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NQR of ^{35}Cl, ^{127}I, and ^{121}Sb in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6

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NQR spectra due to ^{35}Cl, ^{127}I, and ^{121}Sb in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6 have been observed in the temperature range 77 K to melting point. The Zeeman effect on the single crystals of these complexes has been examined. In $I_3Cl_2SbCl_6$ the η-values for the I atoms contributing to the higher and the lower NQR frequencies are 0.73 to 0.09, respectively, whereas in ICl_2SbCl_6 the η-value for the I atom is 0.15. In these complexes the ^{35}Cl NQR lines which yield large η-values (0.42 to 0.56) are assigned to the bridging Cl atoms. The η-values for the other Cl atoms, except the Cl atoms in the ICl_2^+ ion which have η-values of 0.13 to 0.15, are negligibly small. The Sb atoms in both complexes have considerably large η-values (0.39). The orbital populations have been calculated from the NQR parameters. The bonding in the cations is explained on the basis of an approximation using only p orbitals of the I atom.

The NQR investigations on a number of polyhalogen anions shed light on the charge distribution and the interaction between these anions and the surrounding cations.[1–8] Above all, the bonding in trihalides was satisfactorily explained in terms of a three-center four-electron (3c-4e) bond or a resonance hybrid $X-Y\ X^- \longleftrightarrow X^-\ Y-X$. On the other hand, polyhalogen cations are less stable,[9] and the crystal structures of a few compounds were determined by X-ray analysis. The NQR data on the polyhalogen cations were reported for the first time by Evans and Lo,[10] who assigned the ^{35}Cl resonance lines in ICl_2AlCl_4 roughly to the ICl_2^+ and the $AlCl_4^-$ ions. Merryman et al.[9,11] observed the resonances of ^{35}Cl and ^{127}I in $I_2ClSbCl_6$, $I_2ClAlCl_4$, I_3AlCl_4, and I_5AlCl_4, and estimated atomic charges and bond populations. From the known crystal structures of polyhalogen derivatives,[12–16] it is inferred that bridging halogen atoms construct infinite chains of cations and anions. It is therefore important to elucidate the bond character in detail.

Birchall and Myers[14] reported the crystal structure of $I_3Cl_2SbCl_6$ and threw doubt on the presence of $I_2ClSbCl_6$ on the basis of the unit cell parameters and the Raman spectrum. They followed the method of Shamir and Lustig[17] in an attempt to prepare $I_2ClSbCl_6$. It is of interest to know whether this complex is present or not. Although ICl_2SbCl_6 is one of the first compounds in which the presence of the polyhalogen cation was well established by crystallographic study,[12] this complex has not been investigated by NQR yet, so far as we know.

In this paper we describe the results of the NQR Zeeman investigations on single crystals of the complexes $I_3Cl_2SbCl_6$ and ICl_2SbCl_6. The choice of the $SbCl_5$-complexes was favored since the resonances of ^{35}Cl, ^{127}I, and ^{121}Sb could be observed in the course of the experiment. Furthermore a comparison of the Zeeman data with the structural ones was considered to yield useful information on the assignment of the NQR lines and charge distribution.

Experimental

Complexes of $I_3Cl_2SbCl_6$ and ICl_2SbCl_6, were prepared in the manner described in the literatures.[14,18] These were identified by the melting points and the halogen contents. The procedure of Merryman and Corbett[11] was followed in an attempt to prepare $I_2ClSbCl_6$. The NQR spectra of this complex were essentially, except for some parts, identical with those in the literature.[11] Single crystals were grown by Bridgman's method.

A superregenerative spectrometer of Dean's type and a superregenerative parallel transmission line spectrometer were used for detecting the NQR lines. The absorption lines were observed on an oscilloscope. The resonance frequencies were determined with a frequency counter, TR-4142G, of Takeda Riken Co. The Zeeman effect was measured by means of the zero-splitting cone method. The Zeeman field was supplied by means of a Helmholtz coil. Temperature was measured by the use of a copper-constantan thermocouple.

