above complexes in the order given. Actually, the activation energies are the same within the experimental errors in aquation of $IrCl_6^{-3}$ ($E_a = 30.4 \pm 2.0$ kcal., log $pZ = 17.5 \pm 1.8$ (sec.$^{-1}$)^2) and $Ir(OH_2)Cl_5^{-2}$ ($E_a = 29.4 \pm 0.6$ kcal., log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$)); presumably other factors are contributing significantly to the activation energies.

Apparently little research on aquation kinetics of other 5d MX^n and $M(OH_2)X^m$ complexes has been published. Martinez[17] studied the aquation of $IrCl_6^{-2}$ and its exchange with Cl^{*-}, but the results may have been affected by a possible catalytic path involving traces of $IrCl_6^{-3}$ formed in the reaction solutions[18]; her value of 1.01×10^{-6} sec.$^{-1}$ for the aquation rate constant at 50° may be only an upper limit, with $E_a = 20.2 \pm 0.9$ kcal. as a lower limit. The kinetics of aquation of $OsCl_6^{-2}$ in HNO_3 and in HCl media has been investigated[19]; in 0.00001–0.1 F H^+ ($\mu = 0.5$–1.32) at 79.53° the aquation rate constant is 3.5×10^{-6} sec.$^{-1}$, $E_a = 33.1 \pm 0.6$ kcal., and log $pZ = 15.1 \pm 0.4$ (sec.$^{-1}$). Thus, at 50° the aquation rate constants for $Ir(OH_2)Cl_5^{-2}$, $OsCl_6^{-2}$, and $IrCl_6^{-2}$ are in the ratio of *ca.* 1000:4:80; activation energies increase in the order d^5 $IrCl_6^{-2}$(?), d^6 $Ir(OH_2)Cl_5^{-2}$, d^4 $OsCl_6^{-2}$. Hydrolysis rates of $PtCl_6^{-2}$ and $PtBr_6^{-2}$ have been measured,[20,21] but meaningful rates and rate laws have not been established.

Additional kinetic studies on 5d complexes are desirable, both as an extension of our knowledge of transition metal complexes and to allow isolation of the important factors governing the rates of substitution reactions of such complexes.

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[17] M. R. Martinez, "Aquation and Radiochloride Exchange of Hexachloroiridate(IV) Ion," Ph.D. Dissertation, U.C.L.A., June 1958.

[18] The same catalytic path presumably would affect the interpretations made by E. Blasius, W. Preetz, and R. Schmitt, *J. Inorg. Nucl. Chem.*, **19**, 115 (1961), in their study of $IrCl_6^{*-2}$–Cl^- exchange rates. They also studied the $IrCl_6^{*-3}$–Cl^- exchange, but reported no rate law or rate constants and did not state the temperature of the system.

[19] R. R. Miano and C. S. Garner, *Inorg. Chem.*, in press.

[20] E. H. Archibald, *J. Chem. Soc.*, 1104 (1920).

[21] E. H. Archibald and W. A. Gale, *ibid.*, 2849 (1922).

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Raman Spectroscopic and E.m.f. Studies on Aqueous Solutions of the *trans*-Tetrahydroxidodimethylstannate(IV) Ion. The Four Acid Dissociation Constants of the Dimethyltin(IV) Aquo Ion[1]

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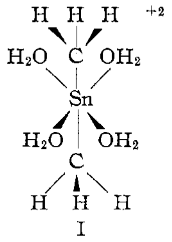
The proton-transfer equilibria of the dimethyltin(IV) ion have been studied in alkaline solutions at 25° by e.m.f. measurements. These data combined with those from earlier studies on acidic solutions give the following values for the four stepwise acid dissociation constants for the dimethyltin(IV) aquo ion in a medium with $[Cl^-] = 0.1\ M$: $\log K_1 = -3.25 \pm 0.01$, $\log K_2 = -5.27 \pm 0.02$, $\log K_3 = -11.5 \pm 0.1$, $\log K_4 = -11.7 \pm 0.1$. The Raman spectra of strongly alkaline solutions of the dimethyltin(IV) ion have been assigned on the basis of a *trans* octahedral structure for the tetrahydroxidodimethylstannate(IV) anion. Proton n.m.r. studies indicate that the tetrahydroxidodimethylstannate(IV) ion decomposes slowly in strong base giving primarily the hexahydroxostannate(IV) and a trimethyltin(IV) species. The solution behavior of the aquodimethyltin(IV) ion and the low Raman intensity of the tin–oxygen bond stretching vibrations indicate that this ion is very similar in its behavior to other simple multivalent cations. The assignment of tin–oxygen stretching frequencies in organotin compounds is also discussed.

