The Molecular Structure of Gaseous Bismuth Trichloride Determined by Electron Diffraction

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Gas-phase electron diffraction data for $BiCl_3$ have been collected with a nozzle temperature of 185 °C. The data are consistent with a model of C_{3v} symmetry having r_a(Bi-Cl) = 242.3(5) pm and ∠ClBiCl = 97.3(2)°. Estimated standard deviations are given in units of the last digit. Secondary bonding Cl→Bi in the solid phase increases the average Bi-Cl bond distance by 8 pm and reduces the average ∠ClBiCl angle by 6°.

Dedicated to Professor Otto Bastiansen on his 70th birthday

While accurate structure parameters are available for the gaseous Group 15 trichlorides NCl_3,[1] PCl_3,[2] $AsCl_3$[3] and $SbCl_3$[4], accurate data on gaseous $BiCl_3$ are lacking, perhaps because of its high reactivity and low volatility. The present study was undertaken to fill the gap.

Experimental

Commercially available $BiCl_3$ (Fluka) was used without further purification. Electron diffraction data were recorded on the EG-100 A apparatus in Budapest,[5] with nozzle-to-plate distances of about 50 (three plates) and 19 cm (four plates). The sample container and nozzle were made of molybdenum,[6] and the vaporising temperature was 183±5 °C. Mass spectra recorded under similar conditions contained no peaks indicating the presence of associated species or impurities.

Atomic intensities ("backgrounds") were subtracted in the manner described by Hargittai and Hargittai.[7] Atomic scattering factors $f_Z'(s)$ were taken from Schäfer *et al.*[8] Molecular intensities were modified through multiplication by $s/|f_{Bi}'(s)||f_{Cl}'(s)|$. The 50 cm curves extended from s = 20 to 140 nm^{-1} with increments of 1.25 nm^{-1}. The 19 cm data were of lower quality and could not be brought into agreement with calculated intensities when $s > 200$ nm^{-1}. The structure refinements were therefore based on intensities ranging from s = 105.0 to 200.0 nm^{-1} with increments of 2.50 nm^{-1} (see Fig. 1).

The molecular symmetry was assumed to be C_{3v}, and r_a distances and vibrational amplitudes l refined by least-squares calculations on the intensity data. The best values are listed in Table 1. An experimental RD curve and a difference curve are shown in Fig. 2.

Discussion

Internuclear distances (r_a), root-mean-square vibrational amplitudes (l) and valence angles of the Group 5 trichlorides as determined by gas-phase electron diffraction are listed in Table 1. Bond distances and valence angles in the gaseous Group 15 element compounds ElH_3, $El(CH_3)_3$ and $ElCl_3$ are displayed in Fig. 3.

As expected, all bond distances increase as the group is descended. The El-H bond distance curve from El = N to El = Sb and the El-Cl bond

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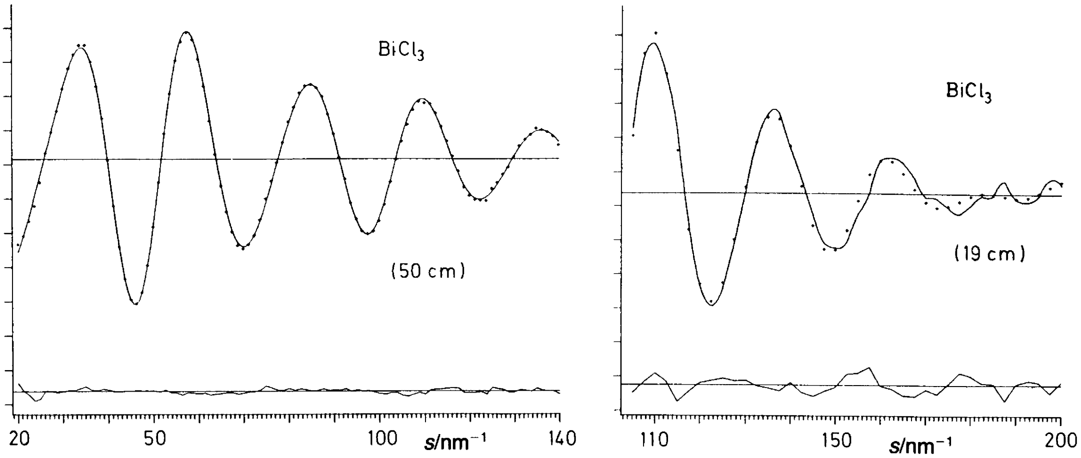

Fig. 1. Modified molecular intensity curves and difference curves for $BiCl_3$.

distance curve from El = P to El = Bi are nearly parallel to the El-C bond distance curve. Only the N-Cl bond distance in the very unstable compound NCl_3 breaks the pattern by being about 10 pm longer than predicted by extrapolation from the other bond distances. The shape of the bond distance curves have been discussed elsewhere.[9]

It is well known that the valence angles in the Group 15 trihydrides approach 90° (or rather 91°) as the group is descended. The valence angles of the trichlorides, on the other hand, approach 97°. The reason for the larger ClElCl angles is not clear: If the angle was determined by non-bonded Cl···Cl repulsions, it would decrease more rapidly with increasing El-Cl bond distance; on going from $SbCl_3$ to $BiCl_3$, the Cl···Cl distance increases by 15 pm but the valence angle remains unaltered.