Results

The NQR frequencies for ^{35}Cl, ^{121}Sb, and ^{127}I in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6 are listed in Tables 1 and 2, respectively. Figures 1 and 2 show the temperature dependence of the resonance frequencies for ^{35}Cl

Table 1. ^{35}Cl, ^{127}I, and ^{121}Sb NQR Parameters in $I_3Cl_2SbCl_6$ at Room Temperature

Atom	Frequency/MHz		η/%$^{a)}$	e^2Qqh^{-1}/MHz$^{a)}$
	77 K	297 K		
Cl_1	21.007	20.784	42.6	40.361
Cl_2	25.175	24.839	1.9	49.675
Cl_3	26.135	25.702	3.2	51.395
Cl_4	38.620	38.293	4.9	76.555
$I_1\ \nu_1$	432.065	429.13	8.8	2837.0
$I_2\ \nu_1$	529.30	522.63	73.4	2373.1
Sb ν_1	22.688	21.054	38.0	122.49
ν_2	36.966	35.730	(38.0)$^{b)}$	

a) These values correspond to 297 K. b) Obtained from the frequency ratio of ν_2/ν_1.

Table 2. ^{35}Cl, ^{127}I, and ^{121}Sb NQR Parameters in ICl_2SbCl_6 at 233 K

Atom	Frequency/MHz			η/%	e^2Qqh^{-1}/MHz
	77 K	233 K	298 K		
Cl_1	19.363	19.198	19.114	56.7	36.490
Cl_2	20.522	20.447	—	48.3	39.409
Cl_3	25.476	25.444	25.127	5.2	50.420
Cl_4	26.059	25.793	25.66$^{b)}$	3.6	50.555
Cl_5	27.145	26.832	25.67$^{b)}$	4.5	53.806
Cl_6	27.159	26.912	26.78$^{b)}$	2.9	53.817
$Cl_7$$^{a)}$	38.654	38.405	38.270	15.4	76.261
$Cl_8$$^{a)}$	40.053	39.829	39.691	13.8	79.155
I$^{a)}$ ν_1	462.569	457.52	454.70	14.9	2962.2
Sb$^{a)}$ ν_1	17.896	17.870	17.857	39.5	102.91
ν_2	30.954	30.337	29.975	(39.5)$^{c)}$	

a) The values of η and e^2Qqh^{-1} for these atoms correspond to 298 K. b) Very weak and broad. c) Obtained from the frequency ratio of ν_2/ν_1.

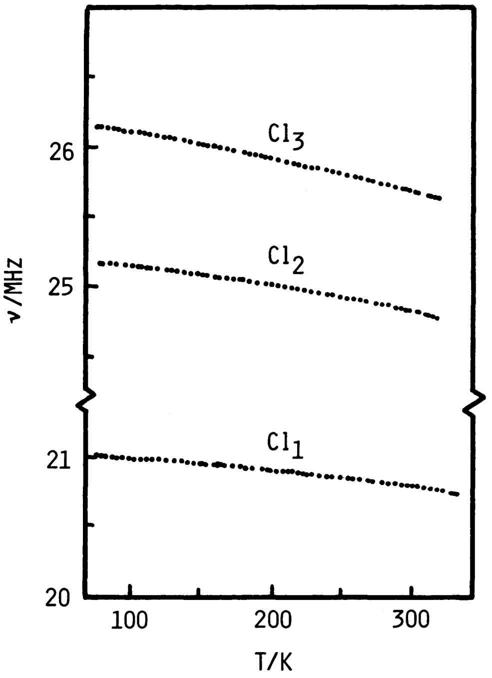

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $I_3Cl_2SbCl_6$.

