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THE PREPARATION AND ELECTRON DIFFRACTION STUDY OF DICHLOROGERMYLENE IN THE VAPOUR PHASE

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Summary

A preparative technique for dichlorogermylene for vapour phase investigation is described. An electron diffraction study on a mixture of $GeCl_2$ and $GeCl_4$ in the vapour phase reproduced earlier results for the tetrachloride structure and showed the bond angle to be 107 ± 5° in $GeCl_2$. This result, with its large error limit, is in conformity with structural variations observed for other dihalide molecules.

Introduction

Spectroscopic and structural data on Group IV dihalides are of great importance for understanding the nature of bonding in these carbene analogues. However, the information that has accumulated to date is rather fragmentary, especially as far as the reactive dichlorides and dibromides are concerned.

There are reliable structural data for the more stable carbon, silicon and germanium difluorides from microwave spectra. The microwave spectroscopic studies on CF_2 by Powell and Lide [1] and more recently by Kirchhoff and Lide [2] showed unambiguously that this triatomic molecule has a symmetric bent structure in agreement with the ultraviolet and infrared spectra [3]. The bond angle F—C—F was determined to be 104.9°. Similar conclusions were made by Rao et al. [4,5] for SiF_2 on the basis of the microwave spectrum and the reported value of $\angle$F—Si—F was 100°59′ in agreement with other spectroscopic evidence [6]. The infrared vibrational spectra for GeF_2 have been recorded in the gas phase and also in neon and argon matrices. The spectra appeared as expected for a triatomic symmetric bent molecule with some dimer present. However, there is some controversy in the spectra reported [7,8]. The most reliable information for the F—Ge—F angle in GeF_2 seems to be the value of 97.17° obtained in a microwave spectroscopic study by Takeo, Curl and Wilson [9].

Most of the structural information for the more reactive dichlorides originates from vibrational spectroscopic studies. An accurate determination was performed for the difference of the ν_3 frequencies in $C^{35}Cl_2$ and $C^{37}Cl_2$ isolated in a matrix [10,11]. The value of $108 \pm 4°$ was estimated for the bond angle Cl—C—Cl vs. the earlier data [12,13]. Similar studies on $SiCl_2$ yielded about 105° [14,15] for the bond angle Cl—Si—Cl.

The molecular geometry of $GeCl_2$ has not yet been determined but its vibrational spectra have been examined by several authors [16—18]. The spectroscopic evidence, including matrix isolation data, indicates a highly bent structure. However, no reliable estimates from the vibrational spectra are available for the bond angle in $GeCl_2$.

Several coordination compounds of $GeCl_2$ have been studied in the crystal phase by X-ray diffraction [19-21]. Thus, e.g. the following parameters were determined r(Ge—Cl) 2.25 Å and ∠Cl—Ge—Cl 94.6° in $GeCl_2 \cdot C_4H_8O_2$ [19] and ∠Cl—Ge—Cl 97.7° in $GeCl_2 \cdot P(C_6H_5)_3$ [20]. No direct evidence is, however, available concerning the geometry of free $GeCl_2$. Structural data for donor-acceptor molecules and the corresponding free molecules show that a substantial decrease in the bond angle of the acceptor part can be expected as the free acceptor molecule enters the donor-acceptor linkage [22].

The present electron diffraction study was initiated with the aim of determining the geometry of the free $GeCl_2$ molecule in the vapour phase.

The source of dichlorogermylene

The early spectroscopic investigations of the $GeCl_2$ molecule in the gas phase [23,24] have been carried out directly in the zone of the reaction 1 [25,26]:

$$Ge(s) + GeCl_4(g) \xrightarrow{350-430°C} 2\,GeCl_2(g) \qquad (1)$$

The excess of $GeCl_4$, however, has always created some difficulties in these studies. In the present work we had an independent goal to find a more suitable source of $GeCl_2$ molecules.

At room temperature germanium dichloride is known to be a polymeric material $(GeCl_2)_x$ that reacts with moisture and oxygen easily. It decomposes into $GeCl_4$ and solid $GeCl_n$ subchlorides ($2 > n > 0.6$) even in an inert atmosphere. The temperature of the decomposition is rather uncertain: from −20 [27] to 75°C [25].

