workers. Since neither Besson, *et al.*, nor Kempter measured the amount of gas evolved, the moles of hydrocarbons produced cannot be compared.

Acknowledgment.—The authors wish to thank T. Hikido and L. Queener of the ORNL Metals and Ceramics Division for preparing the specimens. We are also indebted to the ORNL Analytical Chemistry Division, in particular A. D. Horton and J. L. Botts for developing the gas chromatographic procedure, R. L. Sherman for the X-ray data, the group of W. R. Laing for most of the chemical analyses, R. R. Rickard for the tungsten analysis, C. K. Talbott for gas combustion, J. R. Sites for mass spectroscopy, and L. M. Brady for the carbon analyses of the water.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SWARTHMORE COLLEGE, SWARTHMORE, PENNSYLVANIA

Solubility Studies on Substituted Ammonium Salts of Halide Complexes. III. Tris(tetramethylammonium) Enneachlorodibismuthate(III)[1,2]

BY G. P. HAIGHT, JR., CHARLES H. SPRINGER, AND OLE JAN HEILMANN

Received October 29, 1963

Tris(tetramethylammonium)enneachlorodibismuthate(III) has been prepared and its solubility studied as a function of chloride ion concentration. The data indicate that $BiCl_4^-$ and $BiCl_6^{-3}$ are the only chlorobismuth complexes present in solution. $\beta_6/\beta_4 = 6.4$ at 25° and ion normality of 4.1. This result required re-examination and reinterpretation of spectrophotometric and potentiometric data previously obtained by other authors.[3,4] All data are consistent with the existence of a single equilibrium $BiCl_4^- + 2Cl^- \rightleftharpoons BiCl_6^{-3}$ in acid solutions containing 0.4 to 4.0 M chloride ion.

Spectrophotometric[3] and electrometric[4] studies of complexes $BiCl_n^{3-n}$ have indicated complexes for n = 1 to 5 with some evidence for formation of $BiCl_6^{-3}$ at high $[Cl^-]$. The unreliability of bismuth amalgam electrodes[4] together with the number of assumptions required to interpret the spectrophotometric data[3] prompted us to see what information, especially for complexes of $n \geq 4$, could be obtained from solubility studies. Our data indicate that for $[H^+] = 4.1$ and $[Cl^-] > 0.4$ M, only $BiCl_4^-$ and $BiCl_6^{-3}$ are present, contrary to the conclusions of Hume and Newman[3] and Ahrland and Grenthe.[4] The spectrophotometric and potentiometric findings of the previous authors have been reinterpreted and their data shown to be consistent with an equilibrium involving only $BiCl_4^-$ and $BiCl_6^{-3}$ and the absence of $BiCl_5^{-2}$.

Experimental

Technical grade $BiCl_3$, which was very wet, was hydrolyzed to BiOCl, which was twice dissolved and reprecipitated using reagent grade hydrochloric acid. $[(CH_3)_4N]_3Bi_2Cl_9$ was prepared by dissolving BiOCl in 3 M hydrochloric acid and adding a concentrated solution of reagent grade tetramethylammonium chloride. Large hexagonal crystals of $[(CH_3)_4N]_3Bi_2Cl_9$ precipitated, were filtered, dissolved in hot 3 M hydrochloric acid, and recrystallized at 0° from the same solution. The final product was washed with cold 3 M hydrochloric acid and dried in a vacuum desiccator over solid sodium hydroxide. The salt is stable in air and can be dried at 100° without decomposition. Analysis of the salt for carbon and hydrogen was made by the Clark Microanalytical Laboratory, bismuth was determined spectrophotometrically by the method of Merritt, Hershenson, and Rogers in 6 M hydrochloric acid,[5] and chloride was measured by titration with silver ion according to the familiar Mohr method after hydrolyzing the bismuth to BiOCl. One mole of chloride ion per mole of bismuth ion in the salt was added to the number of moles of chloride precipitated by silver ion.

Anal. Calcd. for $[(CH_3)_4N]_3Bi_2Cl_9$: C, 15.02; H, 3.78; Bi, 43.56; Cl, 33.26. Found: C, 15.26; H, 3.92; Bi, 43.5; Cl, 33.21.