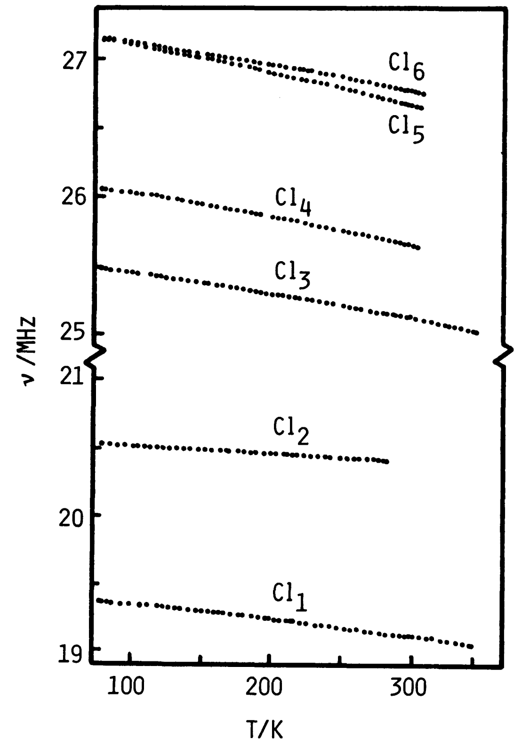

Fig. 2. Temperature dependence of ^{35}Cl NQR frequencies in ICl_2SbCl_6.

bonded to the Sb atom in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6, respectively, in the temperature range from 77 K to the melting points. In $I_3Cl_2SbCl_6$, the NQR lines of the Cl_2 and Cl_3 atoms faded out at around 320 K, whereas the resonance of the Cl_1 atom could be detected up to the melting point. In ICl_2SbCl_6, similarly, the resonance lines of the Cl_1 and Cl_3 atoms could be detected up to near 350 K, and those of the other Cl atoms faded out in the range from 280 to 300 K. This suggests that the Sb–Cl_1 bond in $I_3Cl_2SbCl_6$ and the Sb–Cl_1 and Sb–Cl_3 bonds in ICl_2SbCl_6 are nearly parallel to the reorientational axis of the $SbCl_6$ group.[19,20] The other lines due to ^{35}Cl, ^{127}I, and ^{121}Sb in these complexes were observed up to their melting points.

The Zeeman effect on ^{35}Cl, ^{123}Sb, and ^{127}I in $I_3Cl_2SbCl_6$ was examined at room temperature. The zero-splitting loci are shown in Fig. 3. A single pattern was obtained for each resonance line. This is in agreement with the crystal structure which belongs to the space group $P\bar{1}$.[14] The calculated asymmetry parameters (η) are listed in Table 1 along with the coupling constants (e^2Qqh^{-1}). The Cl_1, I_2, and Sb atoms are characterized by their large η-values. The assignment of the NQR lines on the Cl atoms is based on a comparison of orientation of the efg axis at the resonant nucleus with the corresponding bond directions, as seen in Table 3. The I_1 and I_2 atoms cannot be unequivocally assigned because of the parallelism of their efg axes and because of unreliability in the intensity ratio of the resonance lines. The assignment of these was decided by considering the relationship between the orientation of the efg axes and the charge distribution, as described below. The efg axes at the atoms Cl_2, Cl_3, and Cl_4 coincide in direction with the bond axes. The

Table 3. Angles between efg Axes and Bond Angles in $I_3Cl_2SbCl_6$

Bond	Cl_1–Sb	Cl_2–Sb	Cl_3–Sb	Cl_4–I_2
Cl_2–Sb	87.25° (89.56)			
Cl_3–Sb	85.80 (89.71)	89.63 (89.97)		
Cl_4–I_1	63.95 [69.3]$^{b)}$	51.52 [51.6]	46.26 [46.0]	
I_1 z-axis	93.51	140.55	50.53	90.11
x-axis	65.0	52.5	44.7	1.7
I_2 z-axis	63.40	51.51	46.6	0.58
x-axis	94.1	139.2	49.0	90.2
I_1–I_2	[92.6]	[141.9]	[52.2]	(92.62)

a) The value in parentheses is the corresponding bond angle. b) The value in brackets was calculated from the atomic positions (Ref. 14).

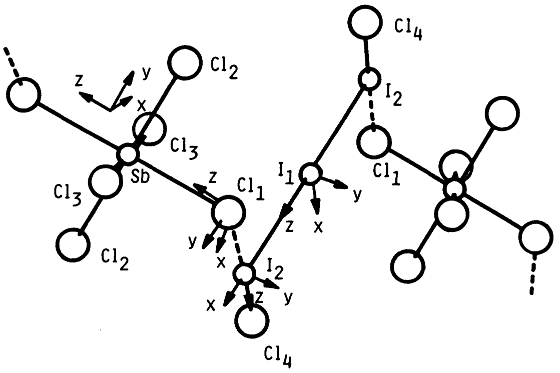

Fig. 4. Molecular shape of $I_3Cl_2SbCl_6$.

