$$R + HCN \rightleftharpoons Mo(CN)_8^{-4} \qquad (5)$$

$$R \longrightarrow \text{final blue product} \qquad (6)$$

The reverse of reaction 5 then accounts for the high quantum yield for photoinduced CN^- exchange. Since the aquo cyano complexes are weak acids, it is possible that at pH 9–10 the actual form of R is $Mo(CN)_7(OH)^{-4}$, and also that the observed pH dependence of reaction 5 is partly due to this acid–base equilibrium. We do conclude, however, that the transient red species is not decacoordinated and is probably a heptacyano complex.

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Solubility Studies on Substituted Ammonium Salts of Halide Complexes.
IV. Tristetramethylammonium Enneachlorodiantimonate(III)[1]

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Knowledge concerning halide complexes of antimony(III) has been extremely difficult to obtain because of the ease of hydrolysis, the irreversibility of antimony electrodes, and the fact that the complexes are weak. The ultraviolet absorption spectrum of antimony(III) is invariant from 6 to 12 M hydrochloric acid, indicating that a limiting coordination number with chloride ion is reached.[2] However, in more dilute acid the absorbance in the ultraviolet decreases generally without the appearance of new, distinctive bands for lower complexes and without the appearance of any crossing points. A limited polarographic study[3] indicated that the average ligand number was approximately four in solutions varying from 0.5 to 6.0 M hydrochloric acid. The present study is an attempt to ascertain the species of Sb(III) present in hydrochloric acid by means of a solubility study on a complex chloride of antimony(III).

Experimental

Preparation of Complex Salts. Tristetramethylammonium Enneachlorodiantimonate(III).—Antimony trichloride was dissolved in 3.0 to 4.0 M hydrochloric acid and treated with tetramethylammonium chloride in the same solvent. From 0.2 M solutions of the salts at 0° large hexagonal crystals were obtained in about 15% yield. The crystals were washed with 3 M hydrochloric acid and air dried in a desiccator over KOH. The salt may also be dried at 100° in air without decomposition. Larger yields may be obtained using more concentrated solutions.

Anal. Calcd. for $((CH_3)_4N)_3Sb_2Cl_9$: C, 18.35; H, 4.63; Sb, 31.00; Cl, 40.7. Found: C, 18.45; H, 4.25; Sb, 31.00; Cl, 40.33.

Tetraphenylarsonium Tetrachloroantimonate(III).—Tetraphenylarsonium ion gave much more insoluble precipitates of composition near that of $(C_6H_5)_4AsSbCl_4$ but the composition varied erratically with treatment and in subsequent solubility studies the saturated solutions never contained the same As:Sb ratio as the solid phase. It was thus necessary to use the tetramethylammonium salt, although its high solubility (0.05 to 0.07 M) made maintenance of constant ionic strength problematical, especially at high chloride ion concentration.

Analysis for antimony(III) in solution was made by titration with standard potassium bromate solution using methyl orange indicator. Analysis for chloride was made by potentiometric titration with standard silver nitrate solution. Analysis for carbon and hydrogen was performed by the Clark Microanalytical Laboratory, Urbana, Ill.

For solubility studies, solutions were saturated either by shaking an excess of salt with solvent in 50-ml. flasks in a thermostat at 25.0 ± 0.1° for 24–96 hr. or by using a Brønsted saturator,[4] one pass being sufficient for saturation. The concentration of antimony(III) was determined by titration with bromate. With 4 M sulfuric acid as the solvent the Sb:Cl mole ratio in solution was 2:9, indicating that the solid phase did not change composition during the study.

The solvent used was H_2SO_4 and HCl with $[H^+]$ maintained at 4.0 M. As in previous studies[5] H_2SO_4 is assumed to be a 1:1 electrolyte, and the ionic strength was essentially constant.

