lifted at room temperature and more completely lifted at low temperatures. Every Rh^{3+} ion brings two extra positive charges into the lattice and causes the Frenkel equilibrium to shift in favor of increased concentration of silver ion vacancies. At the low temperatures used in these experiments, the vacancies are expected to be coulombically bound to the $RhBr_6^{3-}$ ion, but they can dissociate partially or completely as the temperature is raised. Examples of this vacancy association process are found in the esr studies of vanadium in silver chloride,[9,10] ferric ions in AgCl and AgBr,[11,12] and chromium in AgCl.[13] The two vacancies associated with $RhBr_6^{3-}$ at 20°K lower the symmetry of the impurity center and result in the lifting of the triplet degeneracy. The room-temperature data where only two lines are observed have been attributed to the partial dissociation of the vacancies from the center. As mentioned earlier, other interactions can also contribute to this splitting. It is conceivable that the coupling between the ν_3 mode of $RhBr_6^{3-}$ and the nearby intense lattice vibration of the host AgBr contributes significantly to the splittings. Except for the effects of the vacancies mentioned above, $RhBr_6^{3-}$ in the AgBr lattice has the same symmetry as the isolated molecule, and no site-group splitting is expected. At the low dopant concentrations employed in this study (200 pm) the correlation field interactions cannot be very important and have not been detected by epr experiments.[3]

Calculations show that the bromide isotope effect can be responsible for the splitting of the 246.4-cm^{-1} line. The other ir-active mode ν_4, expected to have a frequency of around 100 cm^{-1}, has not been observed because of the intense lattice absorption of the host crystal in this spectral region. Reflectivity studies are currently under way to search for this band.

To substantiate these assignments further, the frequencies are compared in Table I with those measured for Cs_3RhBr_6.

The assignment of 136 cm^{-1} as ν_5 is somewhat tenuous, since the ν_5 of $PtBr_6^{2-}$ is at 97 cm^{-1},[14] and that of $ReBr_6^{2-}$, at 112 cm^{-1}.[15] The relative broadness of the band suggests it may be an impurity-induced multiphonon band of AgBr.

The optical spectrum of single crystals of rhodium-doped AgBr at 77°K is similar to one taken at ambient temperatures.[3] The broad absorption peaked at 550 nm has been attributed to the spin-allowed ($^1A_1 \rightarrow {}^1T_1, {}^1T_2$) transition. It is noted that this electronic transition of the scattering molecule occurs at the wavelength of the exciting light (5682 Å); hence, one expects to observe the resonance Raman effect (RRE). The high intensity of the fundamental observed in the Raman spectrum with 5682-Å irradiation is believed to be a manifestation of the RRE. A comparison of the preresonance Raman effect with the RRE is not possible because of the broadness of the electronic absorption band and because of the available laser exciting lines. However, the relative peak intensities of the Raman-scattered lines with the exciting laser lines have been studied. It is observed that as the exciting line moves away from the absorption maximum at 550 nm, the ratio of the intensity of ν_1 to ν_2 decreases. This is in agreement with the contention[16,17] that in RRE the totally symmetric vibration (ν_1 in this case) is preferentially enhanced. No overtone progression has been observed, although a number of authors[10,11] have reported their appearance in conjunction with the observation of RRE. Further work is in progress to look for these overtones, although the appearance of such progressions is not a necessary condition for the observation of RRE.

Table I. Vibrational Frequencies (cm^{-1}) and Assignments

AgBr/Rh (20°K)	AgBr/Rh (300°K)	Cs_3RhBr_6 (300°K)	Assignment
246.4	245	253	ν_3 (F_{1u})
248.8			
253.8	251		
		130	ν_4(F_{1u})
183	183	185	ν_1 (A_{1g})
171	171	164	ν_2 (E_g)
136			ν_5 (F_{2g})

Registry No. AgBr, 7785-23-1; Rh(III), 16065-89-7; Cs_3RhBr_6, 50986-67-9.

