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The Molecular Structure of Antimony Trichloride as Determined by Gas-electron Diffraction[1]

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The molecular structure and mean amplitudes of $SbCl_3$ have been determined, by the sector-microphotometer method of gas-phase electron diffraction, to be as follows: r_g(Sb–Cl) = 2.333±0.003 Å, r_g(Cl–Cl) = 3.50±0.02 Å, $\theta_\alpha = 97.2° \pm 0.9°$, l(Sb–Cl) = 0.063±0.004 Å, and l(Cl–Cl) = 0.147±0.014 Å. The zero-point average structure derived from the diffraction results by the use of the estimated potential constants is consistent with the rotational constants, B_z, derived from the B_0 of microwave measurements. The joint use of the ED and MW data has given a value of 2.326±0.001 Å for r_z(Sb–Cl).

Some regularities exist among the molecular structures of trihalides of the Vb-group elements.[2–5] That is, the experimental bond length is generally shorter than the sum of the covalent radii by an amont which can be related to the difference between the electronegativities of the central atom and the halogen. Valence angles increase with a decrease in the electronegativities of halogens relative to the Vb-group atom.

The molecular structure of antimony trichloride was previously investigated by the visual method of electron diffraction (ED)[6,7] and by microwave spectroscopy (MW)[8] (Table 1). The reported uncertainties in the MW structure are much smaller than those in the visual ED data. However, the bond angle given by MW seems to be too large by 2 or 3 degrees, whereas the bond length is reasonable, as judged from the trend found in the structures of many trihalides of the Vb-group atoms (see Figs. 3 and 4 of Ref. 4).

TABLE 1. PREVIOUS RESULTS ON THE MOLECULAR STRUCTURE OF $SbCl_3$

	r(Sb–Cl)	θ(ClSbCl)
ED(visual)[a]	2.37 ±0.02 Å	104° ±2°
ED(visual)[b]	2.37 ±0.02 Å	96° ±4°
MW[c]	2.325±0.005 Å	99.5°±1.5°

a) Ref. 6 b) Ref. 7 c) Ref. 8

The present study was undertaken in order to determine the geometry of this molecule more accurately by the sector-microphotometer method of ED. At just the same time, Matsumura[9] reinvestigated the microwave spectra and obtained the rotational constants, B_0, for $^{121}Sb^{35}Cl_3$ and $^{123}Sb^{35}Cl_3$, which were very close to the previous values, and also the B_0 values for $^{121}Sb^{37}Cl_3$ and $^{123}Sb^{37}Cl_3$, which had not been measured before. The structure determined from these rotational constants is: r_0(Sb–Cl) = 2.323±0.005 Å and θ(ClSbCl) = 96°50′±30′.[9] The bond length is essentially equal to the previous MW value, but the angle is not. This structure is in fair agreement with the existing regularities in relation to the structures of related molecules.

In the present report, an electron-diffraction determination of the thermal average structure will be described. Furthermore, the consistency between the ED and MW data will be examined and the zero-point average structure will be derived by the joint use of both sets of data.

Experimental

A sample of antimony trichloride (over 99% pure) obtained from Wako Pure Chemical Industries, Inc., was used without further purification. Electron-diffraction photographs were

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[2] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

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[6] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Farad. Soc.*, **33**, 852 (1937).

[7] S. M. Swingle, quoted by P. W. Allen and L. E. Sutton, *Acta Crystallogr.*, **3**, Pt. 1, 46 (1950).

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taken with a diffraction unit employing an r^3-sector[10] and a high-temperature nozzle made of stainless steel[11] under the following conditions: camera length, 12.39 cm; accelerating voltage, about 42 kV; exposure time, 3—4 minutes; electron-beam current, about 0.24 μA and nozzle temperature, about 70°C. The pressure in the diffraction chamber during exposures was about 7×10^{-5} Torr. Diffraction patterns of CS_2 molecules were taken at the same nozzle temperature just after taking the sample patterns in order to measure the scale factor accurately.[12]

Photographs were recorded on Fuji process hard plates and were developed at 20°C for 5 min with a FD-131 developer diluted twice. The photographic densities were measured with a digital microphotometer at intervals of 1/3 mm.[4] The densities were converted to intensities by using the relation[4] $E=D(1+0.03D)$; they were also corrected for the imperfection of the sector opening from an ideal r^3-shape. Seven plates, four for $SbCl_3$ and three for CS_2, taken in the same sequence of exposures, were selected for structure analysis.