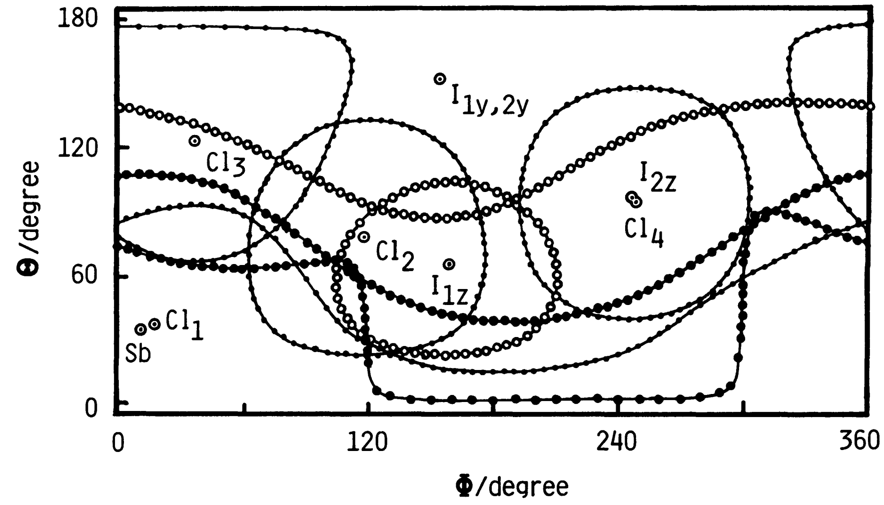

Fig. 3. Zero-splitting loci of ^{35}Cl, ^{127}I, and ^{121}Sb (ν_1, ν_2) Zeeman lines in $I_3Cl_2SbCl_6$.

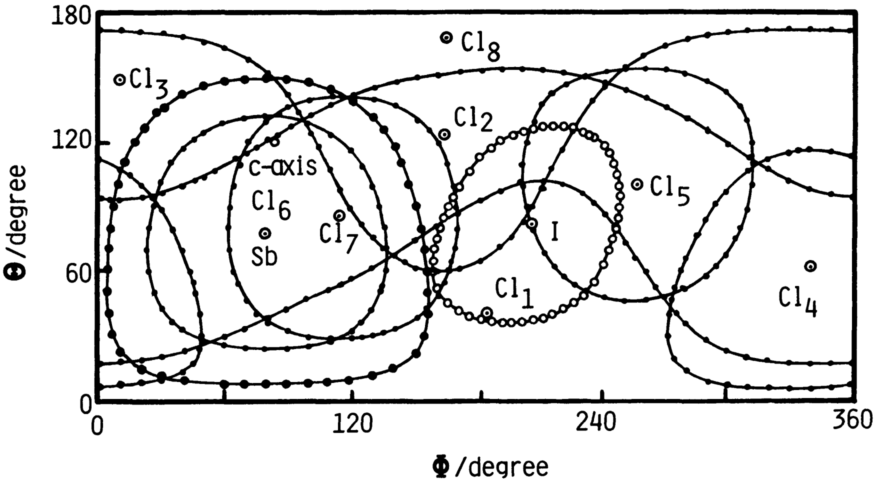

Fig. 5. Zero-splitting loci of ^{35}Cl, ^{127}I, and ^{121}Sb (ν_2) Zeeman lines in ICl_2SbCl_6. Cl_8 indicates the direction of the efg z axis calculated from the other crystal sites.

z axis at the bridging atom Cl_1 deviates from the Sb–Cl bond axis by ca. 6°, as shown in Fig. 4.