The formula is of a general type $(M_I)_3(M_{II})_2Cl_9$ obtained by Wheeler[6] and Cavalca[7] where M_I is an alkali metal and M_{II} may be As, Sb, or Bi.

Standard solutions of Bi^{+3} for spectrophotometry were prepared by dissolving bismuth metal in nitric acid and destroying the nitrate ion with fuming sulfuric acid at 300°. Analysis for bismuth in solutions was done spectrophotometrically at 328 mμ in 6 M hydrochloric acid using a Beckman Model DU spectrophotometer.

All equilibrium studies were made in solutions which were 4 M in hydrogen ion to prevent hydrolysis. Varying concentrations of Cl^- were obtained by substituting sulfuric for hydrochloric acid, assuming H_2SO_4 to be a 1:1 electrolyte.[1,2]

Solubility measurements were made with the aid of a Brönsted saturator.[8] The salt was placed in a filter tube containing a medium fritted glass disk and connected by a capillary U-tube to a sampling tube. One pass of solvent over the salt was usually sufficient for saturation, although in practice several passes were employed. Suction from a water pump was used to pull solvent through the salt bed. Each sample of solvent was analyzed in duplicate by taking aliquots and at least two runs were made with each particular solvent employed. The saturator was maintained at 25.0 ± 0.1° in a thermostat during all manipulations.

The $[Cl^-]/[Bi(III)]$ ratio in 4 M H_2SO_4 saturated with the salt was unchanged from that in the salt, indicating that no change takes place in the solid phase.

---

[1] Paper I: G. P. Haight, Jr., *Acta Chem. Scand.*, **16**, 209 (1962).

[2] Paper II: G. P. Haight, Jr., J. Zoltewicz, and W. Evans, *ibid.*, **16**, 311 (1962).

[3] D. N. Hume and L. Newman, *J. Am. Chem. Soc.*, **79**, 4576 (1957).

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

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

[6] H. L. Wheeler, *Am. J. Sci.*, **46**, 88 (1893).

[7] L. Cavalca, M. Nardelli, and A. Brailvanti, *Gazz. chim. ital.*, **85**, 1239 (1955).

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

TABLE I

SOLUBILITY OF $[(CH_3)_4N]_3Bi_2Cl_9$ AT ION NORMALITY = 4.13 ± 0.08

$[Cl^-]_0$, M	$[(CH_3)_4N^+]_0$, M	S, M	$[Cl^-]$,[a] M	$[(CH_3)_4N^+]$,[b] M
4.057	0.590	0.00873	4.00	0.616
4.057	0.295	0.01965	3.98	0.354
4.057	0.197	0.02715	3.96	0.278
4.057	0.000	0.05680	3.95	0.1704
3.042	0.000	0.04795	2.90	0.1439
2.028	0.000	0.03770	1.92	0.1131
1.014	0.000	0.02560	0.954	0.0768
0.5070	0.000	0.0194	0.479	0.0582
0.3042	0.000	0.0182	0.301	0.0546
0.1217	0.000	0.0179	0.136	0.0537
0.1014	0.000	0.01835	0.112	0.05505
0.0811	0.000	0.0190	0.0980	0.0570
0.0507	0.000	0.02055	0.0705	0.06165
0.0203	0.000	0.0223	0.0505	0.0669
0.0101	0.000	0.02315	0.0440	0.06945
0.0000	0.000	0.02415	0.0390	0.07245

[a] Obtained by successive approximations from slopes at points on a graph of S *vs.* $[Cl^-]$. [b] $[(CH_3)_4N^+]_0 + 3S$.

Results of Solubility Studies

The effects of changing concentrations of chloride ion and of tetramethylammonium ion on the solubility of the salt are summarized in Table I.

Test for Polynuclear Complexes.—If only mononuclear complexes are formed, the concentration of Bi(III) in all forms in equilibrium with solid salt should be inversely proportional to the $^3/_2$ power of the tetramethylammonium ion concentration if the chloride ion concentration is held constant. The straight line passing through the origin of Fig. 1 is convincing evidence that the salt $[(CH_3)_4N]_3Bi_2Cl_9$ dissolves in acid chloride solutions to form only mononuclear complexes of $BiCl_n^{3-n}$.

Determination of Equilibrium Constants.—Symbolism will follow that employed in articles I and II wherever possible.

