3^- medium, it was necessary to fit E_j with a least squares procedure to a function quadratic in $[H^+]$, $E_j = -0.421$ mv. mM^{-1} $[H^+] + 0.00130$ mv. mM^{-2} $[H^+]^2$.

Computational Procedure and Results

Hydrolytic Equilibria in 0.1 M Nitrate Medium.—Earlier studies in a 3 M perchlorate medium[12] have shown that the data for $0 < \bar{n}_{OH} \leq 0.7$ can be fitted using two constants for the formation of $(CH_3)_2SnOH^+$ (11) and the dimer $((CH_3)_2Sn)_2(OH)_2^{+2}$ (22). Here $\bar{n}_{OH}$ is the average number of hydroxo groups bound per dimethyltin(IV). If the total dimethyltin(IV) concentration is no greater than 10 mM, this corresponds to pH values up to *ca.* 3.6. The primary data, $\bar{n}_{OH}(\log [H^+])_B$, where B is the total dimethyltin(IV) concentration, obtained for the nitrate medium were transformed to $\log B(\log [H^+])_{\bar{n}}$. The values of B were 10, 5, and 2.5 mM (duplicates). These data were fitted with the normalized projection map calculated for the (11) and (22) complexes,[12] and a good fit was obtained with the following equilibrium constants

$$(CH_3)_2Sn^{+2} + H_2O = (CH_3)_2SnOH^+ + H^+; \quad \log {}^*\beta_{11} = -3.2 \pm 0.2$$

$$2(CH_3)_2Sn^{+2} + 2H_2O = ((CH_3)_2Sn)_2(OH)_2^{+2} + 2H^+; \quad \log {}^*\beta_{22} = -4.6 \pm 0.3$$

The errors are estimated from the fit to the projection map; the fit is shown in Fig. 1. The comparable values for the 3 M ClO_4^- medium were $\log {}^*\beta_{11} = 3.45 \pm 0.1$ and $\log {}^*\beta_{22} = -4.74 \pm 0.2$. The uncertainty in the constants for the 0.1 M NO_3^- medium is greater than that for the 3 M ClO_4^- medium, and no appreciable medium effect was observed. In part, this uncertainty is a result of having to keep $B \leq 10$ mM so that changes in the ionic medium would not become excessive. Even with this restriction, a rather large fraction of the K^+ of the medium had been replaced with H^+ when $\bar{n}_{OH} < 0.2$. In addition the correction term for the cell potentials, E_j, is quite large in the dilute ionic media, and this introduces an additional uncertainty in the measurements at high hydrogen ion concentrations.

As a check on these values of the constants, a 200-ml.

TABLE I

PHENANTHROLINE COMPLEXING OF THE DIMETHYLTIN(IV) ION[a]

B = 2.51 mM; $[\text{phen}]_{\text{total}}$ = 5.00 mM

C_H, mM	h, mM	$[(CH_3)_2Sn^{+2}]$, mM	[phen], mM	$[(CH_3)_2Sn(phen)^{+2}]$, mM	[phenH], mM	$[(CH_3)_2SnOH^+]^2$, mM	$[((CH_3)_2Sn)_2(OH)_2^{+2}]$, m$M$	log K_1, M
17.403	12.650	2.253	0.00441	0.149	4.851	0.100	0.002	4.18
15.639	10.954	2.194	.00504	.196	4.803	.113	.003	4.28
13.941	9.448	2.003	.00561	.387	4.611	.119	.003	4.54
12.305	7.838	1.978	.00676	.387	4.160	.142	.004	4.46
10.727	6.303	1.936	.00840	.392	4.604	.173	.006	4.38
9.205	4.837	1.883	.0109	.396	4.597	.219	.010	4.29
7.735	3.461	1.793	.0152	.406	4.583	.291	.018	4.17
7.019	2.794	1.748	.0189	.382	4.603	.352	.026	4.06
6.315	2.187	1.655	.0241	.389	4.591	.425	.038	3.99
5.623	1.659	1.498	.0314	.447	4.526	.508	.054	3.98
4.942	1.201	1.287	.0423	.543	4.419	.602	.076	4.00
4.273	0.798	1.041	.0622	.621	4.321	.733	.113	3.98
3.942	.632	0.891	.0770	.693	4.234	.792	.132	4.00
3.614	.483	.733	.0984	.771	4.135	.852	.152	4.03
3.289	.359	.561	.127	.907	3.970	.878	.162	4.10