In ICl_2SbCl_6, forty zero-splitting loci for ^{35}Cl, ^{127}I, and ^{121}Sb are expected to be observed from its crystal structure, which belongs to the tetragonal space group $P4_1$.[12] However, only thiry-one loci could be found, since some efg z axes are nearly parallel to the rf field. The Zeeman effect on the Cl atoms bonded to the Sb atom was observed at 233 K, and that for the other atoms was observed at room temperature. The zero-splitting loci relating to one of the crystal sites are shown in Fig. 5. The NQR parameters are listed in Table 2. The η-value for the Cl_1 atom at room temperature was 0.6 percent less than that at 233 K. The efg axes and the corresponding bond directions are compared in Table 4, and the significant efg axes are shown in Fig. 6. The coupling constant of the I atom is comparable to the value of 3066±37 MHz at 4.2 K obtained from the ^{127}I Mössbauer effect.[13]

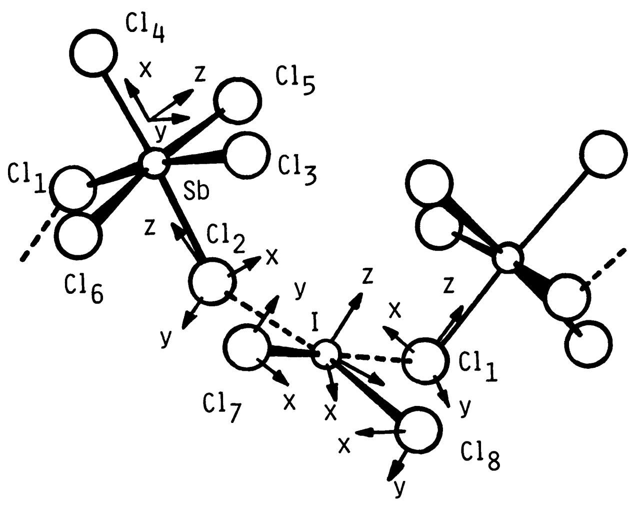

Fig. 6. Molecular shape of ICl_2SbCl_6.

Discussion

$I_3Cl_2SbCl_6$. The NQR spectrum is very similar to that reported previously for $I_2ClSbCl_6$,[11] except for some parts. The sample prepared by the method of Merryman and Corbett[11] exhibited the same spectrum as $I_3Cl_2SbCl_6$. This is verified by examining some samples. They reported that the absorption line due to ^{35}Cl was veiled by the very broad ^{121}Sb line and the corresponding ^{37}Cl line. These lines could not be seen, although the NQR spectrum was examined at various temperatures. The other parts of the spectrum in $I_3Cl_2SbCl_6$ were identical with that reported for $I_2ClSbCl_6$, except that the resonance frequency for the I_2 atom was somewhat different.

The I–I–I bond in the centrosymmetric planar $I_3Cl_2^+$ ion is completely linear. The I–I distance (2.906 Å) is considerably longer than a covalent I–I distance,[14] and is comparable to that in a symmetrical I_3^- ion of $(C_6H_5)_4AsI_3$ (2.90 Å).[21] In the present study the bonding in the I_3 part of the $I_3Cl_2^+$ ion was interpreted in terms of the 3c-4e bond. The atoms Cl_1, Cl_4, I_1, and I_2 are almost coplanar. The bridging $Cl_1 \cdots I_2$ bond and the terminal Cl_4–I_2 bond make angles of 89.55° and 92.62°, respectively, to the I_1–I_2 bond. The $Cl_1 \cdots I_2$–Cl_4 bond is almost linear and is orthogonal to the I–I–I bond. The $Cl_1 \cdots I_2$ distance (2.94 Å) is considerably shorter than the sum of van der Waals radii (3.9 Å), although the Cl_4–I_2 distance (2.33 Å) is nearly equal to the sum of the covalent radii. The $Cl_1 \cdots I_2$–Cl_4 bond can therefore be regarded as an asymmetrical three-center bond.