Introduction

In 1953, Rochow and Seyferth studied the hydrolysis of dimethyltin dichloride and also observed that freshly precipitated dimethyltin oxide dissolved when about 2 moles of sodium hydroxide per mole of oxide had been added.[2] This led them to suggest the formation of $Na_2[(CH_3)_2Sn(OH)_4]$ as the soluble species in the alkaline solutions.

Recent Raman, infrared, and n.m.r. spectroscopic studies[3] have shown that aqueous solutions of dimethyltin(IV) compounds contain an aquo ion with a linear C–Sn–C skeleton, and the vibrational spectra were assigned on the basis of effective D_{3d} symmetry. In all probability the cation contains four water molecules in the first coordination sphere bound essentially by ion–dipole forces and has the structure I. By comparison with I, it would be expected that a tetrahydroxidodimethylstannate(IV) could be formed in strongly alkaline solutions by removal of one proton from each of the coordinated water molecules in the aquo ion.



I

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[1] Abstracted, in part, from the M.Sc. thesis of C. E. F., 1963; supported under grant GP-653 from the National Science Foundation.

[2] E. G. Rochow and D. Seyferth, *J. Am. Chem. Soc.*, **75**, 2877 (1953).

[3] M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, **3**, 1157 (1964).

The first two proton-transfer equilibria of I have been studied in some detail.[4,5] The solubility of the neutral molecule $(CH_3)_2Sn(OH)_2$ in water is low, so the second proton-transfer equilibrium can be investigated only in solutions where the dimethyltin(IV) concentration is about 10 m*M* or less. In the earlier studies, the upper limit of the pH range studied was set by the behavior of the glass electrodes used in the experiments. Above about pH 8.5, they began to respond appreciably to the sodium ions present in the 3 *M* $(Na)ClO_4$ ionic medium. Nevertheless, it was shown that the neutral dimethyltin dihydroxide was the only species present in solution at pH 8.

Considering the structure of the aquodimethyltin(IV) cation (I), one can, at least formally, treat it as a tetrabasic acid. It has been suggested[3] that the C–Sn–C angle in the monohydroxo complex is appreciably less than 180° because of the difference in the donor strength of hydroxo and aquo groups, and this also may be accompanied by a weakening of the tin–oxygen bonds to the water molecules. Some distortion from the regular octahedral arrangement of bonds in the different intermediate conjugate bases would be expected to accompany the decrease in symmetry. The neutral dimethyltin dihydroxide would not be expected to coordinate water molecules strongly, and it may have a structure similar to dimethylgermanium dihydroxide, which has been shown to be tetrahedral in aqueous solution by Raman studies.[6] Because of the low solubility of the dimethyltin dihydroxide and the fact that it exists only in aqueous solution, it is not possible to obtain any structural information on this compound.

It was decided to attempt to measure the final two expected proton-transfer equilibria of the aquodimethyltin(IV) ion and to determine the structure of the species present in strongly alkaline solutions using Raman and n.m.r. spectroscopy.

Experimental

Preparation of Reagents and Solutions.—Dimethyltin oxide was prepared by the hydrolysis of dimethyltin dichloride with ammonium hydroxide, and the precipitated oxide was stirred with conductivity water and filtered successively until no chloride ion could be detected. Stock solutions of the dimethyltin ion were prepared by dissolving the oxide in standard perchloric or hydrochloric acid.

Sodium perchlorate was prepared by neutralization of reagent sodium carbonate with perchloric acid, and recrystallization was continued once beyond that necessary to remove all traces of chloride ion. Sodium chloride and hydrochloric acid solutions were prepared from reagent grade chemicals. Sodium hydroxide solutions were prepared from a 50% solution of reagent sodium hydroxide by dilution with conductivity water saturated with nitrogen.

Potassium hexahydroxostannate(IV) obtained from Alfa Inorganics, Inc., was purified by precipitating it from a saturated aqueous solution with KOH and by washing with alcohol and ether.

Apparatus and Procedure for Solution Measurements.—Several different electrochemical cells were used in the measurements. Initially, attempts were made to use a special, large-envelope glass electrode, Beckman No. 78074V, low resistance, E2 glass. Neither this electrode nor other E2 glass electrodes came to stable potentials in strongly alkaline solutions even in simple acid–base titrations, and so a hydrogen electrode was used for the equilibrium studies.