The monotonic increase of the bond vibrational amplitudes from As to Bi and of the non-bonded Cl···Cl amplitudes from N to Bi, reflect both increasing gas temperature and decreasing stretch and bend force constants.

The decrease in the bond vibrational amplitude on going from NCl_3 to PCl_3 is undoubtedly due to the decrease in zero point vibrational energy resulting from a doubling of the mass of the Group 15 element: The bond-stretch force constants are very similar, viz. f(N-Cl) = 2.73 mdyn Å^{-1} and f(P-Cl) = 2.83 mdyn Å^{-1},[2,10] and the vibrational amplitudes at 298 K calculated from the molecular force fields are l(N-Cl) = 5.5 pm and l(P-Cl) = 5.1 pm.[1,2]

The structure of the $BiCl_3$ molecule is significantly modified when it enters the crystalline phase: In the crystal, each Bi atom enters into "secondary bonding" interactions with five Cl atoms from neighbouring molecules.[11] These in-

Table 1. Molecular structures of the Group 15 element trichlorides, $ElCl_3$, as determined by gas-phase electron diffraction. Estimated standard deviations in parentheses in units of the last digit.

	Temp /°C	r_a(El-Cl) /pm	l(El-Cl) /pm	∠ClElCl /°	r_a(Cl···Cl) /pm	l(Cl···Cl) /pm
NCl_3[a]	25	175.7(2)	6.1(3)	107.1(5)	283	7.4(2)
PCl_3[b]	27	203.9(1)	5.0(1)	100.3(1)	313	8.3(2)
$AsCl_3$[c]	18	216.1(1)	4.7(1)	98.6(2)	327	9.5(3)
$SbCl_3$[d]	70	233.1(1)	6.3(2)	97.2(4)	350	14.7(6)
$BiCl_3$[e]	185	242.3(5)	6.8(3)	97.3(2)	364	16.7(5)

[a]Ref. 1. The temperature is not explicitly stated. [b]Ref. 2. [c]Ref. 3. [d]Ref. 4. [e]This work.

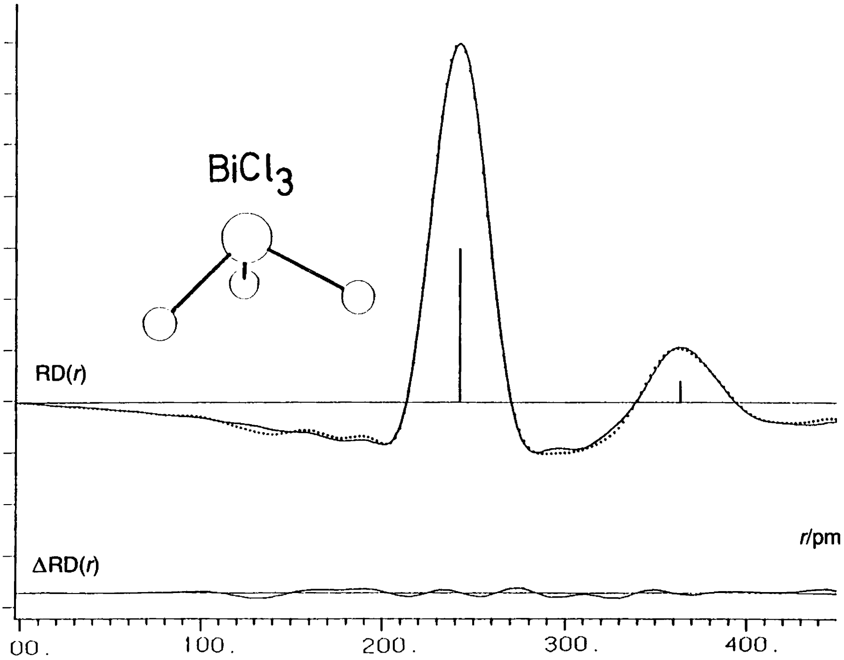

Fig. 2. Full line: calculated radial distribution (RD) curve for $BiCl_3$. Dots: experimental RD curve. Below: Difference curve. Artificial damping constant $k = 20\ pm^2$.