[a] $^*\beta_{11} = 5.62 \times 10^{-4}\ M$; $^*\beta_{22} = 3.31 \times 10^{-5}\ M^2$; $K_{\text{HL}} = 1.15 \times 10^{-5}\ M$.

sample of 5 mM $(CH_3)_2Sn^{+2}$ solution was titrated with base. The total dimethyltin(IV) concentration was not held constant. A trial value for $^*\beta_{11}$ was obtained assuming that $(CH_3)_2SnOH^+$ was the only complex formed. This value increased with pH, and the value 6.63×10^{-14} was selected from the calculations at relatively high values of $[H^+]$ where the monomer should tend to predominate. The mole balance equations for the system are

$$B = b + bh^{-1*}\beta_{11} + 2b^2h^{-2*}\beta_{22} \qquad (1)$$

$$H = h - bh^{-1*}\beta_{11} - 2b^2h^{-2*}\beta_{22} \qquad (2)$$

where B is the total $[(CH_3)_2Sn^{+2}]$, b is the equilibrium $[(CH_3)_2Sn^{+2}]$, H is the analytical $[H^+]$ assuming no complex formation, and $h = [H^+]$. Combining (1) and (2)

$$B + H - h = b \qquad (3)$$

Thus the free $[(CH_3)_2Sn^{+2}]$ is determined from the primary data. With the trial value of $^*\beta_{11}$, (1) is solved for $^*\beta_{22}$, and the following values were obtained on iteration: $10^{4*}\beta_{11}$ = 6.63, 6.60, 6.57, 6.54; $10^{5*}\beta_{22}$ = 2.06, 2.13, 2.19. The last values correspond to log $^*\beta_{11} = -3.18$ and log $^*\beta_{22} = -4.66$, in good agreement with the graphically determined constants.

Phenanthroline Complexes.—Since 157 data items were collected in the study of the three ligands, these have been deposited with the American Documentation Institute.[14] The acid dissociation constant of the phenanthrolinium ion was determined by titration of phenanthroline solutions with HNO_3 in the nitrate medium. A value log $K_{\text{Hphen}} = -4.94$ was obtained, which is in good agreement with the literature values for 0.1 M KNO_3 and 0.4 M $NaNO_3$ media, -4.92[15] and -4.96,[16] respectively.

If it is assumed that mixed hydroxophenanthroline complexes are absent, the following equations apply; L = the ligand, phenanthroline, and charges are omitted in the complexes.

$$B = b + bh^{-1*}\beta_{11} + 2b^2h^{-2*}\beta_{22} + [(CH_3)_2SnL] \qquad (4)$$

$$[L]_{\text{total}} = [L] + K_{\text{HL}}^{-1}[L]h + [(CH_3)_2SnL] \qquad (5)$$

$$C_H = H + [L]_{\text{total}} = h + K_{\text{HL}}^{-1}[L]h - bh^{-1*}\beta_{11} - 2b^2h^{-2*}\beta_{22} \qquad (6)$$

K_{HL} is the dissociation constant for the conjugate acid of the ligand L. Adding (4) and (6) and subtracting (5)

$$B + C_H - [L]_{\text{total}} - h = b - [L] = B + H - h \qquad (7)$$

B and $[L]_{\text{total}}$ were held constant in all measurements. Values of [L] = [phen] and b were obtained by an iterative procedure. First it was assumed that [phen] was negligible and (7) was solved for the equilibrium $(CH_3)_2Sn^{+2}$ concentration, b. This value was then inserted into (6) together with the experimental hydrogen ion concentration, and a first approximation to [phen] was obtained. The procedure was repeated until convergence was obtained.