S = solubility of $[(CH_3)_4N]_3Bi_2Cl_2$ in moles/l.
$[Cl^-]_0$ = concentration of chloride ion originally in solvent
$[X]$ = concentration of species X in moles/l.
$K_n = [BiCl_n^{3-n}]/[Cl^-][BiCl_{n-1}^{4-n}]$
$\beta_n = \prod_0^n K_n = [BiCl_n^{3-n}]/[Bi^{+3}][Cl^-]^n$
$K_s = [(CH_3)_4N^+]^3[BiCl_4^-]^2[Cl^-]$
$\bar{n}$ = average n in $BiCl_n^{3-n}$ species in any given solution

Assuming only mononuclear chloro complexes of Bi(III) in solution, and assuming the absence of hydrolysis of Bi^{+3} in solutions 4.0 M in hydrogen ion, the following relations can be derived (*cf.* papers I and II of this series). For cases where $S = {}^1/_2[Bi(III)] = {}^1/_3[(CH_3)_4N^+]$

$$S^{5/2}[Cl^-]^{1/2} = \frac{K_s^{1/2}}{10.4\beta_4[Cl^-]^4}\sum_0^n \beta_n[Cl^-]^n \tag{1}$$

$$\frac{d \log S}{d \log [Cl^-]} = \frac{2\bar{n} - 9}{5} \tag{2}$$

$$[Cl^-] = \frac{[Cl^-]_0}{1 + 5\, dS/d[Cl^-]} \tag{3}$$

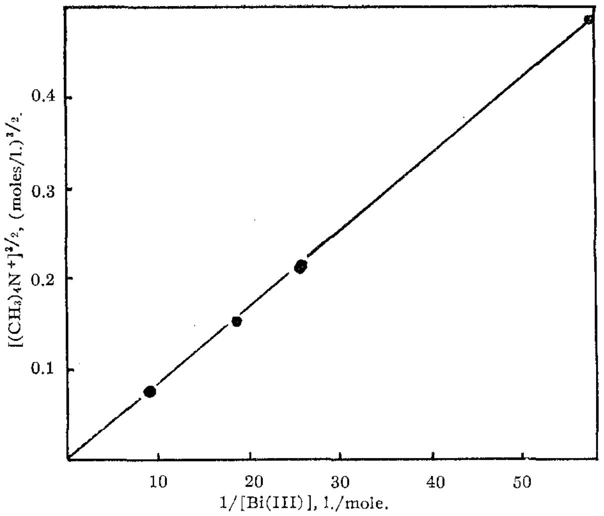

Fig. 1.—Test for the absence of polynuclear complexes. Dependence of [Bi(III)] on $[(CH_3)_4N^+]$ at constant $[Cl^-]$ = 4.1 M.

Equation 3 may be used to determine the concentration of free chloride ion using the slope of the solubility curve at a particular $[Cl^-]_0$ and correcting the curve by successive approximations. The corrected curve must have a limiting slope of −0.2 at $[Cl^-]_0 = 0$. The corrected $[Cl^-]$ values are listed in Table I. Values of $\bar{n}$ may be estimated from the slope of the solubility curve at any given $[Cl^-]$.

Equation 1 is used to evaluate K_s and various K_n values by plotting $S^{5/2}[Cl^-]^{1/2}$ *vs.* various powers of $[Cl^-]$. In this case $S^{5/2}[Cl^-]^{1/2}$ *vs.* $[Cl^-]^2$ gives a straight line over the range $0.1\ M < [Cl^-] < 4.1\ M$ although $\bar{n}$ varies from 4 to 6 (Fig. 2). The relationship indicated by Fig. 2 suggests that $BiCl_4^-$ and $BiCl_6^{-3}$ are the only species present which contain bismuth. From the slope and intercept of the straight lines in Fig. 2 one obtains the values

