$BiCl_n^{3-n}$ 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 $BiCl_5^{-2}$ 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 $[(CH_3)_4N]_3Sb_2Cl_9$. 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 $BiCl_n^{3-n}$ than for $SbCl_n^{3-n}$.

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[10] B. Yoder and G. P. Haight, Jr., unpublished results.

CONTRIBUTION FROM THE AEROSPACE RESEARCH LABORATORIES,
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Pure Quadrupole Resonance of Chlorine-35 in Metal Chlorates

BY ROSS W. MOSHIER

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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 $Ba(ClO_3)_2 \cdot H_2O$ 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] $Ba(ClO_3)_2 \cdot H_2O$,[23] and $Mg(ClO_3)_2 \cdot 6H_2O$.[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

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was drained off and the wet crystals further desiccated to remove surface moisture.

Dry beryllium and magnesium carbonates were dissolved in chloric acid solution for the preparation of the chlorates.

Attempts to prepare manganous and chromic chlorates met with failure because of formation of manganese dioxide and chromic acid even at 0°.

By reactions of the hydroxides of Be^{+2}, Ca^{+2}, Sr^{+2}, Al^{+3}, Ga^{+3}, In^{+3}, Hg^{+2}, and Pb^{+2} with excess chloric acid solution to obviate hydrolysis products, these metal chlorates were prepared. (Filter paper and organic solvent should not be brought in contact with chlorates.) The Be^{+2} and In^{+3} chlorates prepared by this technique were not crystalline. They desiccated to glassy solids and were unsuited for measurements. The method used in the preparation of the hydrated metal chlorates yields crystals of the salts with the degree of hydration shown in Table I.

The measurable values of Cl^{35} pure quadrupole resonance of chlorates at room temperature and liquid nitrogen temperature are given in Table I. Resonance frequencies were sought but not found for the chlorates of Li^+, Rb^+, Cs^+, Be^{+2}, Hg^{+2}, In^{+3}, Tl^+, Nd^{+3}, and Zr^{+4}.

Shimomura, Kushida, and Inoue[24,25] state that the quadrupole resonance frequency of Br^{79} in alkali and alkaline earth metal bromates increases monotonically with the electronegativity[26-28] of the metals. The reported resonance of I^{127} in alkali iodates[29] and of Cl^{35} in alkaline earth chlorate monohydrates[22] also increases monotonically with the electronegativity of the metals. Although the data reported here show rough correlations of this type even though different hydrates and crystal forms are compared, additional data are needed for substantiation and the extension of this correlation to these salts of the other periodic group metals.

TABLE I

Cl^{35} PURE QUADRUPOLE RESONANCES OF METAL CHLORATES

Salt	Crystal habit[a]	eQq 25 ± 1°	 −197°
$NaClO_3$	Cub. or trig.	29.920[19]	30.632[19]
$KClO_3$	Monocl.	28.086[2]	28.953[19]
$Mg(ClO_3)_2 \cdot 6H_2O$	.....	.....	29.885[21]
$Ca(ClO_3)_2 \cdot 6H_2O$	Monocl.	.....	30.11
$Sr(ClO_3)_2$	Rhom.	29.161	29.869[21]
$Ba(ClO_3)_2 \cdot H_2O$	Monocl.	29.399	29.922[23]
$AgClO_3$	Tetr.	28.720	29.430
$Cu(ClO_3)_2 \cdot 6H_2O$	Cub.	29.21	30.064[21]
$Zn(ClO_3)_2 \cdot 4H_2O$	Cub.	30.34	31.001
$Cd(ClO_3)_2 \cdot 2H_2O$	.....	.....	29.893
$Al(ClO_3)_3 \cdot 6H_2O$	Rhom.	29.210	29.86
$Ga(ClO_3)_3 \cdot mH_2O$	.....	29.388	29.832
$Ni(ClO_3)_2 \cdot 6H_2O$	.....	29.682	30.498
$Co(ClO_3)_2 \cdot 6H_2O$	Cub.	.....	30.080
$Pb(ClO_3)_2 \cdot H_2O$	Monocl.	29.233	29.712
$Pt(ClO_3)_4$	.....	.....	30.94

[a] "Handbook of Chemistry and Physics," 40th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958.

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The Effect of Metal Fluoroborates on the Absorption of Ethylene by Silver Ion

BY BERTSIL B. BAKER

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The addition of fluoroboric acid or metal fluoroborates to aqueous silver nitrate or fluoroborate gives a surprisingly large increase in ethylene absorption. The degree of enhancement by various cations correlates well with their charge-to-radius ratio and may be related to degree of hydration.

Introduction

Metal–olefin complexes have been extensively studied because of interest in their structure[1-6] and are the subject of many patents for the separation of paraffins from olefins. With silver, the nitrate salt has received by far the greatest attention, although the perchlorate has also been examined,[7,8] and the fluoroborate was used in a thermodynamic study.[9] Recent patents[10] show silver fluoroborate and silver fluorosilicate to be several times more efficient than silver nitrate for the absorption of ethylene. Further, the amount of ethylene absorbed per mole of silver nitrate decreases with increasing concentration, while with fluoroborate it increases.

We have noted a surprisingly large increase in the ethylene absorption efficiency of silver nitrate or fluoroborate produced by the presence of fluoroboric acid or metal fluoroborates. The practical aspects of this discovery were disclosed in a recent patent.[11] This

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