The first measurements were carried out in a medium with 3 *N* $(Na)ClO_4$ as the supporting electrolyte. After difficulties were encountered during the use of the hydrogen electrode in the perchlorate medium, it was decided to study the equilibria in solutions with a 0.1 *M* (Na)Cl medium, since the stability of the chloro complexes has been found to be low.[7] The final cell employed in these studies was: $Pt(H_2)/\mathbf{M}$ m*M* $(CH_3)_2Sn(IV)$, **OH** m*M* (OH^-), $(100 - 2\mathbf{M})$ m*M* NaCl//100 m*M* NaCl//AgCl (satd.), 100 m*M* NaCl/AgCl/Ag. The cell design was similar to that used previously.[4] The titration vessel was maintained gas-tight by the use of ground glass joints and stoppers machined from Teflon rod. Hydrogen was purified by passing it through a Deoxo catalytic purifier, 6 *N* sulfuric acid, 6 *N* KOH, water, a second Deoxo cylinder, and finally through 0.1 *M* NaCl solution. Tygon tubing was used in all of the gas trains. The solutions were covered with an atmosphere of nitrogen. The nitrogen (99.99%) was passed through alkaline pyrogallol, KOH, and 0.1 *M* NaCl.

Cell potentials were measured to ±0.01 mv. by opposing the cell e.m.f. with a Leeds and Northrup K-3 potentiometer and connecting these in series with a Leeds and Northrup microvolt indicating amplifier, No. 9835-B. The microvolt amplifier served as a preamplifier for the Varian G-10 potentiometer recorder which was used to record the potentials. All measurements were carried out at 25 ± 0.1°. The cell potentials in mv. were described by the equation $E = E^\circ + 29.57 \log P_{H_2} + 59.15 \log [OH^-] + k[OH^-]$, where the term $k[OH^-]$ represents a correction for the liquid–liquid junction potential. Values for E° and k were determined by acid–base titrations in the ionic medium, and k was found to be -0.171 mv./m*M* for 0.1 *M* (Na)Cl. At the highest pH values, the potentials were somewhat erratic, and a fresh electrode was used for each experimental point.

Raman Spectra.—The Raman spectra were recorded photoelectrically with a Cary Model 81 spectrophotometer, and the general procedure for the measurements on solutions has been described earlier.[3] All spectra were recorded within a few hours after the preparation of a given solution.

Raman crystal spectra were determined on powdered samples using conical and straight cells[8] containing approximately 1 g. of sample.

Proton N.m.r. Spectra.—Proton resonance measurements were made with either a Varian DP-60 spectrometer at 56.4 Mc./sec. or with a Varian A-60 spectrometer. Coupling constants were determined with the side-band technique and are believed accurate to ±1 c.p.s. Because of the strongly alkaline nature of the solutions, an external standard was used for measurements of the chemical shifts. A capillary containing benzene was immersed in the sample. The chemical shifts are believed to be accurate to ±0.02 p.p.m.

Results

E.m.f. Measurements.—The equilibrium data are given in Figure 1 as $\bar{n}$, the average number of protons transferred or hydroxo groups bound per dimethyltin(IV), as a function of $\log [OH^-]$. The dimethyltin(IV) concentration had to be maintained at a low value to avoid precipitation at low hydroxide ion concentrations. This led to rather large errors in $\bar{n}$, and it was not possible to determine if small concentrations of polynuclear species were formed. Since the system was essentially mononuclear at these low concentrations in the acid range and entirely so in the neutral region, it

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

(5) R. S. Tobias and M. Yasuda, *Can. J. Chem.*, **42**, 781 (1964).

(6) R. S. Tobias and S. Hutcheson, unpublished work.

(7) H. N. Farrer, M. M. McGrady, and R. S. Tobias, unpublished work.

(8) M. M. McGrady and R. S. Tobias, unpublished work.