Results and Discussion

Analysis of data is based on the assumption of reactions 1 and 2 contributing to the solubility of the salt. A test was made for the presence of polynuclear

$$[(CH_3)_4N]_3Sb_2Cl_9 \rightleftharpoons 3(CH_3)_4N^+ + 2SbCl_4^- + Cl^- \qquad (1)$$

$$SbCl_4^- + (n - 4)Cl \rightleftharpoons SbCl_n^{3-n} \qquad (2)$$

complexes by substituting up to 0.15 M $(CH_3)_4NCl$ for HCl at 4.0 M Cl^-. The product $[(CH_3)_4N^+]^{3/2} \cdot [Sb(III)]$ was $7.24 \pm 0.30 \times 10^{-3}$ over a twofold variation in solubility (Table I). Its constancy indicates no significant concentration of polynuclear species.

TABLE I
TEST FOR POLYNUCLEAR COMPLEXES
$[HCl] + [(CH_3)_4NCl] = 4.0$

$[(CH_3)_4NCl]_0$, M	[Sb(III)], M	$[(CH_3)_4N^+]$, M	$10^3[Sb(III)] \cdot [(CH_3)_4N^+]^{3/2}$
0	0.1105	0.166	7.6
0.025	0.099	0.173	7.1
0.050	0.090	0.185	7.2
0.100	0.0725	0.209	6.9
0.150	0.0625	0.244	7.5

In the absence of polynuclear complexes the solubility data may be analyzed using the equations

$$S^{5/2}[Cl^-]^{1/2} = \frac{K_S{}^{1/2} \sum\limits_{\Delta}^{n} \beta_n [Cl^-]^{n-4}}{10.4\beta_4} \qquad (3)$$

$$[Cl^-] = [Cl^-]_0/(1 + 5dS/d[Cl^-]) \qquad (4)$$

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(1) Presented in part at the 7th International Conference on Coordination Chemistry in Uppsala, Sweden, June 1962.

(2) N. A. Bonner and W. Goishi, *J. Am. Chem. Soc.*, **83**, 85 (1961).

(3) G. P. Haight, Jr., *ibid.*, **75**, 3843 (1953).

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

(5) G. P. Haight, Jr., C. Springer, and O. J. Heilman, *Inorg. Chem.*, **3**, 195 (1964).

$$dS/d[\mathrm{Cl}^-] = (S/[\mathrm{Cl}])(2\bar{n} - 9)/5 \qquad (5)$$

where S is the solubility (M) of the complex salt, $K_S = [(CH_3)_4N^+]^3[SbCl_4^-]^2[Cl^-]$, β_n is the over-all formation constant for $SbCl_n^{3-n} = [SbCl_n^{3-n}]/\{[Sb^{+3}][Cl^-]^n\}$, K_n is the step formation constant for formation of $SbCl_n^{3-n}$ from $SbCl_n^{4-n}$, $\bar{n}$ is the average ligand number for all $SbCl_n^{3-n}$ in solution, and $[Cl^-]_0$ is the chloride ion concentration (M) in the solvent before saturating it with solute.

Observations are summarized in Table II. The corrected values of $[Cl^-]$ were found by a method of successive approximations using eq. 4 and slopes of the solubility curve obtained at the data points. The corrected slope of -0.2 at $[Cl^-]_0 = 0$ is required by the equation. The minimum in the solubility curve denotes $\bar{n} = 4.5$, indicating that species with $n = 4.0$ must be present in significant concentrations. The value of $\bar{n}$ calculated from slopes of the curve using eq. 5 varies from 3.5 to 5.5.

Table II

Solubility Data for $[(CH_3)_4N]_3Sb_2Cl_9$ at Various $[Cl^-]$ at 25°[a]

$[Cl^-]_0$, M	$[Cl^-]$,[b] M	S, M	$10^3S^{5/2}[Cl^-]^{1/2}$
0.00	0.150	0.0785	0.662
0.10	0.215	0.0700	0.598
0.20	0.300	0.0630	0.554
0.30	0.369	0.0585	0.513
0.40	0.465	0.0553	0.492
0.50	0.559	0.0525	0.472
0.60	0.656	0.0500	0.463
0.70	0.752	0.0492	0.466
0.80	0.852	0.0480	0.459
0.90	0.938	0.0473	0.469
1.00	1.031	0.0470	0.480
1.10	1.110	0.0475	0.511
1.20	1.20	0.0473	0.530
1.30	1.30	0.0460	0.490
1.50	1.50	0.0464	0.552
2.00	1.98	0.0470	0.694
3.00	2.95	0.0504	1.008
4.00	3.90	0.0550	1.508

[a] All solutions 4 M in H^+ assuming H_2SO_4 is a 1:1 electrolyte.
[b] Corrected value using eq. 4.