Apparently, Andrews and Frederick [17] were the first who used $(GeCl_2)_x$ as a source of the monomeric $GeCl_2$ molecules. They prepared $(GeCl_2)_x$ by a known technique [27] from $HGeCl_3$ pumping HCl off in vacuum at −22°C over several hours.

In the present work $(GeCl_2)_x$ was prepared by the faster reaction 1 in a flow system at 370—400°C and under a $GeCl_4$ pressure of 1 Torr. The polymeric $(GeCl_2)_x$ condensed on the wall at room temperature and the unreacted $GeCl_4$

was recycled. About 1 g of light yellow $(GeCl_2)_x$ was collected over a period of 1.5—2 h. Then the collector with the deposit was sealed off from the vacuum system.

The molecular composition of the gas over the $(GeCl_2)_x$ sample has been studied at different temperatures with mass spectrometry and IR-spectroscopy.

The vapour composition

Mass spectrometry

The mass spectra were obtained by means of units AEI MS-902 (Budapest) and CH-6 Varian Mat (Moscow). The sample was handled in an inert gas atmosphere with a direct inlet to the ion source.

The identification of $GeCl_2$ in the presence of $GeCl_4$ is difficult under usual conditions of the mass spectrometric experiment with 70 eV electrons since $GeCl_2^+$ ions are formed in the fragmentation process of the tetrachloride [28]. However, the appearance potential of the $GeCl_2^+$ ions originating from $GeCl_4$ is higher by about 7 eV than the ionization potential of $GeCl_2$. The latter was determined to be 10.2 ± 0.1 eV from our measurements*, in good agreement with data in the literature (10.4 ± 0.3 eV) [23]. Accordingly, utilizing an ionizing energy of about 12 eV, the $GeCl_2$ content in the mixture of $GeCl_2$ and $GeCl_4$ could be determined.

The mass spectrometric information can be summarized as follows: (1) The only volatile components of the $(GeCl_2)_x$ sample are $GeCl_2$ and $GeCl_4$. (2) With increasing temperature from 20 to 80°C, the ratio $GeCl_2{:}GeCl_4(I_{144}{:}I_{214})$ increased from 2.5 to 6.8. (3) The $GeCl_4$ content could also be decreased by lengthening the time spent by the sample in the vacuum chamber of the mass spectrometer.

The comparison of mass spectra for various samples facilitated selection of a sample with the smallest $GeCl_4$ content. It also showed, on the other hand, that the $GeCl_4$ content decreased 2.5 times, if the sample was kept at room temperature for 20 days, as a consequence of gradual decomposition of the $(GeCl_2)_x$ polymer.

IR spectroscopic analysis

A glass collector with a sample of $(GeCl_2)_x$ was fitted to the optical helium cryostat without admitting air into the system and was warmed to 60°C. The molecules evaporating from the sample were frozen along with the excess of argon (1000:1) on the CsI window cooled by liquid helium down to 10 K. The molecules isolated in the argon matrix were then identified by their IR spectra (1000—200 cm^{-1}; Hitachi—Perkin—Elmer 225 Spectrophotometer, Moscow). The spectra contained only three bands with maxima at 457.5, 398.6 and 373.4 cm^{-1}. The first corresponds to the strongest absorption of $GeCl_4$ and the others result from the ν_1 and ν_3 vibrational modes of $GeCl_2$, respectively [16-18].

Only after 1 hour of pumping the sample at 60—80°C and 5×10^{-6} Torr could we obtain the spectrum of the matrix-isolated gaseous products (Fig. 1)

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* To determine the IP, the semilog-plot technique [29] was used with benzene as an internal standard; IP(benzene) 9.40 ± 0.01 eV [30].

