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Structural Study of the Molecular Complex of Antimony Trichloride with Benzene by Means of the Pure Quadrupole Resonance

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The Zeeman effect of ^{35}Cl pure quadrupole resonance was studied on a single crystal of the $2SbCl_3 \cdot C_6H_6$ molecular complex at room temperature; it was found that the Cl-Sb-Cl bond angles of two nonequivalent $SbCl_3$ molecules are 96.2°, 94.7°, 92.2°; 94.5°, 92.8°, and 95.2°, with an uncertainty of 1°. The asymmetry parameters for the six chlorine atoms were found to be 0.085 ± 0.001, 0.055 ± 0.004, 0.117 ± 0.005, 0.119 ± 0.005, 0.112 ± 0.005, and 0.160 ± 0.007, listed in the order of decreasing resonance frequencies. The bond character of the Sb-Cl bond was also calculated from the quadrupole coupling constant. It was found that the Sb-Cl bond corresponding to the lowest resonance lines in each nonequivalent $SbCl_3$ molecule has a larger ionicity than the remainder. Moreover, the former has less of a temperature dependence than the latter. Finally, this complex may be assigned to the C_i or C_1 symmetry class from the patterns of zero-splitting and from the intensity ratios of the multiplet of the spectrum.

It is well known that antimony trichloride forms 2 : 1 or 1 : 1 molecular complexes with a number of aromatic compounds. These complexes have been studied by various methods, but their crystal structures are still unknown. Studies of the pure quadrupole resonance on these complexes have been performed by several authors.[1-3] All of them, however, used polycrystalline samples, and their information was limited to the bond nature of the component. The aim of the present work is to deduce the asymmetry parameters of the electric-field gradient at the relevant nuclei, the nature of the Sb-Cl bond, and the bond angles of Cl-Sb-Cl, as well as to assign the resonance lines and find the crystallographic symmetry. The 2 : 1 molecular complex of antimony trichloride with benzene was chosen as the sample for the basic research in order to see how the molecular shape and the bond character of antimony trichloride change in forming the complex.

The study of antimony trichloride itself was performed prior to that of the complex. Fortunately, its crystal structure had already been established by X-ray analysis[4,5] as well as by the pure quadrupole resonance.[4,6]

Experimental

The molecular complex was prepared in the following way.[7] One mole of pure benzene and two moles of pure antimony trichloride were dissolved in carbon disulfide individually, and then these solutions were mixed together. After the solution had been concentrated, the crystal was filtered and dried *in vacuo*. The complex was identified by determining the melting point and the chlorine content. The single crystal of the complex was obtained by a melting method described previously.[8] It was 10 mm in diameter and 25 mm long.

The spectrometer consisted of a super-regenerative oscillator, an amplifier, and a detector. The absorption lines were displayed on an oscilloscope. A Zeeman field of about 200 gauss was applied by a Helmholtz coil. The crystal could be rotated about a fixed axis of the crystal, and its angle Φ could be measured to within ±0.1°. On the other hand, the magnetic field could be rotated on a horizontal plane, and its angle Θ could be measured to within ±1′. The patterns of zero-splitting were observed at about 21°C.

Results and Discussion

The $2SbCl_3 \cdot C_6H_6$ molecular complex has six resonance lines of the same intensity, all due to ^{35}Cl, at room temperature as well as at the temperature of liquid nitrogen,[3] as is shown in Table 1. Let us now label the six resonance lines $\nu_1, \nu_2, \cdots, \nu_6$ from the lower to the higher, and the chlorine atoms contributing to $\nu_1, \nu_2, \cdots \nu_6$, $Cl_1, Cl_2 \cdots, Cl_6$.

