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 Cs symmetry having \( r_{d}(\text{Bi-Cl}) = 242.3(5) \) pm and \( \angle \text{ClBiCl} = 97.3(2)^\circ \). 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 \( \angle \text{ClBiCl} \) angle by 6°.

Dedicated to Professor Otto Bastiansen on his 70th birthday

While accurate structure parameters are available for the gaseous Group 15 trichlorides NC 3, 1 PCl 3, 2 AsCl 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 vapourising 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 \( f_{\text{d}}(s) \) were taken from Schäfer et al. 8 Molecular intensities were modified through multiplication by \( s/[f_{\text{d}}(s)]/[f_{\text{d}}(s)] \). 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 \( r_{d} \) 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 \( (r_{d}) \), 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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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 NCl₃ 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 ClEICl 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 SbCl₃ to BiCl₃, 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 NCl₃ to PCl₃ 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⁻¹,¹⁰ 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.¹²

The structure of the BiCl₃ 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-

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**Table 1.** Molecular structures of the Group 15 element trichlorides, ElCl₃, as determined by gas-phase electron diffraction. Estimated standard deviations in parentheses in units of the last digit.

<table>
<thead>
<tr>
<th></th>
<th>Temp /°C</th>
<th>rₑ(El-Cl) /pm</th>
<th>lₑ(El-Cl) /pm</th>
<th>∠ClEICl °</th>
<th>rₑ(Cl···Cl) /pm</th>
<th>l(Cl···Cl) /pm</th>
</tr>
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<tbody>
<tr>
<td>NCl₃</td>
<td>25</td>
<td>175.7(2)</td>
<td>6.1(3)</td>
<td>107.1(5)</td>
<td>283</td>
<td>7.4(2)</td>
</tr>
<tr>
<td>PCl₃</td>
<td>27</td>
<td>203.9(1)</td>
<td>5.0(1)</td>
<td>100.3(1)</td>
<td>313</td>
<td>8.3(2)</td>
</tr>
<tr>
<td>AsCl₃</td>
<td>18</td>
<td>216.1(1)</td>
<td>4.7(1)</td>
<td>98.6(2)</td>
<td>327</td>
<td>9.5(3)</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>70</td>
<td>233.1(1)</td>
<td>6.3(2)</td>
<td>97.2(4)</td>
<td>350</td>
<td>14.7(6)</td>
</tr>
<tr>
<td>BiCl₃</td>
<td>185</td>
<td>242.3(5)</td>
<td>6.8(3)</td>
<td>97.3(2)</td>
<td>364</td>
<td>16.7(5)</td>
</tr>
</tbody>
</table>

GASEOUS BISMUTH TRICHLORIDE

Fig. 2. Full line: calculated radial distribution (RD) curve for BiCl₃. Dots: experimental RD curve. Below: Difference curve. Artificial damping constant $k = 20$ pm².

![BiCl₃ diagram]

Fig. 3. Bond distances and valence angles of the gaseous compounds EIH₅, EI(CH₃)₃ and EICl, where EI is a Group 15 element. The valence angle in Bi(CH₃)₃ is very uncertain: $\angle$CBIC = 96.7 (10)°.

Interactions 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

411
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), \([\text{NH}_2(\text{C}_2\text{H}_5)_2]_3\text{[BiCl}_6]_\text{[BiCl}_6]\), is shown in Fig. 4c.\(^1\) 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 \([\text{SnCl}_6]^{2-}\).

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References


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