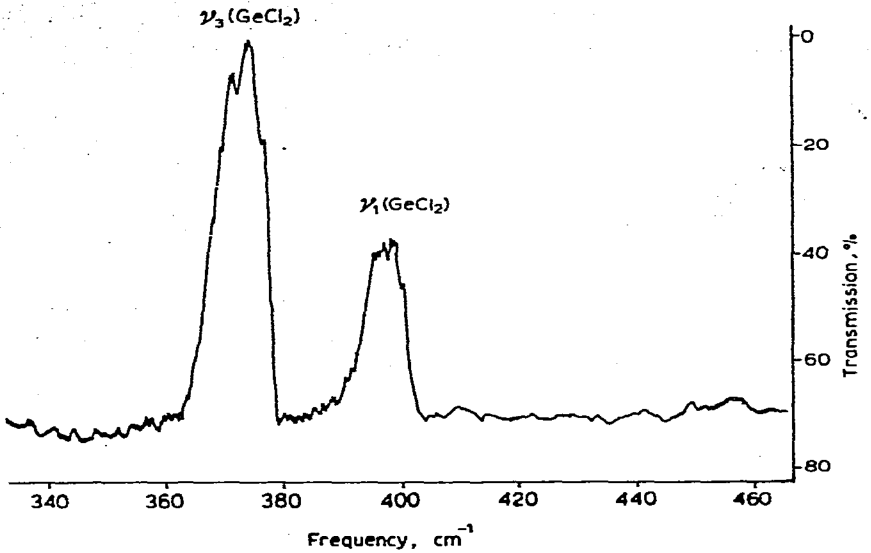

Fig. 1. Part of the IR spectrum of dichlorogermylene (the experimental conditions are described in the text).

practically free from $GeCl_4$. Probably adsorption or trapping of $GeCl_4$ in $(GeCl_2)_x$ during the synthesis leads to its presence in the sample, and high vacuum pumping with simultaneous mild warming is the most effective way of getting the sample of $(GeCl_2)_x$ free from $GeCl_4$ impurity.

As for the electron diffraction experiment, the necessary high density vapour beam of $GeCl_2$ was produced in the nozzle system at about 80°C. The pressure in the sample container was then at least several Torr. Under such conditions the system rapidly approaches equilibrium which is shifted to the right.

$2\,GeCl_2 \rightleftharpoons Ge + GeCl_4$

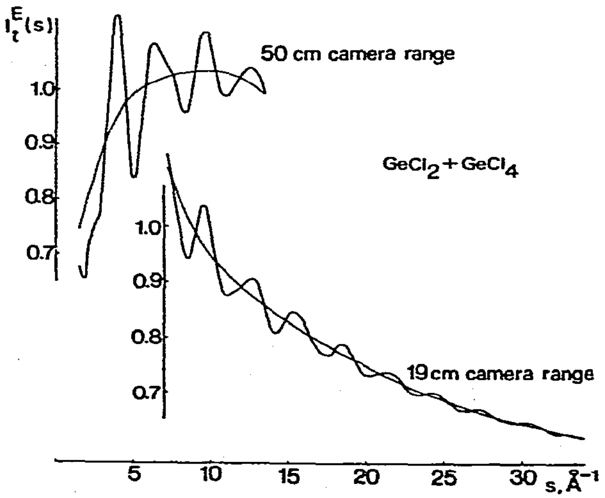

Fig. 2. The total experimental intensities with the experimental backgrounds drawn in.

Thus the vapour beam in the electron diffraction experiment, unfortunately, consisted of both $GeCl_2$ and $GeCl_4$ molecules.

Electron diffraction structure analysis

The electron diffraction patterns were taken with the EG-100A unit and the usual technique of the Budapest laboratory [31,32].

The optical densities of the diffraction patterns were produced essentially the same way as described elsewhere [33]. The procedure used in reducing the data and obtaining the molecular intensities via gradually improved experimental backgrounds followed our usual practice [34]. The ranges of intensity data were $1.50 \leqslant s \leqslant 13.50$ Å^{-1} and $7.25 \leqslant s \leqslant 34.00$ Å^{-1} with $s = 0.25$ Å^{-1}. For both data intervals averaged data sets from the individual diffraction patterns were used since a careful inspection did not reveal any appreciable difference between the individual data sets that might have indicated variations in the vapour composition. The total experimental intensities and the final versions of the experimental backgrounds are shown in Fig. 2 and the corresponding molecular intensities in Fig. 3.