Analysis of Data

The intensities were leveled by the theoretical backgrounds calculated by the use of the elastic and inelastic scattering factors taken from the literature.[13–15] The experimental backgrounds and molecular intensities were determined by using the criterion that there should appear no ghost peak in the range of $r\leqq1.05$ Å in the radial distribution curve, which was itself calculated in a manner described elsewhere.[4]

The interatomic distances, r_a(Sb–Cl) and r_a(Cl–Cl), the mean amplitudes, l(Sb–Cl) and l(Cl–Cl), and the index of resolution, k, were determined by a least-squares fitting of the experimental molecular intensities to the following theoretical expression:

$$qM(q) = k\sum_{i\neq j} A_{ij}\mu_{ij}\cos\Delta\eta_{ij}\exp\left\{-\frac{1}{2}\left(\frac{\pi}{10}q\right)^2 l_{ij}{}^2\right\}$$
$$\times\sin\left\{\frac{\pi}{10}q\left(r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa_{ij}\right)\right\} \qquad (1)$$

Here, all the notations follow usual usage.[16] The asymmetry parameter, $\kappa_{\text{Sb-Cl}}$, was estimated to be 1.2×10^{-5} Å^3 by the diatomic approximation[17] and was fixed in the least-squares analysis. The $\kappa_{\text{Cl-Cl}}$ was ignored. The thermal average distances, r_g, were obtained as sums of r_a and l^2/r_a.

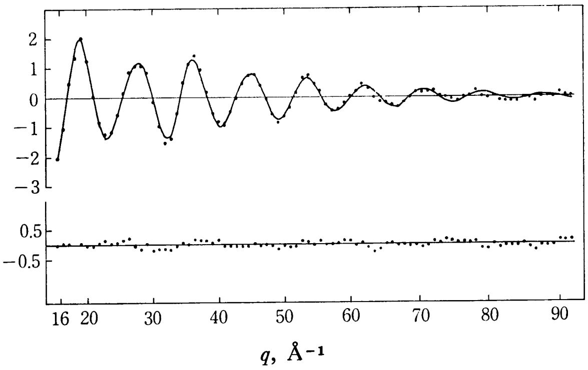

Fig. 1. Molecular intensity (dots for observed values and the solid curve for the best-fit theoretical intensity) and the residuals.

Table 2. Results of the least-squares analysis

	Average[a]	σ_1[b]	σ_2[b]
k	0.882	0.014	0.006
r_a(Sb-Cl)	2.3307	0.0010	0.0003
l(Sb-Cl)	0.0632	0.0017	0.0004
r_a(Cl-Cl)	3.4926	0.0072	0.0034
l(Cl-Cl)	0.1467	0.0054	0.0014

a) The averages of the results from four plates are listed.
b) The definitions of σ_1 and σ_2 are given in Ref. 19.

Table 3. Error matrix[a]

	k	r_a(Sb-Cl)	l(Sb-Cl)	r_a(Cl-Cl)	l(Cl-Cl)
k	231	9	72	66	71
r_a(Sb-Cl)		16	−1	2	7
l(Sb-Cl)			29	19	22
r_a(Cl-Cl)				118	9
l(Cl-Cl)					89

a) $\sigma_{ij}=\text{sgn}[(\boldsymbol{B}^{-1})_{ij}][|(\boldsymbol{B}^{-1})_{ij}|\cdot\boldsymbol{V}^*\boldsymbol{PV}/(n-m)]^{1/2}$, where the notations follow Ref. 19. Units for r_a and l are 10^{-4} Å and the index of resolution, k, is dimensionless.

The experimental molecular intensity and the theoretical one calculated from the best-fit parameters are shown in Fig. 1.[18] The least-squares results are listed in Table 2. An error matrix is given in Table 3.

Results and Discussion

The final results are summarized in Table 4, along with the limits of error estimated in the procedure described in a previous paper.[4] In order to derive a bond angle with a physically clear meaning,[20] the r_g distances were converted to the r_α distances by the following relation:[21,22]

$$r_\alpha = r_g - \frac{\langle\Delta x^2\rangle+\langle\Delta y^2\rangle}{2r_e} - \delta r_{\text{rot}} \qquad (2)$$

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[12] The r_a(C–S) and r_a(S–S) distances at 70°C were estimated to be 1.5572 Å and 3.1080 Å, respectively, by the use of the spectroscopic constants taken from T. Ijima and Y. Morino, This Bulletin, **35**, 1661 (1962).