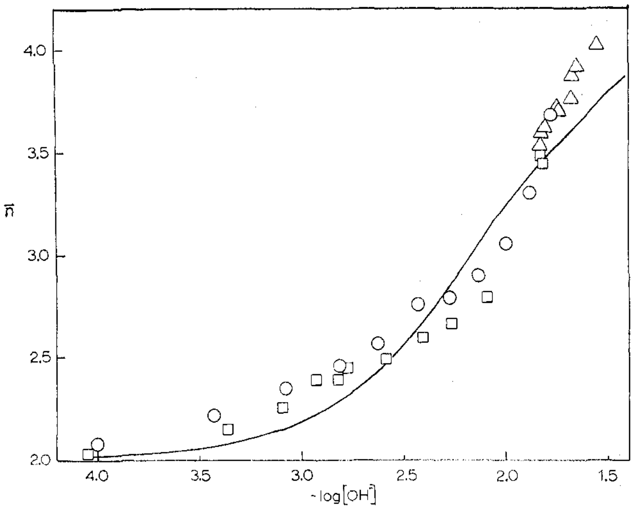

Figure 1.—Average number of protons transferred per $(CH_3)_2$-Sn(IV): △, 5.775 m*M*; □, 5.250 m*M*; ○, 2.313 m*M* $(CH_3)_2$-Sn(IV).

seems unlikely that appreciable concentrations of polymeric species exist in the alkaline range. If polycondensed species were present, the points in Figure 1 for the 5.250 m*M* solutions should lie above those for the 2.313 m*M* solutions.

The data were fitted using the least-squares refinement program GAUSS Z[9] and the University of Minnesota's CDC-1604 computer. All points were weighted equally. The trial values of the hydroxo complexing constants were obtained from the values of log $[OH^-]$ at $\bar{n} = 2.5$ and 3.5, and these were used as input to the computer program. The values of the cumulative hydroxo complexing constants and their standard errors calculated for complexing of $(CH_3)_2Sn(OH)_2$ are: log $\beta_1 = 2.2_7 \pm 0.11$ and log $\beta_2 = 4.35 \pm 0.06$. The few data obtained for the 3 *M* (Na)ClO$_4$ medium gave the value log $\beta_1 = 2.6$.

The hydroxo complexing constants were converted to acid dissociation constants using the value of the ion product of water in 0.11 *M* KCl, $pK_w = 13.78$. This value was obtained from the thermodynamic dissociation constant at 25° and the activity coefficient data of Harned and Mannweiler.[10] The calculated protolysis constants were combined with the values for the first two proton-transfer equilibria also determined for a 0.1 *M* chloride medium,[5] and Table I lists the four stepwise dissociation constants. The ratios of the stepwise constants K_n/K_{n+1} are also tabulated.

Proton Nuclear Magnetic Resonance.—Since erratic electrode behavior was experienced when $\bar{n}$ values of *ca.* 4 were reached, the stability of strongly alkaline solutions was studied using proton n.m.r. Solutions 0.6 *M* in $Na_2[(CH_3)_2Sn(OH)_4]$ and 1.8 *M* in NaOH were prepared by dissolving dimethyltin oxide in standard sodium hydroxide. The spectrum of freshly prepared solutions showed only the water proton plus a single methyl proton signal at δ 6.03 p.p.m. with respect to benzene indicating that no decomposition had occurred.

TABLE I

DISSOCIATION CONSTANTS OF THE TETRAAQUODIMETHYLTIN(IV) ION AT 25° IN A 0.1 *M* CHLORIDE MEDIUM

n	log stepwise constant, K_n	log ratio K_n/K_{n+1}
1	-3.25 ± 0.01^a	
		2.02 ± 0.02
2	-5.27 ± 0.02^a	
		6.2 ± 0.1
3	-11.5 ± 0.1	
		0.2 ± 0.1
4	-11.7 ± 0.1	

[a] Data from ref. 5.

The values of the tin–methyl proton coupling constants were: $J_{^{117}Sn-H} = 78.4$; $J_{^{119}Sn-H} = 82.7$ c.p.s. At the end of 24 hr., a weak additional signal appeared at 6.14 p.p.m. with respect to benzene. This peak became much more intense with time, and a new one also appeared at δ 6.40 p.p.m. The principal decomposition product was identified as a trimethyltin species by a comparison of the chemical shift and coupling constants with those of a solution of $(CH_3)_3SnOH$ in NaOH. At the end of 2.5 months, the integrated signals were in the ratio 1:2:0.5 for the signals at 6.03, 6.14, and 6.40 p.p.m., respectively. There was no evidence for any reduction to tin(II), so hexahydroxostannate(IV) ions must have been produced by the redistribution reaction.