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Synthetic and Nuclear Quadrupole Resonance Study of Chlorodiiodinium Hexachloroantimonate(V), $I_2Cl^+SbCl_6^-$

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The I_2Cl^+ ion was evidently first postulated to account for the properties of appropriate solutions of HIO_3, I_2, and ICl in sulfuric acid.[1] Later work in this laboratory established that the reported[2] phase $2ICl{\cdot}AlCl_3$ not only had the indicated stoichiometry but also was correctly formulated as $I_2Cl^+AlCl_4^-$, the assignment being based on its halogen nqr and aluminum nmr spectra relative to those of ICl_2^+-$AlCl_4^-$, $I_3^+AlCl_4^-$, and $I_5^+AlCl_4^-$.[3] The work reported herein was undertaken to examine the possible formation of similar cations in the system I_2-ICl-$SbCl_5$. The only solid phase stable at room temperature is, however, $2ICl{\cdot}SbCl_5$. This compound does exhibit an unusually strong nqr spectrum for all isotopes possible (^{35}Cl, ^{37}Cl, ^{121}Sb, ^{123}Sb, ^{127}I) which allows appreciable information to be deduced regarding not only its formulation as $I_2Cl^+SbCl_6^-$ but also interactions in the solid structure. A different synthesis and Raman data for the same compound have recently also been reported by Shamir and Lustig.[4]

Experimental Section

Commercial $SbCl_5$ (Research Inorganic/Organic Chemical

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Corp., 99%) was vacuum-distilled once in a sealed glass apparatus and then transferred in a N_2-filled glove bag to a second glass system containing a 5-ml microburet and equipped with Teflon needle valves (Fischer-Porter). The material was then vacuum-distilled into the buret, whereafter the amount of $SbCl_5$ to react with previously weighed ICl or I_2 was measured volumetrically to ±0.01 ml and transferred under vacuum.

Purified ICl or I_2 was sublimed from an evacuated storage flask into an evacuated, preweighed container which was closed and weighed on an analytical balance. The contents were then transferred quantitatively *in vacuo* to a reaction vessel containing the $SbCl_5$; the tube was sealed and heated for a few hours at 120°. Microscopic and nqr identification of the reaction products *in situ* in the sealed reaction containers proved to be useful additions to more conventional means of characterization.

The general nqr techniques employed have been described elsewhere.[5] Briefly, initial spectral measurements were recorded on a Wilks NQR-1A superregenerative spectrometer. These allowed the approximation of transition frequencies to ±10–30 kHz and ±1 MHz in the respective ranges studied, 12–50 and 350–600 MHz. Precise frequency measurements (±1 kHz) were then obtained and overlapping transitions (>20-kHz separation) resolved for chlorine and antimony on a wide-line spectrometer.

Results and Discussion

The phase $2ICl{\cdot}SbCl_5$ ($=I_2Cl^+SbCl_6^-$) is readily formed "neat" according to the described procedures. The compound melts at about 70° and sublimes at room temperature. General reactions of $nI_2 + ICl + SbCl_5$ were investigated for $n = 1$-3 since these stoichiometries would correspond to the formation of $I_{2n+1}{}^+SbCl_6^-$ salts analogous to some known tetrachloroaluminates.[3] However all gave multiphase mixtures containing free I_2 plus the same compound $2ICl{\cdot}SbCl_5$. Other studies of the I_2–$SbCl_5$ and ICl–$SbCl_5$ binary systems demonstrated that the additional ICl necessary for the formation of $2ICl{\cdot}SbCl_5$ is formed substantially quantitatively by oxidation of I_2 by $SbCl_5$ according to the reaction

$$I_2 + 2SbCl_5 \rightarrow 2ICl{\cdot}SbCl_5 + SbCl_3$$

until either I_2 or $SbCl_5$ is consumed. This reaction, which of course precludes the formation of $I_3^+SbCl_6^-$, etc., at least as equilibrium phases, was evidently first noted by Ruff,[6] although he concluded the adduct formed was a mixture (or mixed crystals) of $2ICl{\cdot}SbCl_5$ and $3ICl{\cdot}SbCl_5$.

The stability of the lone adduct $2ICl{\cdot}SbCl_5$ is also demonstrated by the fact that the phase may be achieved using ICl as the oxidizing agent, according to

$$4ICl + SbCl_3 \rightarrow 2ICl{\cdot}SbCl_5 + I_2$$

There is no reaction between $SbCl_3$ and I_2. The only other related compound, $ICl_2^+SbCl_6^-$, requires ICl_3 or Cl_2 for its synthesis.[4]

The 16 resolved transitions observed in the nqr spectrum of $I_2ClSbCl_6$ are listed in Table I together with their assignments. The latter process is greatly aided by both the greater measurement precision possible with the wide-line spectrometer and the likelihood that all transitions have been observed, the strengths of the signals being much greater than those obtained for the same cation in $I_2Cl^+AlCl_4^-$ as well as those reported[7] for other $SbCl_6^-$ salts. Precise verification of some assignments may be made according to required relationships between transitions of different isotopes of the same element in the same chemical environment, while others can be interpreted by comparison with other compounds.