The results of a typical run are given in Table I. The quantity $\bar{n}_{\text{phen}} = [(CH_3)_2Sn(\text{phen})^{+2}]/b + [(CH_3)_2Sn(\text{phen})^{+2}]$ also was calculated where phenanthroline complexing was measurable after the data were corrected for hydrolysis. The data $\bar{n}_{\text{phen}}(\log [\text{phen}])_B$ are illustrated in Fig. 2. The values of log K_1 obtained for each run are given in Table II. All of the data illustrated in Fig. 2 were given equal weights and were used in the calculations; the errors are the standard errors. The $\bar{n}_{\text{phen}}(\log [\text{phen}])_B$ data also were fitted with the normalized curve[17] calculated for a single 1:1 complex. The best fit was obtained with log K_1 = 4.02, and this is illustrated in Fig. 2. The graphical procedure gives a slightly smaller value of K_1, for it weights the points at high $\bar{n}_{\text{phen}}$ values heavily.

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[14] Material supplementary to this article has been deposited as Document Number 7350 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[15] K. Yamasaki and M. Yasuda, *J. Am. Chem. Soc.*, **78**, 1324 (1956).

[16] R. T. Pflaum and W. W. Brandt, *ibid.*, **76**, 6215 (1954).

[17] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 87.

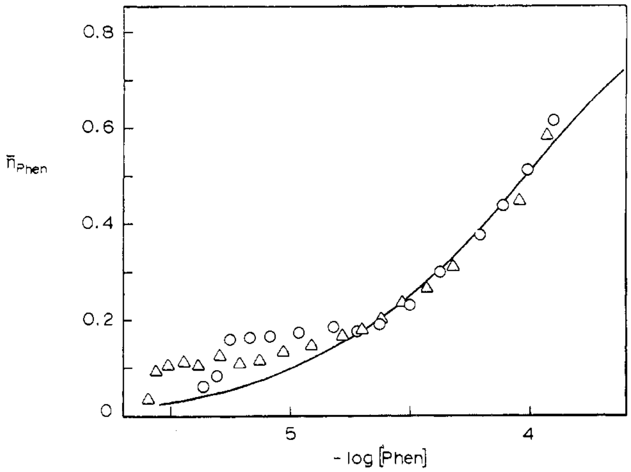

Fig. 2.—Average number of phenanthroline ligands bound per dimethyltin(IV), $\bar{n}_{phen}$, as a function of log [phen]; the B and $[phen]_{total}$ values are: O 2.51 mM, 5.02 mM; Δ 5.02 mM, 5.02 mM. Curve calculated for $\log K_1 = 4.0_2$.

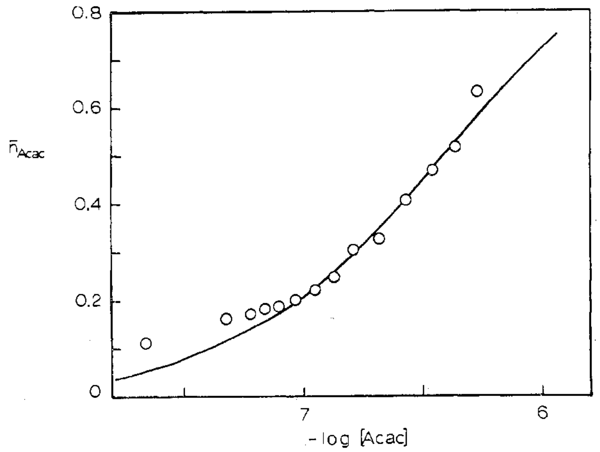

Fig. 3.—Average number of acetylacetonato ligands bound per dimethyltin(IV), $\bar{n}_{acac}$, as a function of log [acac]; $[acac]_{total}$ = 65.8 mM, B = 2.52 mM. Curve calculated for $\log K_1 = 6.4_2$.

Since these points are more accurately determined, the graphical procedure probably gives the better value.

Acetylacetonato Complexes.—It soon became apparent that the stability of the acetylacetonato complex was less than had been anticipated on the basis of the strong tin–oxygen bonds in $(CH_3)_2Sn(OH_2)_2{}^{+2}$ and the hydroxo complexes. This necessitated working at rather high total ligand concentrations.