$$K_s = 2.3 \times 10^{-8}$$

$$\beta_6/\beta_4 = 6.4 = [BiCl_6^{-3}]/[Cl^-]^2[BiCl_4^-]$$

The minimum in the plot of $S^{5/2}[Cl^-]^{1/2}$ *vs.* $[Cl^-]^2$ occurs between 0.1 and 0.2 M $[Cl^-]$. It is reasonable that this point where $\bar{n} = 4.0$ occur below 0.4 M $[Cl^-]$, which by spectrophotometric evidence[3] is the lowest $[Cl^-]$ at which only the two species $BiCl_n^{3-n}$ of highest n are observed. At $\bar{n} = 4.0$ species of $n > 4$, $n = 4$, and $n < 4$ must all be present in significant concentration. The data obtained from $0 \lesssim [Cl^-]_0 \lesssim 0.1\ M$ must be given very tentative treatment. The corrections using eq. 3 become very large compared with $[Cl^-]_0$. Since $[Cl^-]$ is obtained by successive approximations from the slopes of curves the chances for error are very great. The data best fit the equation

$$S^{5/2}[Cl^-]^{1/2} = \frac{K_s^{1/2}}{10.8}\left[\frac{\beta_2}{1 + \beta_4[Cl^-]^2}\right]$$

with $\beta_4/\beta_2 \sim 380$. The points show considerable scatter and the value of the constant can be given only order of magnitude significance. The corrected data are not reliable enough to suggest the absence of $BiCl_3$ as a solute species.

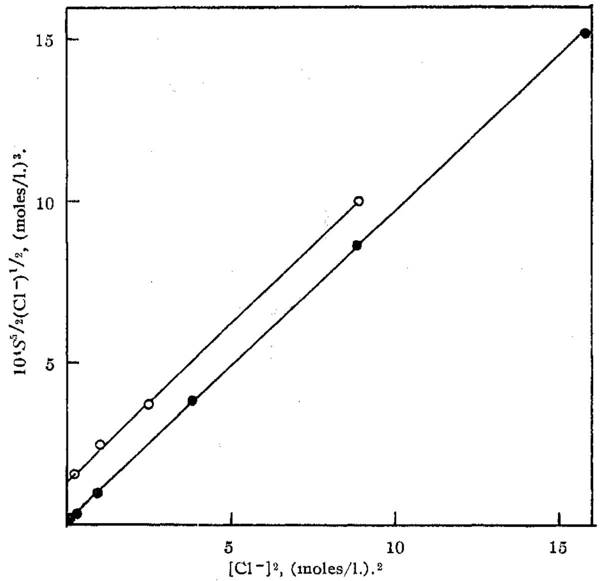

Fig. 2.—A plot of solubility data showing dependence on terms for $n = 4$ and $n = 6$ in the equation

$$S^{5/2}[\text{Cl}^-]^{1/2} = \frac{K_s{}^{1/2}}{10.4\beta_4[\text{Cl}^-]^4} \sum_0^n \beta_n[\text{Cl}^-]^n$$

Closed circles scale as indicated; open circles scale × 0.1 on each axis.

Discussion

The interpretation of data at high ion normalities is complicated by the lack of knowledge of activity effects and the lack of a good theory for the behavior of concentrated electrolytes. The fact that the law described by Fig. 2 holds even up to 4 *M* chloride ion suggests that activity coefficients of the various species involved in the equilibria under study change very little over the range 0.1 to 4.1 *M* chloride ion as long as $[\text{H}^+] = [\text{HSO}_4^-] + [\text{Cl}^-] = 4.1$. Deviation from constant ion normality occurs at 3.0 and 4.0 *M* $[\text{Cl}^-]$ due to high solubility of the salt but never exceeds 2.5% of the total.

This study gives definite information on only the two complexes of $\text{BiCl}_n{}^{3-n}$ for which n is largest, namely 4 and 6. Hume and Newman[3] found highest values of n as 4 and 5 in their spectrophotometric study using chloride concentrations up to 4.0 *M*. Ahrland and Grenthe[4] proposed species with $n = 4$, 5, and 6 even though they employed solutions containing no more than 1.0 *M* chloride in their potentiometric study. Both previous studies yielded information on complexes with lower n, but we shall concern ourselves only with the disagreement concerning higher n values.