Raman Spectra.—The spectrum of a solution *ca.* 0.6 *M* in $Na_2[(CH_3)_2Sn(OH)_4]$ and 1.8 *M* in NaOH is illustrated in Figure 2. Since the n.m.r. data indicated that

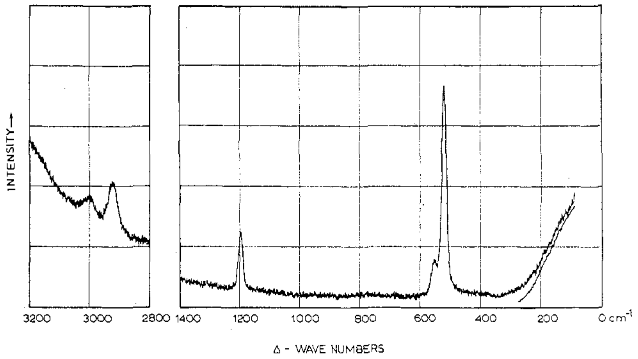

Figure 2.—Raman spectrum of $(CH_3)_2SnO$ dissolved in sodium hydroxide solution.

the tetrahydroxidodimethylstannate(IV) decomposed slowly, the spectra were run on the solutions immediately after preparation. The six Raman shifts are given in Table II together with the states of polarization and the integrated intensities. Frequencies are also given for the tetraaquodimethyltin(IV) cation as determined from measurements on nitrate solutions.[3]

To assist in the vibrational assignments, Raman spectra were measured for both crystals and solutions containing the hexahydroxostannate(IV) ion. Only a single sharp line was observed for 1 *M* KOH saturated with $K_2[Sn(OH)_6]$. This Raman shift was at 556 cm.$^{-1}$ and was found to be strongly polarized. In the crystal spectrum, a sharp line was observed at 546 cm.$^{-1}$ together with a very broad band from 350 to 500 cm.$^{-1}$.

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[9] R. S. Tobias and M. Yasuda, *Inorg. Chem.*, **2**, 1307 (1963).

[10] H. S. Harned and G. E. Mannweiler, *J. Am. Chem. Soc.*, **57**, 1873 (1935).

TABLE II

RAMAN SPECTRA OF $[(CH_3)_3Sn(OH)_4^{-2}]$

ν solution, cm.$^{-1}$[a]	$A\nu$[b]	ν $[(CH_3)_2Sn^{+2}](aq)$, cm.$^{-1}$
180[c]	...	180
523 p	1412	529
555 dp(?)	190	...
1200 p	322	1226
2924 p	530	2933
3000 dp	285	3020

[a] p, polarized; dp, depolarized. [b] Integrated intensity (cm.$^{-1}$ × % deflection). [c] Shoulder on Rayleigh line.

Discussion

The ratio of the first to the second dissociation constant is considerably smaller than the value log $(K_n/K_{n+1}) \simeq 4.9$[11] found for tetrahedral oxy acids. It is not surprising that charge effects are less efficiently transmitted in a large octahedral acid such as the tetraaquodimethyltin(IV) ion, which has rather polar metal–oxygen bonds compared to the tetrahedral oxy acids. Indeed, in the few examples available previously for the ratios of first and second dissociation constants of aquo acids,[12] there seemed to be almost no difference between the constants. Unfortunately, because of the tendency of the conjugate bases of simple aquo metal ions to polymerize *via* condensation reactions, few examples are available, and the errors associated with the second dissociation constants are usually quite large.

The neutral dimethyltin dihydroxide has a wide region of stability indicated by the large value of the ratio log $(K_2/K_3) = 6.2$. This large value is probably associated with the very unfavorable entropy change accompanying the dissociation of an uncharged acid[13] compared to a positively charged acid. The singly charged anion has a very short range of existence as is shown by the value log $(K_3/K_4) = 0.3$, and in strongly alkaline solutions the only species present is the doubly charged anion.

On the basis of the known structure of the aquo acid, the doubly charged anion would be expected to have the formula $[(CH_3)_2Sn(OH)_4^{-2}]$, although the e.m.f. measurements cannot distinguish between this and $[(CH_3)_2SnO_2^{-2}]$. Since the indications are that there is relatively little p_π–d_π bonding in tin compounds,[14] a hydroxo rather than an oxo complex would be expected. This is supported by the known structure of the ion $[Sn(OH)_6^{-2}]$,[15,16] which is isoelectronic with $[(CH_3)_2Sn(OH)_4^{-2}]$ in the sense that CH_3^- can be produced by transferring two protons from the oxygen nucleus to lone pairs on OH^-. By analogy with the aquo ion, the methyl groups would be expected to occupy *trans* positions, and this structure has also been observed in complexes of the dimethyltin ion with a variety of β-diketo ligands.[8]