The same equations given for the phenanthroline system apply here. The acid dissociation constant of Hacac was determined for the 0.1 M NO_3^- medium by potentiometric measurements to be $\log K_{Hacac} = -8.75$. Izatt, *et al.*, gave the value -8.95 at 30° and extrapolated to infinite dilution.[18,19] Since the measurements were made at rather high hydrogen ion concentrations, the equilibrium concentration of acetylacetonate, *i.e.*, [L], was small compared to the other terms in eq. 7. The free $[(CH_3)_2Sn^{+2}]$ was calculated and inserted into eq. (6) to calculate [L]. The procedure was repeated using the trial value of [L], and convergence was obtained after two cycles. The values of the constants obtained are given in Table II. The data $\bar{n}_{acac}(\log\ [acac])_B$ for the run with 65.8 mM $[acac]_{total}$, B = 2.25 mM where fairly large $\bar{n}_{acac}$ values were attained are illustrated in Fig. 3. The solid curve is calculated for $\log K_1 = 6.4_2$, the value obtained by the curve fitting procedure. Even though the acetylacetonato complex is considerably more stable than the phenanthroline complex, accurate values of K_1 could not be obtained. Since acetylacetone is such a weak acid, it was impossible to avoid appreciable hydroxo complex formation. The high total ligand concentration employed to reduce hydroxo complex formation made it difficult to calculate the concentration of bound acetylacetone, and the constants obtained tended to decrease as the solution pH increased.

TABLE II

LOG K_1 VALUES FOR THE FORMATION OF $(CH_3)_2SnL$ AT 25°

B, mM	$[L]_{total}$, mM	No. of detns.	Av. value	Est. std. error
		L = Phenanthroline		
2.51	5.00	15	4.2	0.2
5.02	5.02	19	4.2	.2
		L = Acetylacetonate		
10.01	51.15	28	6.5	0.3
2.52	65.8	24	6.8	.5
2.52	65.8	15	6.5	.3
		L = Picolinate		
4.00	10.05	27	5.0	0.1
4.00	7.04	29	5.1	.2

It seems very unlikely that complexes containing more than one acetylacetonato group are formed in finite concentrations in dilute aqueous solutions. Unlike $(CH_3)_2Si^{+2}$, which coördinates two acetylacetonato groups through only one oxygen each,[20] $(CH_3)_2Sn^{+2}$ coördinates both oxygen atoms. This is demonstrated clearly by the infrared spectra of bis-(acetylacetonato)-dimethyltin(IV), which shows the presence of chelate rings.[21] The reluctance of $(CH_3)_2Sn^{+2}$ to attain a coördination number of greater than two again was demonstrated by the following experiment. Titrations were carried out for solutions with the following $[acac]_{total}$ and B values: 10.25 mM, 5.02 mM; 10.25 mM, 0 mM; 0 mM, 5.02 mM. As in all of the measurements, these values were held constant during the titration. The titration curves for the two experiments with B = 5.02 mM, $[acac]_{total}$ = 10.25 and 0 mM were very similar up to pH ≃ 7, and this reflects mainly the formation of the hydroxo complexes.[12] At pH values greater than 7, the titration curves for the experiments with B = 5.02 and 0 mM, $[acac]_{total}$ = 10.25 mM were identical within the experimental error when the two equivalents of base used to form $(CH_3)_2Sn(OH)_2$ were subtracted from the total quantity added, and these data reflect the neutralization of

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[18] R. M. Izatt, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **59**, 80 (1955).

[19] R. M. Izatt, C. G. Haas, B. P. Block, and W. C. Fernelius, *ibid.*, **58**, 1133 (1954).

[20] R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

[21] M. M. McGrady and R. S. Tobias, unpublished results.

Hacac. Earlier studies have shown that $(CH_3)_2Sn(OH)_2$ is the only hydroxo complex present in appreciable concentrations in the range pH 7 to 9.[12] These data therefore indicate that there is no appreciable tendency for the reaction $(CH_3)_2Sn(OH)_2 + \text{acac}^- = (CH_3)_2Sn(OH)_2\text{acac}^-$ to occur.