Taking the Sb–$Cl_1 \cdots I_2$ angle of 109.75° into account, the orbitals on the bridging Cl atom can be approximated by sp^3 hybridization. The orbital directed toward the Sb atom (ϕ_1) is nonequivalent to that directed toward the I_2 atom (ϕ_2). The latter is

Table 4. Angles between efg Axes and Bond Angles in ICl_2SbCl_6

Bond	Cl_1–Sb	Cl_2–Sb	Cl_3–Sb	Cl_4–Sb	Cl_5–Sb	Cl_6–Sb	Cl_7–I
Cl_2–Sb	86.78°						
	(81.6)[a]						
Cl_3–Sb	169.31	95.19					
	[172.4][b]	(91.3)					
Cl_4–Sb	96.71	175.38	91.36				
	(91.0)	[173.3]	(95.2)				
Cl_5–Sb	81.18	87.20	91.39	90.36			
	(88.9)	(86.5)	(92.4)	(93.1)			
Cl_6–Sb	84.45	89.03	91.60	91.67	176.34		
	(86.5)	(88.3)	(91.5)	(91.6)	[173.6]		
Cl_7–I	79.18	59.34	77.54	55.10	38.64	35.03	
	[72.7]	[55.1]	[78.4]	[57.4]	[40.3]	[34.2]	
Cl_8–I	51.49	44.4	41.46	49.46	80.12	79.41	93.41
	[46.9]	[53.3]	[39.7]	[46.9]	[79.7]	[79.8]	(92.5)
Sb z-axis	83.2	88.5	89.7	91.1	2.2	1.5	
x-axis	78.7	13.1	71.7	16.8	89.5	89.9	

a) The value in parentheses is the corresponding bond angle. b) The value in brackets was calculated from the atomic positions (Ref. 12).

presumed to be intermediate between ϕ_1 and the lone pair orbitals (ϕ_3 and ϕ_4). The orbital populations of ϕ_1 and ϕ_2 cannot be determined unequivocally. The populations, however, can be estimated by considering the following extremes: in one extreme ϕ_2 is equivalent to ϕ_1 (C_{2v} symmetry) and in another ϕ_2 is equivalent to the lone pair orbitals (C_{3v} symmetry). The hybrid orbitals belonging to the symmetry C_{2v} are expressed as follows;

$$\begin{aligned}
\phi_1 &= s\psi_s + (1 - s^2)^{1/2}\psi_{p_z},\\
\phi_2 &= s\psi_s + (1 - s^2)^{1/2}\{\psi_{p_z}\cos\theta + \psi_{p_x}\sin\theta\},\\
\phi_3 &= \{(1 - 2s^2)/2\}^{1/2}\psi_s\\
&\quad - s\{\psi_{p_z}\cos(\theta/2) + \psi_{p_x}\sin(\theta/2)\} + 2^{-1/2}\psi_{p_y},\\
\phi_4 &= \{(1 - 2s^2)/2\}^{1/2}\psi_s\\
&\quad - s\{\psi_{p_z}\cos(\theta/2) + \psi_{p_x}\sin(\theta/2)\} - 2^{-1/2}\psi_{p_y},
\end{aligned} \tag{1}$$

where $s^2=2^{-1}\{1-\cot(\theta/2)\}$ and θ is the angle between the bonds Sb–Cl_1 and $Cl_1\cdots I_2$. The z axis is taken along the Sb–Cl_1 and the x axis in the plane $SbCl_1I_2$, although the efg z axis deviates slightly from the Sb–Cl_1 bond. If ϕ_1 and ϕ_2 are occupied by a and b electrons, respectively, then the coupling constant data may be analyzed by the equations;

$$\begin{aligned}
&(2 - a)\cos^2(\theta/2) = \eta U_p/3,\\
&(2 - a) + (2 - b)\{1 - (3/2)\sin^2\theta\} = 2U_p\sin^2(\theta/2),
\end{aligned} \tag{2}$$

where $U_p=(e^2Qq)_{obs}/(e^2Qq)_{atom}$.