The pattern of the zero-splitting was obtained by measuring the Zeeman effect on the resonance

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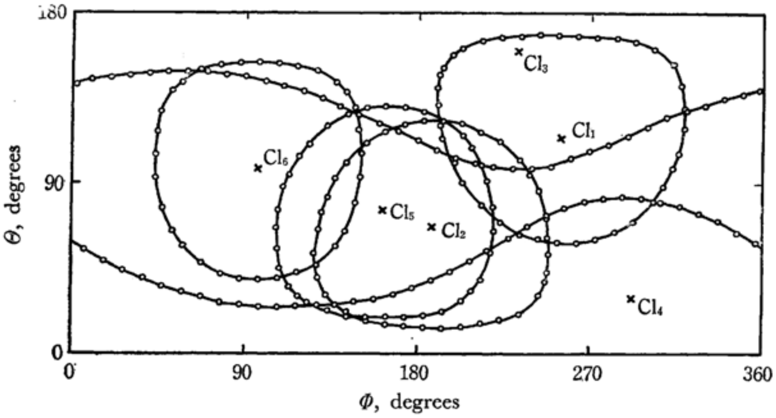


Fig. 1. Zero-splitting patterns of Zeeman lines of the complex $2SbCl_3 \cdot C_6H_6$. The axis of $\Theta=0$ is taken as the rotational axis of the sample tube. The plane of $\Phi=0$ is arbitrarily chosen.

TABLE 1. PURE QUADRUPOLE RESONANCE FREQUENCIES DUE TO ^{35}Cl IN ANTIMONY TRICHLORIDE AND ITS COMPLEX WITH BENZENE

Compound		Resonance frequency, Mc/sec 21°C	Resonance frequency, Mc/sec −196°C	$\Delta\nu$[a] kc/sec
$2SbCl_3 \cdot C_6H_6$	ν_1	18.543	18.655	112
	ν_2	18.647	18.749	102
	ν_3	19.606	20.068	462
	ν_4	19.973	20.349	376
	ν_5	20.047	20.459	412
	ν_6	20.077	20.509	437
$SbCl_3$	ν'_1	19.179	19.304	116
	ν'_2	20.419	20.912	480

a) $\Delta\nu$ is the difference between the resonance frequencies at 21 and −196°C.

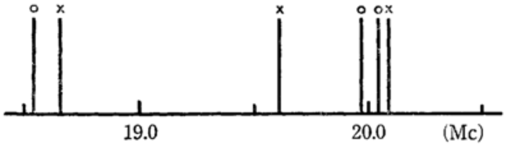
line; it is reproduced in Fig. 1. Although the Zeeman patterns of six resonance lines are shown in Fig. 1, one of them was missing in the original sample because the principal z axis of the field gradient at the chlorine atom contributing to the missing line was nearly parallel to the rf coil axis, thus reducing its intensity considerably. In order to observe the pattern, we had to use another sample, a single crystal in which the crystal axes were oriented differently. For this sample, however, another resonance line was missing. Combining both results, the six patterns shown in Fig. 1 were obtained.

The direction of the principal z axis of the field gradient of the chlorine atom can be determined by the zero-splitting pattern.[9] Generally the z axis is parallel to the direction of the Sb-Cl bond in the complex. Consequently, the angle between any two Sb-Cl bonds can be deduced; these angles are listed in Table 2. It should be remarked here that the z axis may deviate slightly from the direction of the bond which is bound to the benzene ring. As has been stated above,

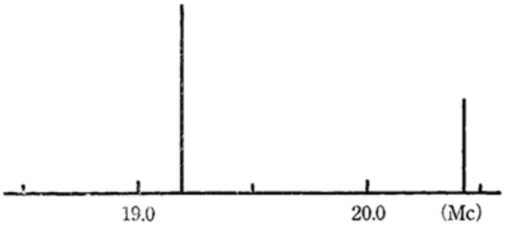
TABLE 2. THE ANGLES BETWEEN THE Sb-Cl BONDS[a]

Bond	Sb-Cl_1	Sb-Cl_2	Sb-Cl_3	Sb-Cl_4	Sb-Cl_5
Sb-Cl_2	69°28′				
Sb-Cl_3	128°46′	94°39′			
Sb-Cl_4	94°48′	93°46′	140°19′		
Sb-Cl_5	94°28′	25°17′	78°24′	95°9′	
Sb-Cl_6	139°15′	96°12′	92°9′	48°29′	78°8′

a) The experimental error is ±1°.



$2SbCl_3 \cdot C_6H_6$



$SbCl_3$

Fig. 2. Pure quadrupole resonance spectra of antimony trichloride and its complex with benzene. Resonance lines with the same mark, circle or cross come from the same antimony trichloride molecule.