Spectrophotometric Studies.—The present authors have made spectrophotometric measurements on Bi(III) solutions containing 4 *M* hydrogen ion and 0.4 to 4.0 *M* chloride ion in the range 300 to 350 mμ and find no disagreement with the data of Newman and Hume. An isosbestic point at 315 mμ tends to confirm the assumption made that only two Bi(III) species are present over this range of chloride ion. Hume and Newman studied the variation of absorbance above 340 mμ on the tail of the peak appearing at 328 mμ. They assumed the following: (1) Only two species containing Bi(III) are present in the concentration range of chloride used, with which we agree. (2) Only the species of highest n absorbs light in this region. (3) The two species differ by *one* in the value of n. They then selected the lowest value of the absorbance for the species of highest n which would force their data to fit the assumption that $\Delta n = 1$. This value for the absorbance should be approached at high chloride ion concentrations and appears to be too high on the graphs they present, although not seriously so.

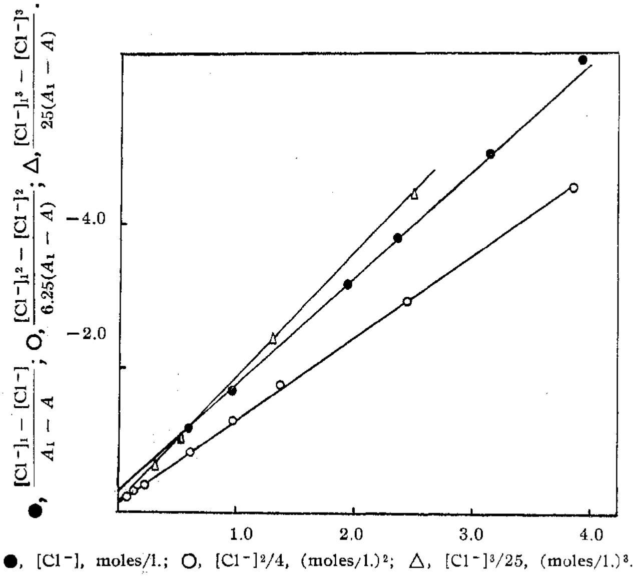

Fig. 3.—Plots showing test of eq. 5 demonstrating the difficulty in determining Δn from spectrophotometric data dependent on the two species absorbing, where the absorbance due to either species alone is unknown: $\lambda = 328$ mμ; $[\text{Cl}^-] = 0.392$ *M* $= L_1$; $A_1 = 0.800$; $\Delta n = 1$, closed circles; $\Delta n = 2$, open circles; $\Delta n = 3$, triangles. Concentrations in moles/l.

It is evidently important to test the consequences of assuming $\Delta n = 1$ *vs.* $\Delta n = 2$ and of assuming a particular value for the absorbance of a species which cannot be measured directly.

Consider a system containing two complex ions in equilibrium. At a constant concentration of metal ion the absorbance at a given wave length is studied *vs.* the concentration of ligand. A_1, A_2, A_3 . . . . are measured values of absorbance. L_1, L_2, L_3 . . . . are corresponding ligand concentrations. A_H is the absorbance if only the species of higher ligand number is present. A_0 is the absorbance if only the species of lower ligand number is present. If

$$K = \frac{(A - A_0)}{(A_\text{H} - A)L^{\Delta n}}$$

is the equilibrium constant for the reaction

$$\text{ML}_n + (\Delta n)\text{L} \rightleftarrows \text{ML}_{(n + \Delta n)}$$

then

$$A = \frac{A_0 + A_\text{H}KL^{\Delta n}}{1 + KL^{\Delta n}} \qquad (4)$$

From the data a reference point (A_1, L_1) is selected.

TABLE II

ABSORBANCE OF 9.55 × 10^{-5} *M* Bi^{+3} IN 4 *M* [H_2SO_4 + HCl]

λ, mμ	[Cl^-], *M* 3.92	3.14	2.36	1.96	1.57	0.98	0.78	0.59	0.392	K^a	A_H^a	A_0^a
350	0.079	0.0745	0.078	0.076	0.069	0.064	0.060	0.054	0.048		0.080	0.018
340	0.508	0.497	0.451	0.478	0.451	0.409	0.382	0.337	0.277	3.3	0.519	0.154
336	1.290	1.271	1.254	1.217	1.177	1.087	1.016	0.910	0.755	3.1	1.295	0.440
328	1.337	1.319	1.296	1.265	1.232	1.144	1.074	0.970	0.800	3.6	1.340	0.495
320	0.988	0.985	0.980	0.970	0.972	0.945	0.910	0.875	0.775	...	0.990	0.668
310	0.363	0.369	0.383	0.392	0.416	0.459	0.473	0.507	0.529	...	0.355	0.618
300	0.118	0.122	0.136	0.143	0.154	0.200	0.224	0.272	0.342	3.3	0.111	0.448
345^b										3.6	0.777	0.233