The experimental radial distribution is shown in Fig. 4 having maxima at about 2.11 Å and 3.45 Å. Of these, the first corresponds to the Ge—Cl bonds and the second to the Cl···Cl nonbond distances. This distribution already provides evidence against a linear $GeCl_2$ structure since there is no maximum above 4 Å.

In agreement with the mass spectrometric findings, a comparison of the distributions from the electron diffraction experiment with those calculated for either $GeCl_2$ or $GeCl_4$ or their mixtures showed that a considerable amount of the tetrachloride was present in the vapour. This fact had to be taken into account and the vapour composition had then to be carefully correlated with the electron diffraction data in any realistic attempt to establish the molecular geometry of germanium dichloride. Note that a germanium tetrachloride mole-

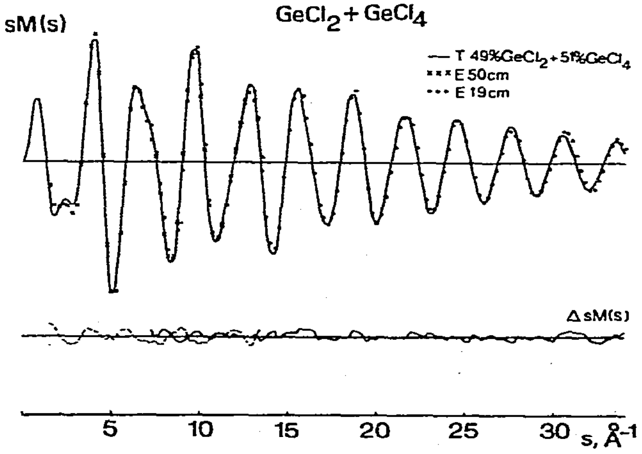

Fig. 3. Experimental (E) and theoretical (T) molecular intensities and the difference curves.

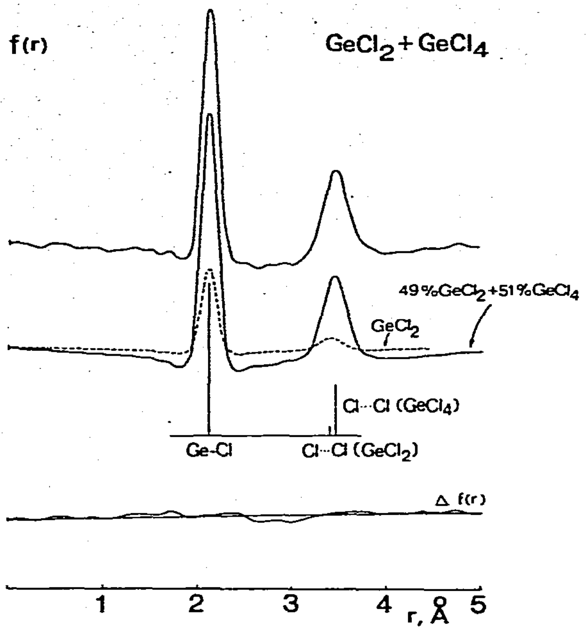

Fig. 4. Experimental (upper curve) and thereoretical (full line) radial distributions and the difference curve $\Delta f(r)$. The dashed line indicates the contribution of $GeCl_2$ to the total theoretical curve.

cule has more than three times as much contribution to the scattering patterns as a germanium dichloride molecule. Fortunately, accurate data are available for the internuclear distance and mean vibrational amplitude parameters of $GeCl_4$ from the study of Morino et al. [35]. These data (see Table 3) were utilized in the initial stages of this structure analysis. Later, however, in order not to introduce a systematic error, a refinement of the structural parameters of $GeCl_4$ was carried out simultaneously with that of the parameters of $GeCl_2$.

Various assumptions have been used and their influence on structural parameters tested throughout different refinement schemes. There was only one assumption that was common to all refinement schemes, viz. for the germanium—chlorine bonds of the two molecules mean values were refined only.