The hybrid orbitals belonging to the symmetry C_{3v} are given by[22]

$$\begin{aligned}
\phi_1 &= s_1\psi_s + (1 - s_1^2)^{1/2}\psi_{p_z},\\
\phi_2 &= s_2\psi_s + (1 - s_2^2)^{1/2}(\psi_{p_z}\cos\theta + \psi_{p_x}\sin\theta),\\
\phi_3 &= s_2\psi_s + (1 - s_2^2)^{1/2}\{\psi_{p_z}\cos\theta - (1/2)\psi_{p_x}\sin\theta\\
&\quad + (3^{1/2}/2)\psi_{p_y}\sin\theta\},\\
\phi_4 &= s_2\psi_s + (1 - s_2^2)^{1/2}\{\psi_{p_z}\cos\theta - (1/2)\psi_{p_x}\sin\theta\\
&\quad - (3^{1/2}/2)\psi_{p_y}\sin\theta\},
\end{aligned} \tag{3}$$

where $s_1^2=2\cot^2\theta$ and $s_2^2=1-2/(3\sin^2\theta)$, and therefore

$$\begin{aligned}
&2 - b = \eta U_p,\\
&\{(2 - a) - (2 - b)/3\}(1 - 2\cot^2\theta) = U_p.
\end{aligned} \tag{4}$$

Using the experimental bond angle, the values of $a=1.46$ and $b=1.84$ are obtained for the symmetry C_{2v}, and those of $a=1.45$ and $b=1.84$, for the symmetry C_{3v}. Even when the deviation of the z axis on the Cl_1 atom from the Sb–Cl_1 axis is taken into account, the variations in the populations of ϕ_1 and ϕ_2 are less than 0.5 percent.

Each I atom in the $I_3Cl_2^+$ ion is positively charged. The efg components can be written in terms of the population N_i on the i-th p orbital as follows;

$$\begin{aligned}
&q_{ii} = [N_i - (N_j - N_k)/2]q_{atom}(1 + \varepsilon)^\rho,\\
&\qquad i, j, k = x, y, z
\end{aligned} \tag{5}$$

where ρ is the charge at the I atom and ε is the correction parameter for the ionization of the I atom. The value of $\varepsilon=0.12$ was used for the I atom.[23] If only the p_z and p_x orbitals on the I atom participate on bonding and the p_y orbital is completely filled, the charge on the I atom is approximated by

$$\rho = [U_p(1 + \eta) - 1]/[U_p\varepsilon(1 + \eta) + 1]. \tag{6}$$

The populations deduced from Eqs. 1—6 are listed in Table 5.

The electron numbers for the I_2–I_1–I_2 and $Cl_1\cdots I_2$–Cl_4 bonds are 3.83 and 3.88, respectively, assuming that the s character for the bonding orbital of the Cl_4 atom is 0.15. These values are close to the expected value 4, notwithstanding neglect of the s and d character of the central I atom, and accordingly these bonds can be explained essentially in terms of the 3c-4e bond. The total charges of the I_1 and I_2 atoms are estimated to be +0.30 and +0.66, respectively. These values are comparable to the values of +0.2 and +0.5 which were calculated by using the relationship between bond length and bond order.[14,24]

Table 5. Electronic Distributions of Polyhalogen Cations and Surrounding Chlorine Atoms in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6

Compound	Atom	N_x[a]	N_y[a]	N_z[a]	N_σ[b]
$I_3Cl_2SbCl_6$	Cl_1	1.90	(2)	1.58	$1.45<a<1.46$ (Sb) $b=1.84$ (I_2)
	Cl_4	(2)	(2)	1.20	1.18
	I_1	1.93	(2)	0.77	
	I_2	1.53	(2)	0.81	
ICl_2SbCl_6	Cl_1	1.87	(2)	1.58	$1.48<a<1.53$ (Sb) $1.78>b>1.75$ (I)
	Cl_2	1.88	(2)	1.58	$1.42<a<1.44$ (Sb) $b=1.81$ (I)
	Cl_7	1.93	(2)	1.27	1.14
	Cl_8	1.93	(2)	1.25	1.11
	I	0.95	0.84	(2)	

a) The value in the parentheses is assumed to be 2. b) The population in the bonding atomic orbital. The symbols in parentheses indicate the atom toward which the hybrid orbital directs.