[a] Calculated assuming Δn = 2. [b] Calculated from data of Hume and Newman.[3]

Then it can be shown from eq. 4 that for other points (A, L)

$$A_1 - A = \frac{K(A_H - A_0)(L_1^{\Delta n} - L^{\Delta n})}{(1 + KL_1^{\Delta n})(1 + KL^{\Delta n})}$$

and

$$\frac{(L_1^{\Delta n} - L^{\Delta n})}{(A_1 - A)} = \frac{1 + KL_1^{\Delta n}}{K(A_H - A_0)}(1 + KL^{\Delta n}) \qquad (5)$$

Hopefully, a plot of $(L_1^{\Delta n} - L^{\Delta n})/(A_1 - A)$ *vs.* $L^{\Delta n}$ will give a straight line when the correct value for Δn is employed. Figure 3 shows that the spectrophotometric data obtained by the present authors at the maximum absorbance for the species of highest *n* gives the desired straight lines with correct sign for the intercepts for values of Δn = 1, 2, or 3. This indicates that one cannot choose between Δn values in the absence of knowledge concerning A_H, A_0, or *K*. Hume and Newman[3] made the reasonable assumption that Δn = 1, which the analysis with eq. 4 shows must fit their data. However, it has now been found that a limiting absorbance is obtained in concentrations of hydrochloric acid that are 6 *M* or more. This value is 1.360 for 9.55 × 10^{-5} *M* Bi(III) *vs.* 1.340 calculated using eq. 5 and Δn = 2. Given this value for A_H one may employ the equation

$$1 + KL^{\Delta n} = \frac{A_H - A_0}{A_H - A} \qquad (6)$$

Figure 4 shows that the plot of L^2 *vs.* $1/(A_H - A)$ is a straight line while *L vs.* $1/(A_H - A)$ is curved. This confirms the result of the solubility study that the two highest chloro complexes of Bi^{+3} are $BiCl_4^-$ and $BiCl_6^{-3}$. Table II gives the spectrophotometric data obtained for the present study including the values of *K*, A_0, and A_H using eq. 5 at various wave lengths and assuming that Δn = 2. The results of analyzing Hume and Newman's data[3] at 345 mμ in this way are included for comparison. The calculated absorption curve for $BiCl_4^-$ no longer drops sharply to zero at 340 mμ as required by their assumption that only the complex with highest *n* absorbs at λ > 340 mμ.

Recently Dyrssen and co-workers[9] measured the spectrum of $R_3NHBiCl_4$ and a higher chlorobismuth(III) complex in carbon tetrachloride. Maximum absorbance is observed at 315 mμ for $BiCl_4^-$ and at 330 mμ for the controversial species designated $BiCl_5^{-2}$ by Hume and Newman and $BiCl_6^{-3}$ by the present authors. The peaks in carbon tetrachloride are broader than those observed in aqueous solution, but it is perhaps significant that $BiCl_4^-$ has absorbance equal to 20 to 30% that of the higher species in the wave length region in which Hume and Newman assumed it to be zero.

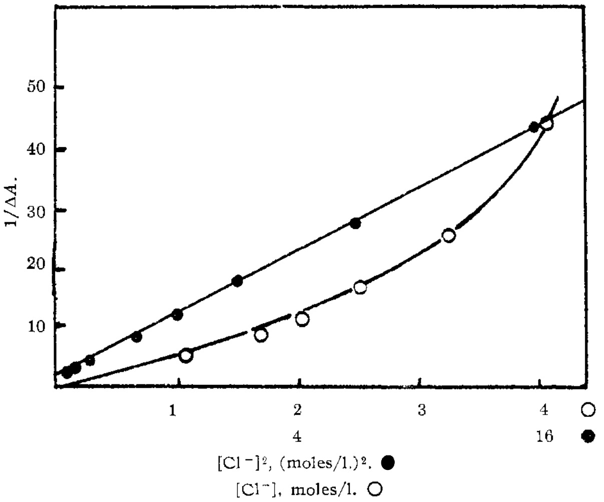

Fig. 4.—Plots showing tests of eq. 6 showing that Δn is clearly determinable if the absorbance of one of two absorbing species can be determined alone: λ = 328 mμ; A_H = 1.360; Δn = 1, open circles; Δn = 2, closed circles.