The least squares refinements were based on the molecular intensities in a manner described earlier (see, e.g. [36]).

The structure analysis can be divided into and characterised by the following steps:

(i) Using the structural parameters for $GeCl_4$ from [35] as starting values, the mean Ge—Cl distance and the nonbond Cl···Cl distances and their mean amplitudes of vibration (l values) were refined for fixed ratios of $GeCl_2$ and $GeCl_4$. The l(Cl···Cl) values for $GeCl_4$ and $GeCl_2$ were assumed to be the same in almost all the refinements. The starting values for the Cl···Cl distance of $GeCl_2$ for each ratio examined were 3.25, 3.42 and 3.60 Å corresponding to ∠Cl—Ge—Cl = 95°, 108° and 117° in that order. The best agreements with the experimental data were obtained for the ratios with 80, 70 and 60% of $GeCl_4$ with the following parameters:

GeCl$_4$ content (%)	input Cl···Cl (Å)	Ge—Cl		Cl···Cl (GeCl$_4$)		Cl···Cl (GeCl$_2$)	
		r (Å)	l (Å)	r (Å)	l (Å)	r (Å)	l (Å)
80	3.25	2.109	0.049	3.439	0.108	3.209	0.107
70	3.25	2.109	0.049	3.442	0.104	3.301	0.103
60	3.25	2.109	0.049	3.441	0.104	3.380	0.103
80	3.42	2.109	0.049	3.434	0.108	3.782	0.107
70	3.42	2.109	0.049	3.432	0.102	3.713	0.101
60	3.42	2.109	0.049	3.426	0.096	3.600	0.095
80	3.60	2.109	0.049	3.435	0.107	3.763	0.066
70	3.60	2.109	0.049	3.433	0.101	3.708	0.113
60	3.60	2.109	0.049	3.430	0.098	3.580	0.148

Note that the value of r(Cl···Cl) 3.444 Å for GeCl$_4$ would correspond to the ideal tetrahedral arrangement.

(ii) Fixing the values of the bond angle Cl—Ge—Cl of GeCl$_2$ and using an assumed geometry for GeCl$_4$ obtained by averaging the parameters produced in the preceding section, the ratio of GeCl$_4$ and GeCl$_2$ was now refined yielding the following results:

assumed bond angle (°) Cl—Ge—Cl of GeCl$_2$	refined percentage of GeCl$_4$ content
95	65
103	53
108	41
117	55
123	59

(iii) The contribution of 40, 50, 60 and 70% of GeCl$_4$ was subtracted from the experimental radial distribution and the residue was examined in order to estimate r(Cl···Cl) for GeCl$_2$. The following data were obtained:

subtracted amount of GeCl$_4$ (%)	residue maximum* for r(Cl···Cl) (Å) at about
40	3.43
50	3.42
60	3.42
70	3.38

(iv) Fixing a consistently tetrahedral geometry for GeCl$_4$ (resulting from previous refinements) and fixing also the ratio of the two components, r(Cl···Cl) and l(Cl···Cl) of GeCl$_2$ were refined. Starting values for the former were used

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* As contributions from larger amounts of GeCl$_4$ were subtracted, an additional peak at about 3.7—3.8 Å became apparent (cf. the small shoulder at the right hand foot of the 3.4 Å maximum on the experimental radial distribution curve). Accordingly, such starting values have also been tested in consequent refinements.

that corresponded to 103° and 124° bond angles in order to utilize a wide angle range. The following results were obtained:

$GeCl_4$ content (%)	starting from 103° ($GeCl_2$) $\angle$Cl—Ge—Cl (°)	l(Cl···Cl) (Å)	starting from 124° ($GeCl_2$) $\angle$Cl—Ge—Cl (°)	l(Cl···Cl) (Å)
60	106.5	0.094	108.3	0.160
50	107.7	0.076	107.8	0.082
40	108.3	0.069	108.3	0.071