For the purpose of assigning the Raman shifts, the tetrahydroxidodimethylstannate(IV) first will be considered as an octahedral XY_2Z_4 unit, and so the *effective* symmetry of the *trans* complex would be D_{4h} and that of the *cis* complex C_{2v}. Raman spectra would be expected to distinguish clearly between these two possibilities. The representation of the normal coordinates of the *trans* complex has the structure

$$\Gamma_{trans} = 2A_{1g} + 2A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3E_u$$

There are therefore five Raman active skeletal modes for the *trans* complex. In contrast the representation for the *cis* complex is

$$\Gamma_{cis} = 6A_1 + 2A_2 + 4B_1 + 3B_2$$

and all 15 normal modes are Raman active. The *cis* complex should exhibit a rather complex Raman spectrum at frequencies below about 700 cm.$^{-1}$, although much accidental degeneracy would be expected because of the heavy tin atom, and this should lead to some simplification.

Since the tin–oxygen bonds should be quite polar and this would lead to very small bond polarizabilities, it also seemed possible that the Raman intensities for vibrations involving predominantly changes in the tin–oxygen bonds might be too low to be detected. If this were true, the problem would be similar to that of the free aquo cation, for which the skeletal vibrations can be assigned in terms of a three-atom model XY_2 with $D_{\infty h}$ or C_{2v} symmetry for the *trans* and *cis* ions, respectively. For this case the normal coordinates would have the representations

$$\Gamma'_{trans} = A_{1g} + A_{2u} + E_u$$

$$\Gamma'_{cis} = 2A_1 + B_2$$

For the *trans* complex, only the A_{1g} symmetrical C–Sn–C stretch is Raman active, while all three skeletal modes of the *cis* complex would be Raman active. On the basis of this three-atom model, the *trans* complex would be expected to show one polarized line, while the *cis* complex would show one polarized and one depolarized line in the tin–carbon stretching region 500–600 cm.$^{-1}$.

The Raman spectrum for the solutions of dimethyltin dihydroxide in base proved to be exceedingly simple and shows only three lines aside from the antisymmetrical methyl stretch at 3000 cm.$^{-1}$, the symmetrical methyl stretch at 2924 cm.$^{-1}$, and the symmetrical methyl deformation at 1200 cm.$^{-1}$. By analogy with the dimethyltin aquo ion, it would be expected that modes involving mainly bending of the tin–carbon bonds would appear in the broad line below 200 cm.$^{-1}$. The very strong, polarized line at 523 cm.$^{-1}$ can also be assigned with certainty to the symmetrical tin–carbon stretch. The assignment of the 555 cm.$^{-1}$ line is less easy. Since the intensity was very low, polarization measurements were difficult and indicated that the line was only weakly polarized if at all. This could be assigned either to tin–oxygen vibrations on the basis of

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(11) J. E. Ricci, *J. Am. Chem. Soc.*, **70**, 109 (1948).

(12) L. G. Sillén, *Quart. Rev.* (London), **13**, 146 (1959).

(13) G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamics," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1961, pp. 305, 524.

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(15) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford, 1962, p. 556.

(16) R. L. Williams and R. J. Page, *J. Chem. Soc.*, 4143 (1957).

the *trans* XY_2Z_4 model or to the antisymmetrical tin–carbon stretch, species B_2, on the basis of the *cis* XY_2 model, although the antisymmetrical tin–carbon stretch would be expected at a somewhat higher frequency. This question was settled by an examination of the Raman spectrum of $K_2Sn(OH)_6$ solutions. Since relatively little coupling of the vibrations should occur through the heavy tin atom, the tin–oxygen stretching frequency should be transferable from this anion to the dimethyl species. The strongly polarized line found at 556 cm.$^{-1}$ could be assigned with certainty to the A_{1g} breathing mode, ν_1,[17] assuming effective cubic symmetry for $[Sn(OH)_6{}^{-2}]$. In the spectra of powdered $K_2Sn(OH)_6$, this tin–oxygen stretching frequency appeared at 546 cm.$^{-1}$. The other two Raman allowed transitions[16] for the $[Sn(OH)_6{}^{-2}]$ were not observed, and even the totally symmetrical stretch was broad and weak. The line at 555 cm.$^{-1}$ in the tetrahydroxidodimethylstannate(IV) is therefore assigned to tin–oxygen stretching, indicating that the complex has the *trans* octahedral configuration.