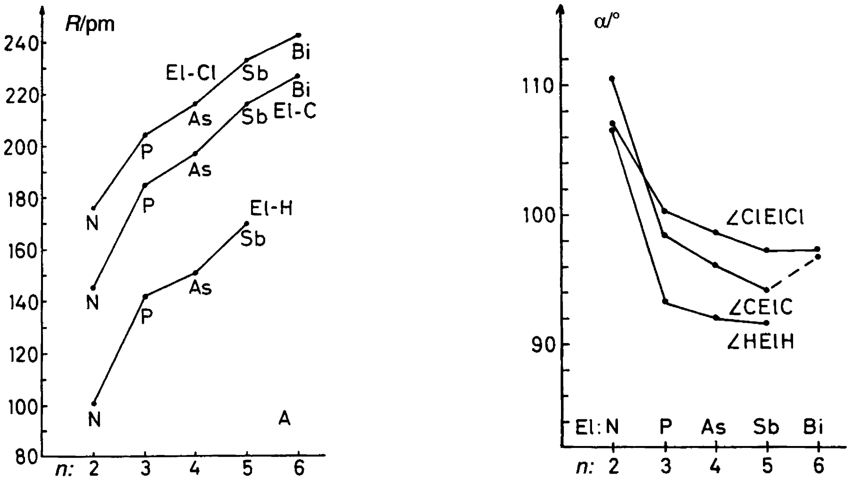

Fig. 3. Bond distances and valence angles of the gaseous compounds ElH_3, $El(CH_3)_3$ and $ElCl_3$ where El is a Group 15 element. The valence angle in $Bi(CH_3)_3$ is very uncertain: ∠CBiC = 96.7 (10)°.

teractions may presumably be described as weak electron donor/acceptor bonds, Cl→Bi. As a result the average ClBiCl angle is reduced by about 6° and the average Bi-Cl bond distance increased by about 8 pm.

The bicapped trigonal prismatic coordination

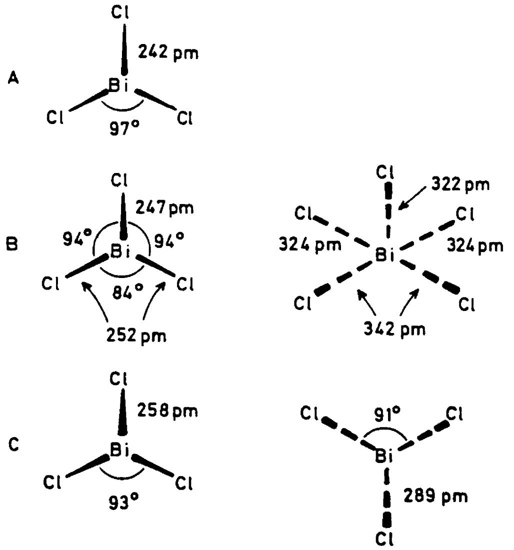

Fig. 4. (A) The structure of $BiCl_3$ in the gas phase. (B) The coordination polyhedron of Bi in crystalline $BiCl_3$. To the left the Bi atom and the three covalently bonded Cl atoms. The Bi is above the Cl_3 plane. To the right the cap consisting of five Cl atoms with secondary bonds to Bi. The coordination polyhedron may be described as a trigonal prism with two face bridging Cl. Interatomic distances and angles have been averaged to C_s symmetry. (C) Coordination polyhedron of $[NH_2(C_2H_5)_2]_3$ $[BiCl_6]$. The coordination is distorted octahedral with three covalently bonded Cl atoms below the Bi atom (left) and three datively bonded Cl^- ions above (right).

around Bi is indicated in Fig. 4B. It is seen that the two bonds that are *anti* (or near-*anti*) to the strongest (shortest) secondary bonds suffer the greatest elongation and span the smallest valence angle.

The coordination around Bi in diethylammonium hexachlorobismuthate(III), $[NH_2(C_2H_5)_2]_3$ $[BiCl_6]$, is shown in Fig. 4c.[12] The Bi atom resides on a C_3 axis, the coordination being distorted octahedral. The three secondary Bi–Cl bond distances are 289.2(7) pm, i.e. about 30 pm shorter than in solid $BiCl_3$, perhaps because Cl^- ions are better electron donors than (approximately) neutral Cl atoms. The covalent Bi-Cl bond lengths have increased by about 16 pm and the angle between them has been reduced by about 4°. The presence of an electron lone pair on Bi presumably prevents the adoption of octahedral symmetry with six equal metal-Cl distances as in $[SnCl_6]^{2-}$.

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