Picolinato Complexes.—Again assuming that only a monopicolinato complex is formed, the equations for the mole balance of picolinate and the proton condition become

$$[\mathrm{L}]_{\mathrm{total}} = K_{\mathrm{H_2L}}{}^{-1}K_{\mathrm{HL}}{}^{-1}h^2[\mathrm{L}] + K_{\mathrm{HL}}{}^{-1}h[\mathrm{L}] + [\mathrm{L}] + [(\mathrm{CH_3})_2\mathrm{SnL}] \quad (8)$$

$$C_{\mathrm{H}} = h + 2K_{\mathrm{H_2L}}{}^{-1}K_{\mathrm{HL}}{}^{-1}h^2[\mathrm{L}] + K_{\mathrm{HL}}{}^{-1}h[\mathrm{L}] - bh^{-1}{}^*\beta_{11} - 2b^2h^{-2}{}^*\beta_{22} \quad (9)$$

Taking (4) + (9) − (8)

$$B - [\mathrm{L}]_{\mathrm{total}} + C_{\mathrm{H}} - h = b + K_{\mathrm{H_2L}}{}^{-1}K_{\mathrm{HL}}{}^{-1}h^2[\mathrm{L}] - [\mathrm{L}] = B + H - h \quad (10)$$

An iterative procedure was used once more to calculate b and [L]. The value of the first dissociation constant of $\mathrm{picH_2}^+$ determined by Green and Tong[22] was used, and the dissociation constant of picH was determined by potentiometric measurements to be $\log K_{\mathrm{HL}} = -5.34$ for the nitrate medium. The calculated values of the complexing constants are given in Table II. The data $\bar{n}_{\mathrm{pic}}(\log\ [\mathrm{pic}])_B$ are given in Fig. 4, and the solid curve is calculated for $\log K_1 = 5.0_2$, the value obtained by curve fitting.

Discussion

The measurements of complex formation at different total dimethyltin(IV) concentrations gave the same values for the stability constants within the experimental error, so there is no indication of polynuclear complex formation with these ligands as bridging groups. These experiments have confirmed the earlier observations from the study of the hydrolytic equilibria of $(CH_3)_2Sn^{+2}$ that this ion tends to bind two water molecules very strongly.

The stability constants for some phenanthroline complexes of divalent metal ions are given in Table III.

The small value for the stability constant of the $(CH_3)_2Sn^{+2}$–phenanthroline complex makes it seem unlikely that appreciable d_π–p_π back bonding occurs in these complexes. The results are also in accord with the recent observation of Alleston and Davies[6] that although the adducts $R_2SnX_2\cdot$phen and $R_2SnX\cdot$dipy are easily prepared and stable, the phenanthroline or dipyridyl is quantitatively displaced upon reaction with a mercury(II) or iron(II) salt. These results also indicate that even the stable adducts formed with α,α′-dipyridyl and 1,10-phenanthroline[6] should be susceptible to hydrolysis.

TABLE III

COMPARISON OF LOG K_1 VALUES FOR FORMATION OF THE FIRST PHENANTHROLINE COMPLEX OF DIVALENT METAL IONS AT 25°

	log K_1	Medium	Author
Copper(II)	6.30	0.4 M $NaNO_3$	Pflaum and Brandt[16]
Zinc(II)	6.43	$\mu = 0.1$	Kolthoff, *et al.*[23]
Cadmium(II)	6.4	0.1 M KNO_3	Douglas, *et al.*[24]
$(CH_3)_2Sn(IV)$	4.2	0.1 M NO_3^-	This work