Symmetry motions of a *trans* XY_2Z_4 complex with D_{4h} symmetry are given in Figure 3. These may be compared with those given recently by Blyholder and Ford[18] for the analogous *cis* complex. On this basis, the line at 555 cm.$^{-1}$ is assigned to ν_1 and also to ν_5 in order to account for the apparent depolarized nature of this line. The strong line at 523 cm.$^{-1}$ is assigned to ν_2. All of the other Raman-active vibrations are bending modes. By analogy with $[Sn(OH)_6{}^{-2}]$ and $[(CH_3)_2Sn(OH_2)_4{}^{+2}]$, these would be expected to be very low in intensity or below 200 cm.$^{-1}$, where a broad line is observed.

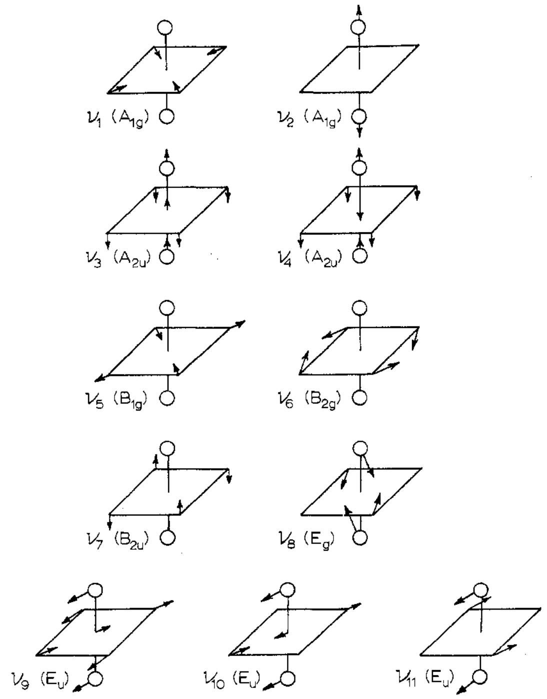

Figure 3.—Symmetry motions of a *trans* XY_2Z_4 molecule.

Recently there has been some discussion in the literature about the frequency of tin–oxygen vibrations. Poller,[19] using Gordy's rule for relating electronegativity, bond length, and stretching force constant, estimated 2.7 × 10^5 dynes/cm., which leads to a frequency of 570 cm.$^{-1}$. Kriegsmann and Kessler[20] assigned the line at 620 cm.$^{-1}$ in the Raman spectrum of the $[SnF_5OH^{-2}]$ ion to a vibration involving essentially Sn–O bond stretching. Kroenke and Kenney[21] have assigned an infrared band at 563 cm.$^{-1}$ in $PcSn(OH)_2$ (Pc = phthalocyanino, $C_{32}H_{16}N_8$) to the antisymmetrical O–Sn–O vibration. Kriegsmann, *et al.*,[22] assigned the tin–oxygen stretch in $(CH_3)_3SnOH$ to a band at 576 cm.$^{-1}$ in the infrared spectrum; the intensity of the transition in the Raman spectrum was so low it was not observed in the spectrum of the pure liquid. Because of the heavy tin atom, relatively little variation in frequency would be expected from one alkyl tin compound to another, and the tin–oxygen stretching frequency should generally appear in the range of 550–575 cm.$^{-1}$. Poller[19] originally reported tin–oxygen stretching frequencies for triphenyltin hydroxide at 912 and 895 cm.$^{-1}$ and for triethyltin hydroxide at 855 cm.$^{-1}$ from studies of infrared spectra. Okawara and Yasuda[23] have shown by means of the shift which occurs upon deuterium substitution that these bands are due to the Sn–O–H deformation.

A comparison of the Raman shifts of the *trans*-tetrahydroxidodimethylstannate(IV) anion to those of the *trans*-tetraaquodimethyltin(IV) cation shows that the hydroxo complexing leads to a general decrease in the vibrational frequencies. A similar effect has been observed with the dimethylthallium(III) cation[24] and dimethylthallium hydroxide, although the thallium–oxygen bond is so polar that no Raman lines attributable to Tl–O vibrations are observed.