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[17] K. Kuchitsu, *ibid.*, **40**, 505 (1967).

[18] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan. A copy may be secured by citing the document number (Document No. 7303).

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TABLE 4. MOLECULAR PARAMETERS OF ANTIMONY TRICHLORIDE DETERMINED BY ED[a)] (r AND l IN Å UNIT)

	Sb-Cl		Cl-Cl
r_g	$2.332_8 \pm 0.003_3$		3.499 ± 0.019
l	0.063 ± 0.004		0.147 ± 0.014
r_α	$2.328_7 \pm 0.003_3$		3.494 ± 0.019
θ_α(ClSbCl)		$97.2 \pm 0.9°$	
r_z	$2.324_8 \pm 0.004_2$		
θ_z(ClSbCl)		$97.2 \pm 1.0°$	

a) All parameters except for r_z and θ_z are given values at 343°K.

The stretchings due to the perpendicular thermal vibrations, $(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2r_e$, were calculated to be 0.0028 Å and 0.0020 Å for Sb–Cl and Cl–Cl respectively by using the harmonic potential constants estimated below.[22)] The centrifugal stretchings, δr_{rot}, were evaluated to be 0.0013 Å and 0.0030 Å for Sb–Cl and Cl–Cl respectively.[23)] The r_α-structure thus obtained is also given in Table 4.

The general quadratic potential field of a pyramidal XY_3-type molecule can be defined by using the following six potential constants associated with the internal symmetry coordinates, as has been described in a previous paper:[22)]

$$\begin{aligned} F_{11} &= f_r + 2f_{rr}\,, \\ F_{12} &= f_{r\theta'} + 2f_{r\theta}\,, \\ F_{22} &= f_\theta + 2f_{\theta\theta}\,, \\ F_{33} &= f_r - f_{rr}\,, \\ F_{34} &= f_{r\theta'} - f_{r\theta}\,, \\ F_{44} &= f_\theta - f_{\theta\theta}\,. \end{aligned} \tag{3}$$

Since not all the potential constants can be determined uniquely from four vibrational frequencies, the experimental mean amplitudes were used as supplementary information. The fundamental frequencies measured in the liquid state[24)] were used because those for the gas phase were not available. A sufficiently large number of sets of mean amplitudes were calculated from the potential fields compatible with the frequencies and compared with the observed mean amplitudes. The potential constants were then estimated to be as is shown in Table 5. The theoretical values of the mean amplitudes corresponding to the estimated potential constants were 0.062 ± 0.006 Å and 0.134 ± 0.008 Å for l(Sb–Cl) and l(Cl–Cl) respectively.

TABLE 5. POTENTIAL CONSTANTS OF $SbCl_3$ ESTIMATED FROM THE OBSERVED MEAN AMPLITUDES AND VIBRATIONAL FREQUENCIES (IN md/Å UNIT)

A_1 species		E species	
F_{11}	$2.0_6{}^{+0.2^{a)}}_{-0.4}$	F_{33}	$1.5_0{}^{-0.2}_{+0.1}$
F_{12}	-0.1 ± 0.2	F_{34}	0.2 ± 0.1
F_{22}	$0.22^{-0.02}_{+0.10}$	F_{44}	$0.20^{+0.07}_{-0.03}$

a) The uncertainties take the upper and lower signs in the same order.

The molecular structure given in Table 4 is very close to the r_0-structure determined by a recent microwave study.[9)] However, this may not necessarily indicate that both the MW and the ED data are consistent, for different definitions of the molecular parameters were used. In order to see the consistency of the data, the r_α-structure measured by ED was converted to the zero-point average structure (r_z) and the rotational constants observed by MW were reduced to the rotational constants, B_z, corresponding to the r_z-structure. The observed ground-state rotational constants are given in Table 6.