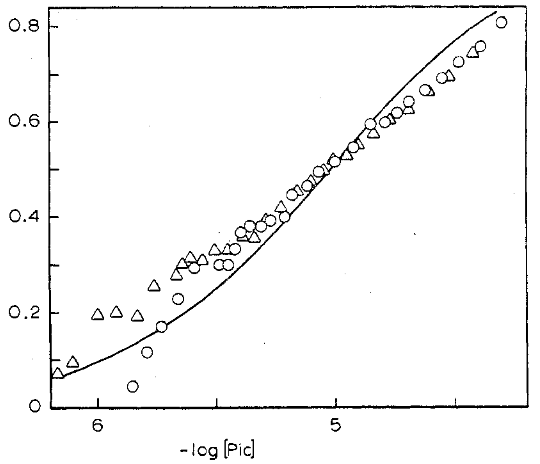

Fig. 4.—Average number of picolinato ligands bound per dimethyltin(IV), $\bar{n}_{\mathrm{pic}}$, as a function of log [pic]; $[\mathrm{pic}]_{\mathrm{total}}$ = ○ 10.05 mM, △ 7.04 mM, B = 4.00 mM. Curve calculated for $\log K_1 = 5.0_2$.

The oxygen donor acetylacetonate was comparatively more successful in displacing coördinated water molecules in the aquo-dimethyltin(IV) ion. The stability constants for some acetylacetonato complexes of divalent metal ions are given in Table IV.

TABLE IV

COMPARISON OF LOG K_1 VALUES FOR FORMATION OF THE FIRST ACETYLACETONATO COMPLEX OF DIVALENT METAL IONS

	log K_1	Medium	Temp., °C.	Author
Beryllium(II)	7.8	→ 0	30	Izatt, *et al.*[18,19]
Zinc(II)	4.98	→ 0	30	Izatt, *et al.*[18,19]
Cadmium(II)	3.83	→ 0	30	Izatt, *et al.*[18,19]
Uranyl	7.74	→ 0	30	Izatt, *et al.*[18,19]
$(CH_3)_2Sn(IV)$	6.6	0.1 M NO_3^-	25	This work

It is seen that the behavior of $(CH_3)_2Sn^{+2}$ is rather like that of the typical "A" type ions Be^{+2} and UO_2^{+2}. In general these ions form quite stable complexes with oxygen donors. Although $(CH_3)_2Sn^{+2}$ exhibits a considerably stronger effect on coördinated water molecules than either UO_2^{+2} or Be^{+2} as shown by the hydrolysis constants, it forms a weaker acetylacetonato complex than either of them, contrary to what one would expect. This may be the result of strain in the chelate ring system if tin is hybridized essentially sp^3. One conclusion drawn from the study[12] of the hydroxo complexes of $(CH_3)_2Sn^{+2}$ was that two strong bonds were formed to water molecules. These studies also indicate that these water molecules are quite resistant to substitution by ligands containing either nitrogen or oxygen donor atoms.

The stability constants of some picolinato complexes of divalent metal ions are given in Table V. The

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(22) R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

(23) I. M. Kolthoff, D. L. Leussing, and T. S. Lee, *ibid.*, **73**, 390 (1951).

(24) B. E. Douglas, H. A. Laitinen, and J. C. Bailar, Jr., *ibid.*, **72**, 2484 (1950).

TABLE V

COMPARISON OF LOG K_1 VALUES FOR FORMATION OF THE FIRST PICOLINATO COMPLEX OF DIVALENT METAL IONS AT 25°

	log K_1	Medium	Author
Copper(II)	8.6	0.1 M NO_3^-	Suzuki, *et al.*[25]
Zinc(II)	5.12	0.1 M NO_3^-	Suzuki, *et al.*[25]
Cadmium(II)	4.36	0.1 M NO_3^-	Suzuki, *et al.*[25]
Lead(II)	4.82	0.1 M NO_3^-	Suzuki, *et al.*[25]
$(CH_3)_2Sn(IV)$	5.1	0.1 M NO_3^-	This work

picolinato complex is more stable than the phenanthroline complex because of the affinity of the dimethyltin-(IV) ion for oxygen donors. The stability of the picolinato complex is not appreciably different from that of the lead(II) complex and probably is similar to that of the tin(II) complex. This is in accord with earlier observations that the dimethyltin(IV) and tin(II) ions exhibit similar chemical behavior.[12,26]