(v) To test the influence of l(Cl···Cl) of $GeCl_2$ on the bond angle, fixing the amplitude at various values, the bond angle of $GeCl_2$ was refined yielding the following:

fixed l(Cl···Cl) (Å) in $GeCl_2$	$\angle$Cl—Ge—Cl in $GeCl_2$ (°)
0.08	106.8
0.09	106.6
0.10	106.5
0.11	106.4
0.12	106.4

(vi) At this stage of the structure analysis a background revision was performed and, accordingly, the main steps of the refinements had to be repeated. In the course of these calculations the relative abundance of $GeCl_4$ and $GeCl_2$ were found to be 51 and 49% with a 3% standard deviation. Fixing then the corresponding ratio, a refinement of the $GeCl_4$ parameters was carried out followed by a simultaneous refinement of the $GeCl_2$ parameters as well. The results* are presented in Table 1 together with the standard deviations from the least squares refinement and the total uncertainties that include also the

TABLE 1

MOLECULAR PARAMETERS OF THE $GeCl_2$ + $GeCl_4$ SYSTEM

Parameter	Value [a]	σ_{LS}	σ_t
$r_a(\text{Ge—Cl})_{av}$	2.109	0.0004	0.004
$r_g(\text{Ge—Cl})_{av}$	2.110		
$l(\text{Ge—Cl})_{av}$	0.048	0.001	0.001
$r_a(\text{Cl}\cdot\text{Cl})_{GeCl_2}$	3.384	0.067	0.096
$r_g(\text{Cl}\cdot\text{Cl})_{GeCl_2}$	3.387		
$l(\text{Cl}\cdot\text{Cl})_{GeCl_2}$	0.095	0.007	0.010
$r_a(\text{Cl}\cdot\text{Cl})_{GeCl_4}$	3.444	0.008	0.014
$r_g(\text{Cl}\cdot\text{Cl})_{GeCl_4}$	3.447		
$l(\text{Cl}\cdot\text{Cl})_{GeCl_4}$	0.098	0.007	0.010
$\angle\text{Cl—Ge—Cl}_{GeCl_2}$	106.7	1.9	2.7

[a] The distances are given in Å, the bond angle in degrees.

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* The scattering factors used in these calculations were taken from Cox and Bonham [37] (coherent) and Tavard et al. [38] (incoherent). The scattering functions were calculated for a one to one mixture of $GeCl_4$ and $GeCl_2$.

TABLE 2

CORRELATION COEFFICIENTS (X 1000)

	$r(\text{Ge—Cl})_{av}$	$r(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	$r(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_2}$	$l(\text{Ge—Cl})_{av}$	$l(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	k_1[a]	k_2[a]
$r(\text{Ge—Cl})_{av}$	1000						
$r(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	21	1000					
$r(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_2}$	−19	−978	1000				
$l(\text{Ge—Cl})_{av}$	5	46	−55	1000			
$l(\text{Cl}\cdots\text{Cl})_{\text{GeCl}_4}$	−23	−946	967	−1	1000		
k_1	5	36	−44	256	−4	1000	
k_2	3	62	−72	767	−2	213	1000

[a] The k_1 and k_2 values are the scale factors for the two camera distances.

TABLE 3

MOLECULAR PARAMETERS OF $GeCl_4$ DETERMINED FROM ELECTRON DIFFRACTION BY MORINO et al. [35]

	Ge—Cl	Cl···Cl
r_g	2.113 ± 0.003 Å	3.444 ± 0.006 Å
l_g	0.047 ± 0.003 Å	0.098 ± 0.003 Å

experimental scale error (cf., e.g. [39]). The correlation coefficients for the parameters refined as independent are collected in Table 2.

(vii) To test the influence of the fixed value of the $GeCl_4$ to $GeCl_2$ ratio on the value of the $GeCl_2$ bond angle, the calculations were repeated assuming 60/40 and 40/60% mixtures. The corresponding values for ∠Cl—Ge—Cl of $GeCl_2$ were 107.7° and 106.5°, while no appreciable effect was observed on the tetrahedral $GeCl_4$ structure.

Discussion

The results of this study are given in Table 1. The internuclear distances are presented as r_a parameters and also as $r_g(\approx r_a + l^2/r_a)$ parameters. The structural data obtained for germanium tetrachloride are in very good agreement with the results of Morino et al. [35] which are summarized in Table 3.