Table I. Nqr Transitions for $I_2ClSbCl_6$ at Room Temperature

No. (t_i)	Freq,[a] MHz	Intens[b]	Line width, kHz	Assignment	Freq calcd from ^{35}Cl datum, MHz
1	15.846 (1)	w	1	^{123}Sb (ν_1)	
2	16.376 (1)	m	2	^{37}Cl	16.373 (1)
3	16.554 (1)	mw	2	^{37}Cl	16.562 (5)
4	19.569 (1)	m	3.5	^{37}Cl	19.569 (1)
5	20.247 (1)	m	4.5	^{37}Cl	20.247 (1)
6	20.778 (1)	s	5.5	^{35}Cl	
7	21.011 (5)[c]	ms	13–17	^{35}Cl + ^{121}Sb (ν_1)[d]	
8	21.029 (4)[c]	mw	12	^{123}Sb (ν_2)[d]	
9	24.829 (1)	vs	7.5	^{35}Cl	
10	25.689 (1)	vs	8	^{35}Cl	
11	30.169 (1)	m	6	^{37}Cl (cation)	30.172 (1)
12	32.896 (1)	m	2	^{123}Sb (ν_3)	
13	35.705 (1)	ms	12	^{121}Sb (ν_2)	
14	38.281 (1)	m	7	^{35}Cl (cation)	
15	429 (1)	s		^{127}I (central) (ν_1)	
16	517 (1)	m		^{127}I (terminal) (ν_1)	

[a] Measurement error in the least significant figure is given in parentheses. [b] As observed on a Wilks instrument. Key: s, strong; m, moderate; w, weak. [c] Incompletely resolved; see text. [d] Assignments may be reversed; see text.

The assignment of the transition at 429 MHz to the central iodine atom in the I_2Cl^+ cation is consistent with the value found for $I_2Cl^+AlCl_4^-$, 417 MHz, the latter falling into proper sequence for the central iodine in the $AlCl_4^-$ salts of the V-shaped I_3^+, I_2Cl^+, and ICl_2^+: 308, 417, and 458 MHz, respectively.[3] A similar expectation for the effect of chlorine substitution on the frequency of the other terminal iodine would suggest that the 415- and 428-MHz transitions for terminal atoms in $I_3^+AlCl_4^-$ translate into 517 MHz in the present I_2Cl^+. This transition has not been observed with $I_2Cl^+AlCl_4^-$. The ν_2 ($\pm{}^3/_2 \rightarrow \pm{}^5/_2$) transitions possible for the iodine atoms in I_2Cl^+ would all be expected to fall beyond the range of the instrument used.

The required ratio (1.26878) for the resonance frequencies of ^{35}Cl and ^{37}Cl readily enables the assignment of four pairs of chlorine transitions in the compound, as shown. The highest frequency observed for ^{35}Cl (38.281 MHz) corresponds well to those obtained for this cation in $I_2Cl^+AlCl_4^-$ (38.127, 37.912 MHz),[3] while the three in the range 20.778–25.689 MHz are in reasonable agreement with those reported for this isotope in a variety of other $SbCl_6^-$ salts.[7] The sharp resonance at 16.554 MHz, which cannot be assigned to antimony or iodine, must be attributed to ^{37}Cl in $SbCl_6^-$, requiring that a fourth transition for ^{35}Cl in $SbCl_6^-$ be located at about 21.003 MHz. A large and unusually shaped band is found in this region with the Wilks instrument, and this feature is clearly but still incompletely resolved on the wide-line spectrometer into a pair of transitions at 21.011 (5) and 21.029 (4) MHz. Although the large line widths (Table I) arise in part from the incomplete resolution, some of the width of the former resonance must also result from the near coincidence of the presumably narrow ^{35}Cl transition with an antimony resonance. The antimony parameters and hence the locations of the transitions are well overdetermined, and two are definitely required near 21.0 MHz.

The multiplicity of antimony transitions arises from the higher spin of the isotopes ^{121}Sb ($I = {}^5/_2$, 57% abundance) and ^{123}Sb ($I = {}^7/_2$, 43%), giving five transitions to be described by three constants, that is, a single asymmetry parameter η and a coupling constant e^2Qq/h for each isotope. Assignment of the antimony transition at lowest frequency

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is obvious, and a consistent solution can be obtained only with the indicated assignment of the pair at highest frequency. There is however no clear choice between the ν_1 transition for ^{121}Sb and ν_2 for ^{123}Sb in the assignment of the overlapping resonances near 21 MHz. Solution of the secular equations by the method of Reddoch[8] according to both possibilities gives the results shown in Table II. Clearly the asymmetry parameters obtained for each isotope are in excellent agreement, and the ratio of the coupling constants obtained for the two antimony isotopes is very close to that reported in the literature. However, no distinction can be made between the two possible assignments of the antimony transitions near 21 MHz based on a significantly better agreement of the derived parameters for one or the other.