TABLE 6. GROUND-STATE ROTATIONAL CONSTANTS AND ZERO-POINT AVERAGE ROTATIONAL CONSTANTS (IN MHz UNIT)

	$^{121}Sb^{35}Cl_3$	$^{123}Sb^{35}Cl_3$	$^{121}Sb^{37}Cl_3$	$^{123}Sb^{37}Cl_3$
B_0[a)]	1753.6_0	1750.0_4	1670.3_5	1667.0_0
B_z	1751.4_3	1747.8_7	1668.3_2	1664.9_7

a) Determined by Matsumura.[9)]

The following relations were used for deriving r_z(Sb–Cl) from r_α(Sb–Cl):[21)]

$$r_z \simeq r_\alpha - (\langle \Delta z \rangle_T - \langle \Delta z \rangle_0) \tag{4}$$

$$\begin{aligned} \langle \Delta z \rangle &\simeq \langle \Delta r \rangle - \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r_e} \\ &\simeq \frac{3}{2} a_3 \langle \Delta z^2 \rangle - \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r_e} \end{aligned} \tag{5}$$

The Morse parameter, a_3, was assumed to be 2 Å^{-1}. The parallel and perpendicular mean amplitudes were computed from the estimated potential constants, and the correction term, $\langle \Delta z \rangle_T - \langle \Delta z \rangle_0$, was evaluated to be $0.003_9 \pm 0.002_5$ Å. On the other hand, the difference in bond angles, $(\theta_z - \theta_\alpha)$, was simply assumed to be $0 \pm 0.3°$.[25,26)] The zero-point average structure thus estimated is also shown in Table 4.

The B_z values were derived from the B_0's as:[5)]

$$B_z = B_0 - \delta B_{\text{vib}} - \delta B_{\text{cent}} \tag{6}$$

The sums of δB_{vib} and δB_{cent} were estimated, according to the theory of rotation-vibration interaction,[27,28)] to be 2.17 ± 0.11 MHz and 2.03 ± 0.10 MHz for (^{121}Sb, ^{123}Sb)^{35}Cl$_3$ and (^{121}Sb, ^{123}Sb)^{37}Cl$_3$ respectively. The B_z values are also listed in Table 6.

In Fig. 2, the relation between r_z(Sb–Cl) and θ_z-(ClSbCl), constrained by zero-point average rotational constants, are shown by four lines. The rectangle denotes the limits of the molecular structure determined by ED. The average structure corresponding to the crossing point of the MW lines is: $r_z = 2.324_8$ Å and $\theta_z = 96.2°$. This is slightly different from the r_0-structure,[9)] $r_0 = 2.323 \pm 0.005$ Å and $\theta = 96°50' \pm 30'$. The MW bond angle appears to be about 1° smaller

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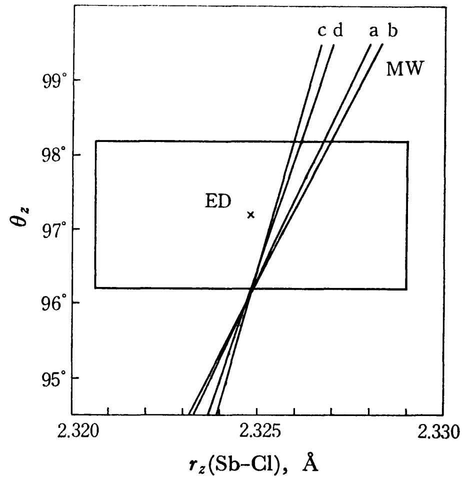

Fig. 2. The zero-point average structure obtained by ED and the relations given by the MW rotational constants (a): ^{121}Sb^{35}Cl$_3$, (b): ^{123}Sb^{35}Cl$_3$, (c): ^{121}Sb^{37}Cl$_3$, (d): ^{123}Sb^{37}Cl$_3$.

than the diffraction value, while the bond lengths from the two sets of data are in perfect agreement. However, it should be noted that the above MW structure is sensitive to a systematic error due to unknown isotopic shifts of the r_z-structure.[5] That is, the crossing point of the MW lines in Fig. 2 may shift remarkably even as a result of an isotope effect of r_z as small as 0.0003 Å. Since all the microwave lines pass near the center of the ED rectangle, we may conclude that the ED and MW data are consistent. By combining the ED valence angle with the MW lines, we can determine r_z(Sb–Cl) to be $2.325_9 \pm 0.001_1$ Å, which may be regarded as much more reliable and precise than the ED value. The corresponding r_g distance is 2.334± 0.003 Å.

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