The properties of the $(CH_3)_2Sn^{+2}$ ion appear to be quite different from those of the $(CH_3)Hg^+$ ion, for the latter forms very stable complexes with nitrogen donors.[10] It is perhaps not surprising that there is no indication of back bonding in the phenanthroline complex of $(CH_3)_2Sn^{+2}$, since the dimethyltin(IV) ion has a net charge of +2. The d orbital contraction caused by this charge also is abetted by the rather high effective nuclear charge acting on the 4d orbitals. On the other hand, these are just the characteristics which confer a large polarizing power on an ion, and it seems likely that it is this property which leads to stable complexes with sulfur donors. This subject has been reviewed by Parry and Keller,[27] and recently Williams[28] has discussed the stability of complexes of the alkyltin(IV) ions and sulfur donors in terms of these concepts.

[25] K. Suzuki, M. Yasuda, and K. Yamasaki, *J. Phys. Chem.*, **61**, 229 (1957).

[26] E. G. Rochow, D. Seyferth, and A. C. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 3099 (1953).

[27] R. W. Parry and R. N. Keller, "Chemistry of the Coördination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Co., New York, N. Y., 1956, Chapter 3.

[28] R. J. P. Williams, *Proc. Chem. Soc.*, 20 (1960).

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Chemistry of Ethylenimines. X. Reactions with Phosphorus Nitrilochloride Trimer[1]

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The stereochemistry of two aziridine derivatives of $(PNCl_2)_3$ has been determined by n.m.r. Geminal chlorines in the trimer are replaced by two and four ethylenimino groups, respectively, following the behavior of a weak nucleophile like *p*-toluidine. This behavior is in contrast to that of the more closely related dimethylamine, which replaces chlorine on successive phosphorus atoms. The stereochemistry of other derivatives is correlated with the two established by n.m.r.

The stereochemistry of derivatives of the trimer of phosphonitrilic chloride, $(PNCl_2)_3$, was suggested for phenyl derivatives obtained by Friedel-Crafts reactions in 1942[2] and for aryl amino derivatives in 1948.[3] These substitutions were established as being for geminal chlorines in the phenylation experiments and Bode suggested the same structure for the aryl amino compounds. Non-geminal substitution has been confirmed for reactions of the trimer with ammonia, methylamine, and dimethylamine by phosphorus nuclear magnetic resonance spectra[4] and by proton n.m.r. in the case of the latter reagent.[5]

The present work establishes the structure of the di- and tetraaziridinyl derivatives, II and IV, by n.m.r. spectra on the P^{31} nucleus by the argument that follows.

It would be expected that the trimer, $(PNCl_2)_3$, and the hexaaziridinyl derivative, VI, would exhibit single peaks in the n.m.r. spectra since they contain a single type of phosphorus atom. The chemical shift of the $(PNCl_2)_3$ peak, relative to orthophosphoric acid, the standard, was measured as 19 ± 1 p.p.m., exactly the figure given by Becke-Goehring[4] for this compound.

Since phosphorus bonded to nitrogen exhibits a greater chemical shift than phosphorus bonded to chlorine,[4] one would predict that the relative positions of peaks in the n.m.r. spectra would be about the same for geminal substitution of two aziridine groups as for non-geminal substitution (Fig. 2). However, the relative intensities of the peaks would be reversed due to the difference in environment of the P atom in the two cases. In geminal substitution, there are one $\equiv PN_2$ and two $\equiv PCl_2$ groups (ratio 0.5); but two $\equiv PNCl$ and one $\equiv PCl_2$ groups (ratio 2.0) for non-geminal substitution. Experimentally the ratios of areas under the peaks was about 0.6–0.9 for the diaziridinyl derivative, suggesting geminal substitution.

[1] The work was supported by Public Health Service Grant CY-3092.

[2] H. Bode and H. Bach, *Chem. Ber.*, **75B**, 215 (1942); R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960).

[3] H. Bode, *Angew. Chem.*, **60**, 67 (1948); H. Bode, K. Bütow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).

[4] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959); M. Becke-Goehring and K. John, *Angew Chem.*, **70**, 657 (1958).

[5] S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961), reporting the work of R. F. M. White.