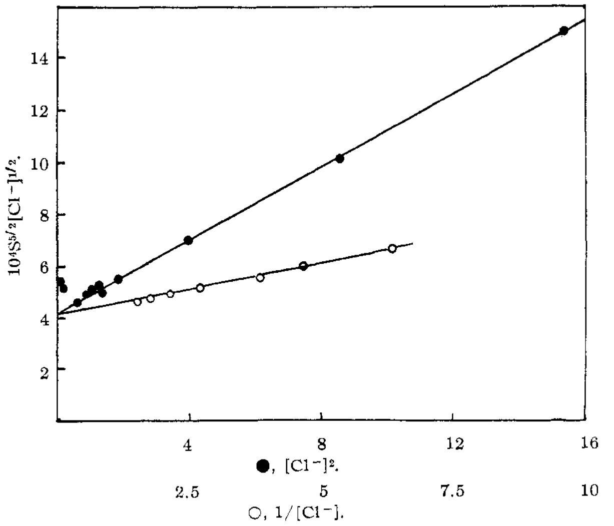

Figure 1.—Plots of the left-hand side of eq. 3 *vs.* $[Cl^-]^2$ (black dots) showing linearity at higher chloride ion concentrations, and *vs.* $1/[Cl^-]$ (open circles) showing linearity at lower chloride ion concentrations. The two plots should have a common intercept.

Figure 1 shows that a plot of the left-hand side of eq. 3 *vs.* $[Cl^-]^2$ gives a straight line over the range $0.8\ M < [Cl^-] \leqslant 4.0\ M$. This indicates that in this region the formation of $SbCl_6^{-3}$ from $SbCl_4^-$ is the dominant equilibrium in solution. A plot of the same quantity *vs.* $1/[Cl^-]$ gives a straight line over the range $0.15\ M < [Cl^-] < 0.8\ M$. This indicates that in this region formation of $SbCl_3$ from $SbCl_4^-$ is the dominant equilibrium in solution. No evidence of the formation of $SbCl_5^{-2}$ is found in these data. The two plots have a common intercept of 4.05×10^{-4} equal to $K_S^{1/2}/10.4$. From the slopes and the intercept the following constants are calculated: $K_5K_6 = [SbCl_6^{-3}]/\{[SbCl_4^-]\cdot[Cl^{-2}]\} = 0.17$; $K_4 = [SbCl_4^-]/\{[SbCl_3][Cl^-]\} = 10$; $K_S = 1.8 \times 10^{-5}$.

The constants are concentration constants and may be subject to activity corrections in view of the large change in solvent from nearly pure 4.0 M sulfuric acid to 4.0 M hydrochloric acid. Due to the relatively high solubility of the salt, the ionic strength is not quite constant but varies from 4.20 to 4.33. Also K_4 has been derived from data in the region where corrections using eq. 4 are large. However, there does appear to be strong evidence that the complex $SbCl_n^{3-n}$ of highest n is $SbCl_6^{-3}$ and not $SbCl_4^-$ as suggested by polarographic data.[3] The suggestion derived from the polarographic data that $SbCl_4^-$ is the only Sb(III) species present between 0.5 and 6.0 M HCl is contravened by observed changes in the absorption spectrum over this range. The possibility that the negatively charged complexes might be protonated is ruled out by the fact that partial substitution of lithium chloride for hydrochloric acid at constant $[Cl^-]$ has no effect on the absorption spectrum of antimony(III). The equilibrium between $SbCl_4^-$ and $SbCl_6^{-3}$ is analogous to that found for bismuth complexes.[5]

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Palladium(II) Complexes of Secondary and Tertiary N-Substituted Ethylenediamines

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Although simple tertiary amines are reported not to form stable transition metal complexes, the coordination stability of a tertiary amino group increases mark-