Table II. Parameters Calculated from Antimony Assignments for $I_2Cl^+SbCl_6^-$

	^{121}Sb		^{123}Sb	
Assignment	Table I	Alternate[b]	Table I	Alternate[b]
Asym parameter[a]	0.3794	0.3805	0.3811	0.3799
e^2Qq/h,[a] MHz	122.244	122.261	155.843	155.766

Q_{123}/Q_{121}: Table I, 1.27486; alternate,[b] 1.27404; ref 9, 1.27474

[a] Data measurement errors alone are estimated to give an uncertainty of ±4 in the last digits shown. [b] t_7 and t_8 reversed in Table I.

The observation of four independent chlorine atoms for the $SbCl_6^-$ anion indicates the group possesses C_s or C_{2v} point symmetry in the crystal, provided of course that all resonances have been observed. *If* intensities are meaningful, each of the higher frequency transitions (t_9 and t_{10}) corresponds to two equivalent atoms, but this conclusion is necessarily speculative.

Although an antimony asymmetry parameter of 0.38 may seem rather large for the central atom in a nominally octahedral complex, Schneider and DiLorenzo[10] have pointed out that such a value can result from only ~3% imbalance in the p-orbital population relative to axial symmetry. Angular distortions are particularly effective in this respect. The spread of almost 5 MHz in the ^{35}Cl transitions is consistent with (but of course not proof of) the observed asymmetry. Transition averages of 23.7 ± 0.7 MHz with ranges of less than 1 MHz have been cited as characteristic of ^{35}Cl in relatively unperturbed $SbCl_6^-$ ions (at 77°K);[7] the present ^{35}Cl transitions still average 23.08 MHz without regard to possible multiplicity. Raman data for this compound also support the presence of an $SbCl_6^-$ ion with appreciable distortion, the e_g mode being split by 36 cm^{-1} or 13%.[4]

A distortion of the $SbCl_6^-$ ion of the amount indicated is certainly not without precedent. Variations of over 0.20 Å in antimony-chlorine distances and 3° in angles in other hexachloroantimonate(V) salts have been observed and attributed to packing effects.[11] In addition specific interactions with the I_2Cl^+ cation may not be negligible. In the presumably similar ICl_2SbCl_6 the V-shaped cation has two more distant chlorine atom neighbors in anions which complete a roughly rectangular arrangement about the iodine.[12] This (and perhaps packing) then gives a 0.15-Å range (6.5% or 4σ) in Sb-Cl distances and a 13.6° range in angles at antimony in ICl_2SbCl_6.

Insufficient nqr data for the present I_2Cl^+ cation, especially ν_2 for the central iodine, make it difficult to judge whether bonding to the anion is reflected in cation transitions. Previous correlations of structural parameters and nqr transitions in ICl_2^+ and I_3^+ were aided by the higher symmetry of the cation. The structures of $ICl_2^+AlCl_4^-$ and $ICl_2^+SbCl_6^-$ [12] have not been determined well enough to allow any predictions to be made regarding the relative basicity of the two anions.

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Registry No. $I_2Cl^+SbCl_6^-$, 38656-79-0; ^{35}Cl, 13981-72-1; ^{37}Cl, 13981-73-2; ^{121}Sb, 14265-72-6; ^{123}Sb, 14119-16-5; ^{127}I, 7553-56-2.

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Hydrogen Bonding. II. Complex Fluoride Salts of Arylammonium Ions[1]

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In the course of investigations[2] into the possible existence of ions of the type $[(OH^-)_nF^-_{4-n}H^+_m]^{m-4}$ we became interested in salts of the $H_3F_4^-$ anion, a simple species where $n = 0$ and $m = 3$. Reported examples of solid-phase, crystalline higher hydrogen fluoride complexes fall into two stability classes. With simple metal cations such as the alkali metals the order of anion stability is $HF_2^- > H_2F_3^- > H_3F_4^-$,[3] which is what would be expected if the $H_3F_4^-$ ion is either a linear extension of the $H_2F_3^-$ ion, which is known[4] to have two hydrogen fluoride moieties hydrogen bonded to a central fluoride ion, or is a less likely species with three hydrogen fluorides hydrogen bonded to a single fluoride. On the other hand, with hydrogen-bonding cations such as hydronium[5] or ammonium[6] the order of anion stability is $HF_2^- > H_3F_4^-$, and the $H_2F_3^-$

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