The Molecular Structure of Selenium Dichloride, \( \text{SeCl}_2 \)
Determined by Gas Electron Diffraction

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The electron diffraction pattern of the vapor from a sample of SeCl\(_4\) has been recorded with a reservoir and nozzle temperature of about 175 °C. The gas jet was found to consist of SeCl\(_2\) (80\%) and Cl\(_2\) (20\%). The bond distance in SeCl\(_2\) is \( r_a(\text{Se-Cl}) = 2.157(3) \AA \), the valence angle \( \angle \text{ClSeCl} = 99.6(5)^\circ \).

Two of the three known selenium chlorides, Se\(_2\)Cl\(_2\) and SeCl\(_4\), are stable in the solid phase but not in the gas phase, while the third, SeCl\(_2\), is stable in the gas phase but does not appear to exist in the solid phase [1]: SeCl\(_2\) forms a molecular solid which melts incongruently at about \(-48 °C \) [2, 3]. On evaporation it dissociates partly or not completely to Se(l) and SeCl\(_2\)(g). SeCl\(_4\) forms cubane-like tetramers in the solid phase [2, 4]. The melting point (in a closed system) is about 306 °C. On evaporation it dissociates completely according to

\[
\text{SeCl}_4(s) \rightarrow \text{SeCl}_2(g) + \text{Cl}_2(g). \quad [5, 6]
\]

The molecular structures of Se\(_2\)Cl\(_2\) and tetrameric SeCl\(_4\) have recently been determined by X-ray crystallography [2-4].

The SeCl\(_2\) molecule has been studied by gas phase Raman spectroscopy [6] and by He(I) photoelectron spectroscopy [7, 8]. We now report the molecular structure determined by gas electron diffraction.

A sample of SeCl\(_4\) was synthesized as described elsewhere [2]. Electron diffraction of the vapor was recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of about 175 °C. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. The data were processed by standard procedures. Six 50 cm plates yielded an average modified molecular intensity curve extending from \( s = 2.00 \) to 14.75 \( \AA^{-1} \) with increment 0.125 \( \AA^{-1} \). Four 25 cm plates yielded an average intensity curve extending from \( s = 5.00 \) to 29.00 \( \AA^{-1} \) with increment 0.25 \( \AA^{-1} \). Atomic scattering factors were calculated from atomic potentials [9] by the partial wave method [10].

An RD curve obtained by Fourier inversion of the experimental intensity is shown in Fig. 1. The composite peak at about \( r = 2.1 \AA \) consists of peaks representing the bond distances Cl-Cl and Se-Cl in Cl\(_2\) and SeCl\(_2\) respectively, the peak at 3.3 \( \AA \) represents the nonbonded Cl⋯Cl distance in SeCl\(_2\). Note that the RD curve contains no peaks in the range 3.8 to 5.0 \( \AA \) indicating the presence of measurable quantities of Se\(_2\)Cl\(_2\) or SeCl\(_4\).

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Fig. 1. (Above): Experimental RD curve for the SeCl\(_2\)/Cl\(_2\) gas mixture emanating from the nozzle. Artificial damping constant \( k = 0.002 \AA^2 \); (Below): difference between the experimental curve and the theoretical curve calculated for best model (Table I).
The bond distance and the root-mean-square vibrational amplitude of the Cl₂ molecule were fixed at the values determined by Shibata, \( r_g = 1.993 \) Å and \( \ell = 0.051 \) Å, respectively [11]. The bond distance, valence angle and R.M.S. vibrational amplitudes of SeCl₂ as well as the mole fractions of SeCl₂ and Cl₂ in the gas jet were refined by least-squares calculations on the intensity data with a program originally written by H. M. Seip [12]. The best parameter values are listed in Table I. The estimated standard deviations have been multiplied by a factor of two to compensate for data correlation and expanded to include a scale uncertainty of 0.1%.

Table I. Mole fraction and molecular structure of SeCl₂ in the molecular beam.

<table>
<thead>
<tr>
<th></th>
<th>( r_a / \text{Å} )</th>
<th>( \ell / \text{Å} )</th>
</tr>
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<tbody>
<tr>
<td>( \chi (\text{SeCl}_2) ) = 0.79(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se-Cl</td>
<td>2.157(3)</td>
<td>0.061(3)</td>
</tr>
<tr>
<td>Cl₁Cl₂</td>
<td>3.295(13)</td>
<td>0.132(9)</td>
</tr>
<tr>
<td>( &lt;\text{ClSeCl}^a )</td>
<td>99.6(5)°</td>
<td></td>
</tr>
<tr>
<td>( \chi (\text{Cl}_2) ) = 0.21(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>1.993^b</td>
<td>0.051^b</td>
</tr>
</tbody>
</table>

- \( a \) Not corrected for shrinkage; \( b \) ref. [11].

The low mole fraction of Cl₂ was initially something of a surprise. Refinements on data from single plates indicated, however, that the amount of Cl₂ present in the gas jet decreased in the course of the experiment. We assume that most of the Cl₂ formed escaped before we began to record the scattering pattern.

The bond distance in SeCl₂ is indistinguishable from the terminal Se–Cl bond distances in the SeCl₄ tetramer [2, 4], but significantly shorter than in crystalline Se₂Cl₂ where the mean Se–Cl bond distance is 2.204 Å [3]. At the same time the valence angle in SeCl₂ is significantly smaller than the valence angle at Se in Se₂Cl₂, \( <\text{SeSeCl} = 104.3° \) (mean value). The same differences have been noted between SC₁₂ and S₂Cl₂ [3].

In a very early electron diffraction investigation of the vapor from solid SeCl₄, Lister and Sutton concluded that the SeCl₄ molecule is (distorted) tetrahedral with a (mean) SeCl bond distance of 2.13 ± 0.04 Å [13]. The possibility that SeCl₄ dissociates in the gas phase was not considered. This study, which has found its way into the literature, must be regarded as invalid. A later study by Akishin, Spiridonov and Mishulima concluded that the sample had undergone partial or complete decomposition, most probably to give SeCl₂ and Cl₂. The degree of dissociation could not be determined, however, and the average SeCl bond distance of the “molecules present in the vapor” given as 2.18 ± 0.02 Å [14]. This result, though less accurate, is consistent with ours.

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