ICl_2SbCl_6. According to X-ray analysis,[12] the atoms I, Cl_1, Cl_2, Cl_7, and Cl_8 are almost coplanar. The z axis for the I atom is normal to this plane, and the x axis almost coincides with the bisector of the angle $\angle Cl_7ICl_8$. The z axes at the Cl_1 and Cl_2 atoms are nearly parallel to the corresponding Sb–Cl bond (see Table 4). The z axis at each bridging atom lies in the Sb–Cl···I plane. According to the ^{127}I Mössbauer effect, the value e^2Qqh^{-1} is positive.[13] This is in agreement with the results of the Zeeman effect of NQR.

The angles $\angle SbCl_7I$ and $\angle SbCl_8I$ are 116.8° and 114.8°, respectively. The valence orbitals at these bridging Cl atoms can be approximated by sp^2 hybridization. The wave functions can be written as follows:

$$\begin{aligned}
\phi_1 &= s_1\psi_s + s_2\psi_{p_z}, \\
\phi_2 &= (1/2)s_2\psi_s + 2^{-1/2}s_1\psi_{p_z} + 2^{-1/2}\psi_{p_x}, \\
\phi_3 &= (1/2)s_2\psi_s + 2^{-1/2}s_1\psi_{p_z} + 2^{-1/2}\psi_{p_x}, \\
\phi_4 &= \psi_{py}, \qquad (7)
\end{aligned}$$

where $s_1=\cot\theta$ and $s_2=(1-\cot^2\theta)^{1/2}$. If the populations in ϕ_1 and ϕ_2 are set equal to a and b, respectively, the relations between the NQR parameters and the orbital populations are given by

$$\begin{aligned}
&2 - b = (4/3)\eta U_p, \\
&\{(2 - a) - (2 - b)/2\}(1 - \cot^2\theta) = (1 - \eta/3)U_p. \qquad (8)
\end{aligned}$$

The ranges of the orbital populations can be estimated in a similar manner as above. These are listed in Table 5. According to X-ray analysis,[12] the distances of the bonds Sb–Cl_1, Sb–Cl_2, Cl_1···I, and Cl_2···I are 2.33, 2.29, 2.85, and 3.00 Å, respectively. The values of a and b correlate to the corresponding bond distance, as can be seen in Table 5. The populations of the valence p orbitals were calculated by assuming $N_z=2$. The net charge on the I atom is estimated to be +1.21. This is comparable to the value (+1.26) for I_2Cl_6[10] and that (+1.13) calculated for the isolated ICl_2^+ ion.[24]

If sp^3 hybridization with C_{2v} symmetry is adopted to the I atom, the interorbital angle is calculated to be 92.6° by using the relation $\eta=-3\cos\theta$.[25] This value is in good agreement with the crystallographically known angle of $\angle Cl_7ICl_8$ (92.5°).[12] The shortness of the distances I···Cl_1 and I···Cl_2 suggests that the interaction between the I atom and the surrounding Cl atoms cannot be described by simple sp^2 hybrid orbitals at the I atom.

The atomic arrangement around the I atom can be represented as a resonance $ICl_2^+SbCl_6^- \longleftrightarrow ICl_4^-$-$SbCl_4^+$, and is similar to that in the ICl_4^- ion.[12] The bonding in the ICl_4^- ion and I_2Cl_6 could be satisfactorily explained by considering only the valence p orbitals.[3,10] If this is the case for the ICl_4 part in ICl_2SbCl_6, the total number of electrons that take part in σ-bonding is 8. Examination of Table 5 reveals that the total electron number is about 7.6. Although this is somewhat smaller than the expected value, it is considered that the I atom in this complex presents essentially only the p orbitals for bonding, as well as the $I_3Cl_2^+$ ion. The comparatively large η-values for the terminal Cl atoms may be ascribed to the π-interaction of the p_x orbital at each Cl atom with the p_x and p_y orbitals at the I atom.

The η-values of ^{121}Sb in $I_3Cl_2SbCl_6$ and ICl_2SbCl_6 are significantly large. There is no experimental atomic coupling constant for ^{121}Sb. If the calculated value of 1300 or 945 MHz is used for $(e^2Qqh^{-1})_{\text{atom}}$,[26,27] the imbalance in the orbital population is estimated to be at most 0.02 to 0.03. Hence, a slight imbalance in the population of the p orbitals brings about the large η-value. This is ascribable to the large ionic character of the Sb atom.

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