TABLE III

COMPARISON OF β_6/β_4 BY DIFFERENT METHODS

	Solubility [H^+] = 4.0 *M* μ^a = 4.1	Spectrophotometric [H^+] = 1.0 *M* μ = 5.0	Potentiometric [H^+] = 1.0 *M* μ = 2.0
β_6/β_4	6.0	3.1–3.6	1.9
β_4/β_2	380	120	250
[Bi(III)]	10^{-2}–10^{-1} *M*	10^{-5}–10^{-4} *M*	10^{-2} *M*

[a] μ = total ion normality.

Potentiometric Studies.—Ahrland and Grenthe[4] have presented potentiometric data on the $BiCl_n^{3-n}$ system. They used graphical techniques of Leden[6] to solve the equation

$$X = 1 + \sum_{1}^{n}\beta_n[Cl^-]^n \qquad (7)$$

where X = [Bi(III)]/[Bi^{+3}] and is evaluated from potential measurements. Values of β_n for n = 3 to 6 were thus obtained. Ahrland and Grenthe also evaluated β_1 and β_2 from data on the solubility of BiOCl. If one considers the possibility that not all possible

---

(9) Private communication from David Dyrssen, Stockholm, Sweden.

$\mathrm{BiCl}_n{}^{3-n}$ complexes are formed, one can fit Ahrland and Grenthe's potentiometric data with the equation

$$X = 1 + \beta_2(\mathrm{Cl}^{-2}) + \beta_4(\mathrm{Cl}^-)^4 + \beta_6(\mathrm{Cl}^-)^6 \qquad (8)$$

with $\beta_2 = 1.45 \times 10^4$, $\beta_4 = 3.6 \times 10^6$, and $\beta_6 = 6.8 \times 10^6$.

These results, summarized in Table III, are all consistent with, though not proof of, the absence of $\mathrm{BiCl}_5{}^{-2}$ in aqueous chloride solutions. The β_6/β_4 values are in excellent agreement considering that they are very sensitive to errors in determining the intercepts of graphical plots and considering the different ionic media employed in the various studies. The results with Bi(III) are also consistent with preliminary findings from solubility studies on $[(\mathrm{CH}_3)_4\mathrm{N}]_3\mathrm{Sb}_2\mathrm{Cl}_9$. These studies indicate a preference of Sb(III) for coordination numbers four and six with chloride ion.[10] β_6/β_4 appears to be an order of magnitude higher for $\mathrm{BiCl}_n{}^{3-n}$ than for $\mathrm{SbCl}_n{}^{3-n}$.

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

[10] B. Yoder and G. P. Haight, Jr., unpublished results.

CONTRIBUTION FROM THE AEROSPACE RESEARCH LABORATORIES,
OFFICE OF AEROSPACE RESEARCH, WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Pure Quadrupole Resonance of Chlorine-35 in Metal Chlorates

BY ROSS W. MOSHIER

Received April 24, 1963

The Cl^{35} pure quadrupole resonance frequency in 16 metal chlorates has been measured at 25 and −197°. The influence of the metal on the resonance frequency is related to the electronegativity of the metal.

Covalently-bonded chlorine, bromine, and iodine possess quadrupole moments, and the pure quadrupole resonance frequencies of one or more of their isotopes have been determined in inorganic and organic compounds. The resonance frequency is influenced by the kind and position of substituents in the molecule. Correlation[1-5] has been obtained between the Cl^{35} pure quadrupole resonance frequency in substituted chloroorganic compounds and Hammett σ parameters[6] for the substituents. Investigations of the Cl^{35} and Cl^{37} pure quadrupole resonance frequencies have been reported for solid chlorine,[7] metal chlorides,[8-17] some oxy chlorides,[8,14,18] and the chlorates of sodium,[11,19,20] potassium,[19] copper(II),[21] magnesium,[21] calcium,[22] strontium,[21,22] and barium.[22,23]

This investigation is concerned with the pure quadrupole resonance of Cl^{35} in metal chlorates. Mixtures of KClO_3, NaClO_3, and $\mathrm{Ba(ClO_3)_2 \cdot H_2O}$ in several ratios were studied. Because the Cl^{35} pure quadrupole resonance frequency has a different value for each metal chlorate, qualitative and possible quantitative analytical applications were envisioned, but analytical applications are not promising. A correlation of the frequency and some property of the metal cation has been sought in the data.