The tin–methyl proton coupling constants are considerably smaller in the *trans*-tetrahydroxidodimethylstannate(IV) ion than in either the *trans*-tetraaquodimethyltin(IV) cation or the *trans*-bis(acetylacetonato)-dimethyltin(IV), $J_{^{117}\text{Sn–H}}$ = 102 and 95.0; $J_{^{119}\text{Sn–H}}$ = 106 and 99.3 c.p.s., respectively.[3] Assuming the Fermi contact term to be the only important one in the expression for the coupling constants and using the linear correlation between the tin–hydrogen spin–spin coupling constants suggested by Holmes and Kaesz,[25] the coupling constants for *trans*-tetrahydroxidodimethylstannate(IV), $J_{^{117}\text{Sn–H}}$ = 79 and $J_{^{119}\text{Sn–H}}$ = 83 c.p.s., indicate that there is about 38% s character in the tin orbitals directed to the methyl carbons compared to 49% in the aquo cation.[3] Whatever the precise amount of s character in the tin orbitals bonding the carbon

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[17] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p. 118.

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atoms may be, there appears to be an appreciable decrease in going from the aquo cation to the anion. This may result from an increase in the utilization of s character in the tin–oxygen bonds as these become more covalent in going from the aquo cation to the anion.

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Thermodynamics of Metal Cyanide Coordination. III. $\Delta G°$, $\Delta H°$, and $\Delta S°$ Values for Ferrocyanide and Ferricyanide Ion Formation in Aqueous Solution at 25°[1a]

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Values for $\Delta H°$ of -85.77 and -70.14 kcal./mole have been determined calorimetrically for the formation of ferrocyanide and ferricyanide ions, respectively, from their constituent ions in aqueous solution at 25°. Combination of these $\Delta H°$ values with literature $\Delta S°$ values gave $\Delta G°$ values of -48.23 and -59.50 kcal./mole for the formation of ferrocyanide and ferricyanide ions, respectively. Corresponding log β_6 values (valid at zero ionic strength) are 35.4 and 43.6.

Introduction

This paper is part of a study to determine the thermodynamic quantities, $\Delta G°$, $\Delta H°$, and $\Delta S°$, for the interaction of cyanide ion with selected metal ions.[2] As recently pointed out by Griffith,[3] reliable formation constants for cyanide complexes are virtually unknown. Equilibrium constants are difficult to measure by the usual procedures for the formation of many of these complexes because of their extremely stable nature, their slow kinetics, and the evolution of gaseous HCN in their acidic solutions.

Ferrocyanide and ferricyanide ions are typical of complexes whose formation constants are not amenable to direct measurement. Formation constant and $\Delta G°$ values for such complexes can be obtained from $\Delta H°$ and $\Delta S°$ data, however, provided these latter data can be experimentally determined. This approach has been used by Stephenson and Morrow,[4] who estimated log β_6 values of 24 and 31 for the formation of ferrocyanide and ferricyanide ions, respectively, from their respective constituent ions in aqueous solution. However, these values appear to be unusually low when compared with the formation constant of $Ni(CN)_4^{2-}$ (log $\beta_4 = 30.1$) determined recently in this laboratory.[5] Stephenson and Morrow[4] state that their β_6 values are uncertain due to the approximate $\Delta S°$ and $\Delta H°$ values used in their calculations. Since no accurate calorimetric $\Delta H°$ value for the formation of the ferricyanide ion was available to these workers, their estimated β_6 value for the formation of this species is particularly uncertain. Recently reported standard entropy values[6] ($S°_{H^+} = 0$) for the ferrocyanide and ferricyanide ions make possible better estimations of the $\Delta S°$ values for the formation of these complexes in aqueous solution by combination of these standard entropy values with available entropy values for Fe^{2+},[7] Fe^{3+},[8] and CN^-.[8]

Müller[9] measured the heat of formation of ferrocyanide ion by the reaction of CN^- with Fe^{2+}. Guzzetta and Hadley[10] report ΔH values for ferrocyanide and ferricyanide ion formation from the interaction of Fe^{2+} and solid ferric alum, respectively, with 1 F CN^- solutions. The ΔH values reported by Müller[9] and Guzzetta and Hadley[10] are not thermodynamically useful because of the high ionic strengths, μ, of the solutions used by these investigators. Also, in the latter study[10] no mention is made of corrections for the dilution of the cyanide ion solution by the metal ion solutions, the heat of dissolution of the ferric alum, and heat effects due to H_2O and HCN formation. Such corrections could be considerable, and the reported values are, therefore, uncertain.

In the present study, $\Delta H°$ values are reported for the formation of ferrocyanide and ferricyanide ions from their respective constituent ions in aqueous solution at 25°. These $\Delta H°$ values are combined with $\Delta S°$ values calculated from literature data[6–8] to give corresponding formation constant values.

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