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9) K. Shimomura, *J. Phys. Soc. Japan*, **12**, 657 (1957).

six resonance lines of the same intensity are observed in a polycrystalline sample, but they can not be grouped into any sets. This problem can, however, be solved easily when the Zeeman effect on the resonance lines is examined. The results are shown in Fig. 2, in which those lines labeled by the same mark, a circle or a cross, come from the same molecule. The ν_1 and ν_2 resonance frequencies are considerably lower than the remainder. These lowering must be caused by some factors other than the crystal field. One possibility is that they correspond to the bonds which reside on the benzene ring.

The values of the asymmetry parameter are determined from the distortion of zero-splitting loci by the following equation:10)

$$\eta = 3(\sin^2\theta_{max} - \sin^2\theta_{min})/(\sin^2\theta_{max} + \sin^2\theta_{min}) \tag{1}$$

where θ_{max} and θ_{min} are maximum and minimum zero-splitting angles, corresponding to $\phi=0°$ and 90° respectively. Consequently, the quadrupole coupling constants are calculated by this equation, substituing the value of η:

$$\nu = (eQq_{zz}/2h)(1+\eta^2/3)^{1/2} \tag{2}$$

The values of η and eQq_{zz} derived in this way are listed in Table 3.

The bond character of the Sb–Cl bond can be determined from η and eQq_{zz}. The resonance structures are considered to be as shown in Fig. 3 in general. There is no doubt about the existence of covalent (1) and ionic (2) structures, but there must be a double-bond structure (3) as well. Since the ground state of antimony is $5s^2 5p^3$, the sp^3 hybrid orbital seems to occur in $SbCl_3$ to some extent. Kimball11) discussed the possibilities of double-bond formation by treating the problem of direct valence from the viewpoint of the group theory. According to him, the sp^3 hybrid orbital is capable of forming a strong π bond with d^2 and a weak π bond with d^3. However, Gordy12) proposed that the tendency to form a double bond by using d orbitals falls off rapidly in descending rows in the periodic table, essentially vanishing for such fifth-row elements as Sn and Sb. The Sb–Cl bond length of $SbCl_3$, as claculated by the equation of Schomaker and Stevenson,13) is in good agreement with the observed value if the Sb–Cl bond has a little double-bond character in $SbCl_3$. If the double-bond character of the Sb–Cl bond can be neglected, the bond character can be derived as follows.

TABLE 3. THE NATURE OF Sb–Cl BONDS IN $SbCl_3$ MOLECULE

Compound	Species	eQq_{zz} Mc/sec	U_p %	η %	i %
$2SbCl_3 \cdot C_6H_6$	Cl_1	36.927	33.7	16.0±0.7	60.4
	Cl_2	37.216	33.9	11.2±0.5	60.1
	Cl_3	39.122	35.7	11.9±0.5	58.0
	Cl_4	39.854	36.3	11.7±0.5	57.3
	Cl_5	40.074	36.5	5.5±0.4	57.1
	Cl_6	40.106	36.6	8.5±0.1	56.9
$SbCl_3$	Cl'_1	38.205	34.8	15.3	59.0
	Cl'_2	40.794	37.2	5.7	56.1

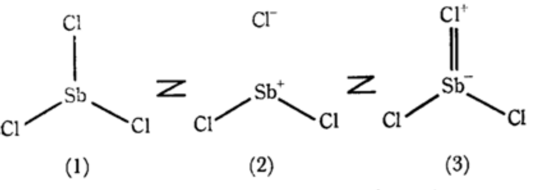

Fig. 3. Resonance structures of antimony trichloride.

The number of the unbalanced p-electron is given by:

$$U_p = (1-i)(1-s) \tag{3}$$

where i is the ionic character and s is the s electron character, which is assumed to be equal to 0.15.14) On the other hand, the value of U_p is evaluated from the observed quadrupole coupling constant:

$$U_p = (eQq_{zz})_{obs}/(eQq_{zz})_{atom} \tag{4}$$

where $(eQq_{zz})_{atom}$ is 109.7 Mc/sec.15) The ionic character, i, can be calculated from Eqs. (3) and (4). The results are listed in Table 3. It may be noted that the $Sb–Cl_1$ and $Sb–Cl_2$ bonds have a larger ionic character than do the other bonds, which have nearly the same ionic character as those of $SbCl_3$ in its pure state. Thus it seems likely that the π electron of the benzene is transferred to the chlorine atom through the $Sb–Cl_1$ or $Sb–Cl_2$ bond.