Experimental

Apparatus.—The super-regenerative spectrometer was similar in design to that of Bray.[4] The resonances were displayed on an oscilloscope. Frequencies were measured using a National Corporation Model 125 receiver using as calibration points the reported Cl^{35} frequencies of KClO_3,[19] NaClO_3,[11,19,20] $\mathrm{Ba(ClO_3)_2 \cdot H_2O}$,[23] and $\mathrm{Mg(ClO_3)_2 \cdot 6H_2O}$.[21] The band spread on the receiver permitted pinpointing of the frequencies of the references, and interpolation and extrapolation to within one kc.p.s. of the resonance frequencies of the Cl^{35} in the new compound. This method of frequency measurement was used by Bray and Ring.[23]

Two to four grams of sample was contained in wax-sealed vials which were inserted into the oscillator coils for measurement of resonance frequencies. Immersion of the oscillator coil containing the sample into liquid nitrogen permitted measurements at low temperature.

Materials.—Sodium chlorate and barium chlorate monohydrate were obtained commercially.

To prepare the chlorates of H^+, K^+, Rb^+, Cs^+, Cu^{+2}, Ag, Zn, Cd, Tl^+, Ni^{+2}, and Co^{+2}, equivalent quantities of solutions of the desired cation sulfate and barium chlorate were mixed, filtered, and then centrifuged to obtain a clear solution free from suspended barium sulfate. Concentration of the solutions resulted in crystallization of the chlorates of K^+, Rb^+, Cs^+, Ag^+, and Tl^+. The deliquescent nature of the chlorates of Li^+, Cu^{+2}, Zn^{+2}, Cd^{+2}, Ni^{+2}, and Co^{+2} required vacuum desiccation over phosphorus pentoxide for 2 days to obtain crystals. The mother liquor

---

[1] H. C. Meal, *J. Am. Chem. Soc.*, **74**, 6121 (1952).

[2] P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **22**, 2023 (1954).

[3] P. J. Bray, *ibid.*, **22**, 1787 (1954).

[4] P. J. Bray and R. G. Barnes, *ibid.*, **27**, 551 (1957).

[5] P. J. Bray, R. G. Barnes, and R. Bersohn, *ibid.*, **25**, 813 (1956).

[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[7] R. Livingston, *J. Chem. Phys.*, **19**, 803 (1951).

[8] H. G. Dehmelt, *ibid.*, **21**, 380 (1953); *Phys. Rev.*, **92**, 1240 (1953).

[9] P. K. Kisliuk, *J. Chem. Phys.*, **22**, 86 (1954).

[10] A. Bassompierre, *Compt. rend.*, **236**, 596 (1953).

[11] T. C. Wang, *Phys. Rev.*, **99**, 566 (1955).

[12] H. G. Robinson, *ibid.*, **100**, 1731 (1955).

[13] H. G. Dehmelt and H. Kruger, *Z. Physik*, **130**, 385 (1951).

[14] R. Livingston, *J. Phys. Chem.*, **57**, 496 (1953).

[15] B. P. Dailey, *ibid.*, **57**, 490 (1953).

[16] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

[17] D. Nakamura, K. Ito, and M. Kubo, *Inorg. Chem.*, **2**, 61 (1963).

[18] P. J. Bray and D. Esteva, *J. Chem. Phys.*, **22**, 570 (1954).

[19] T. C. Wang, C. H. Townes, A. L. Schawlow, and A. N. Holden, *Phys. Rev.*, **86**, 809 (1952).

[20] Y. Ting, E. R. Manring, and D. Williams, *Phys. Rev.*, **96**, 408 (1954).

[21] P. J. Bray, *J. Chem. Phys.*, **23**, 703 (1955).

[22] V. S. Grechishkin and F. I. Skripov, *Dokl. Akad. Nauk SSSR*, **126**, 1229 (1959).

[23] P. J. Bray and P. J. Ring, *J. Chem. Phys.*, **21**, 2226 (1953).