The molecular shape of the $SbCl_3$ in the complex and its pure crystal are shown in Fig. 4, the bond angles being taken from Table 2. Two nonequivalent $SbCl_3$ molecules in the complex crystal have almost the same shape, but show differently-spaced resonance frequencies. That is, in the $Sb–Cl_3$ molecule (A) the smallest angle is between $Sb–Cl_3$ and $Sb–Cl_6$, which correspond to the middle and the highest frequencies respectively, whereas in the other molecule, $SbCl_3$ (B), the smallest angle is between $Sb–Cl_1$ and $Sb–Cl_4$, the lowest and the middle frequencies. The shape

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10) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).

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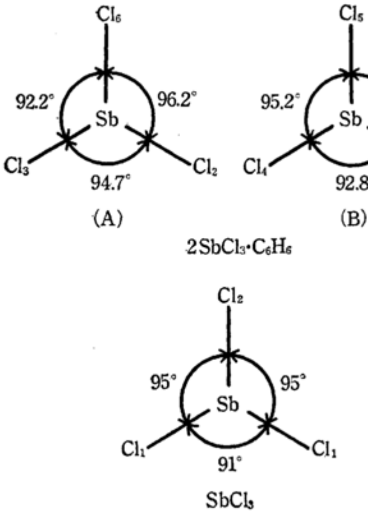

Fig. 4. Shapes of antimony trichloride molecule in the pure state[4] and its complex with benzene.

of $SbCl_3$ (B) is similar to that of $SbCl_3$ in its pure crystal; accordingly, the asymmetry parameter of Sb in the former should be equal to that in the latter. This is really the case; the findings on the ^{123}Sb resonance will be reported elsewhere. In this complex, benzene may combine with the chlorine atom to form the complex; that is, some charge may be transferred to the chlorine atom from benzene. Therefore, the bond angles of $SbCl_3$ in the complex may be expected to increase as a result of the stronger coulombic repulsion between chlorine atoms; however, only a little change may be seen, as is shown in Fig. 4.

We will now discuss the structure of $SbCl_3$ in the complex further. Daasch[16] assumed, from its infrared spectrum, that the $2SbCl_3 \cdot C_6H_6$ molecular complex has C_{2v} symmetry in the solid state and C_{3v} symmetry in the liquid state. Perkampus and Baumgarten[17] proposed, from the infrared spectrum, that the possible symmetry of the complex crystal was C_{2v}, C_s, or C. From the present Zeeman analysis it may be concluded that this complex has C_i or C_1 symmetry in the solid state; there is only one kind of pattern for each resonance line, as is shown in Fig. 1, and the intensities of all the resonance lines are equal.[18] If the structure of this complex has C_{2v} or C_s symmetry, at least one resonance line has two kinds of patterns. However, it is impossible to distinguish C_i from C_1 by the Zeeman analysis, because both positive and negative directions of the z axis of the field gradient give the same result.

Ashkanaji *et al.*[19] and Raskin[20] have reported on the Raman spectrum of a solution of antimony trichloride in benzene. The former authors observed two new lines which Raskin could not observe; they attributed these lines to the bending and stretching vibrations of the bond between antimony and benzene. On the contrary, it seems more probable, for the following reasons, that benzene combines with the chlorine atom. First, the lowest resonance frequency, ν_1, or ν_2, in each $SbCl_3$ molecule has the least temperature dependence, as may be seen in Table 1. This runs parallel to the more restricted motion of the chlorine atom bound to benzene. Second, the chlorine, Cl_1 or Cl_2, corresponding to the lowest line has the largest ionic character, which may be interpreted as having been brought about by the charge transfer from benzene. A somewhat similar situation arises in the molecular complex of carbon tetrabromide with *p*-xylene.[21] Two bromine atoms of the carbon tetrabromide in this complex are bound to benzene rings, while the other two bromine atoms are free from complexing. Hooper[22] tentatively assigned the lower frequency to the complexing bromine atoms. These results may support our conclusion, although the final decision should be made on the basis of X-ray analysis.

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