Mean values for the lengths and the mean amplitudes of vibration of the Ge—Cl bonds in $GeCl_4$ and $GeCl_2$ were determined in the present study. That these values are not different from those determined for germanium-tetrachloride itself suggest that the Ge—Cl bond in $GeCl_2$ is little different from that in $GeCl_4$. On the other hand, the relative weight in the scattering from the bonds of the dichloride is half of that from the bonds of the tetrachloride, provided there are an equal number of $GeCl_2$ and $GeCl_4$ molecules present. Thus the above statement on the length of the dichloride bond should be treated cautiously. It is also interesting to note in this connection that the length of the Ge—Cl bond seems to vary appreciably as its environment changes. This is illustrated by some data for methylchlorinegermane derivatives collected in Table 4.

The present electron diffraction study provides direct evidence for the highly bent structure of $GeCl_2$. The high relative abundance of $GeCl_4$ in the vapour phase and strong correlations between parameters made it impossible

TABLE 4

THE VARIATION OF THE Ge—Cl BOND LENGTH IN GERMANIUM TETRACHLORIDE AND ITS METHYL DERIVATIVES

Substances	r(Ge—Cl) (Å)
$GeCl_4$	2.113 ± 0.003 [a]
CH_3GeCl_3	2.135 ± 0.006 [b]
$(CH_3)_2GeCl_2$	2.155 ± 0.004 [c]
$(CH_3)_3GeCl$	2.170 ± 0.001 [d]

[a] r_g, electron diffraction [35]. [b] r_s, microwave spectroscopy [40]. [c] r_g, electron diffraction [41]. [d] r_s, microwave spectroscopy [42].

to determine an accurate value for the bond angle in dichlorogermilene. In fact, the relative weight in the scattering from the Cl···Cl nonbond interaction of the dichloride is only one third of that from the nonbond interactions of the tetrachloride, provided there are an equal number of $GeCl_2$ and $GeCl_4$ molecules present.

As the geometry of the $GeCl_2$ molecule and its relationship with other molecular geometries are discussed, the very large uncertainty of the ∠Cl—Ge—Cl determined in $GeCl_2$ has to be kept in consideration. The total error given in Table 1 was calculated using one standard deviation from the least squares refinements. For comparisons with other data it is better to calculate the total error with two or even two and a half standard deviations corresponding to higher confidence limits (99 and 99.5%, respectively). The respective σ_t values are 4.6 and 5.4°. It is hoped that future electron diffraction investigations will be able to use samples with a much higher $GeCl_2$ concentration and thus determine more accurately the geometry of this molecule.

As the uncertainty of the bond angle of $GeCl_2$ is large at the present time, only a very qualitative discussion can be attempted.

As the bond angles in GeF_2 (see Introduction) and $GeCl_2$ are compared, it is seen that the valence shell electron pair repulsion (VSEPR) model [43] is applicalbe for these structures.

Another interesting structural variation has been observed for some AX_2 triatomic molecules, viz. the bond angle decreases in molecules with central atom A having larger atomic number (in a group of the Periodic Table) while the ligand X remains uncharged. Thus, e.g. ∠X—A—X is 180° in $MgCl_2$ and $CaCl_2$, 120° in $SrCl_2$ and 100° in $BaCl_2$ [44], or 140° in CaF_2 and 108° in SrF_2 [45]. Note that the chlorine derivative here again has a larger angle than the fluorine derivative.

As the bond angles in the series CF_2, SiF_2 and GeF_2 are considered, i.e. 105°, 101° and 97°, respectively, and also the available data for CCl_2 (108°), and $SiCl_2$ (105°) (for refs. see Introduction), according to the variations described above, the bond angle ∠Cl—Ge—Cl in $GeCl_2$ can be expected to be between 105 and 97°, i.e. smaller than in $SiCl_2$ but larger than in GeF_2. This expectation is also in agreement with the cited observation concerning the structural changes in donor-acceptor complexes as compared with the geometry of the uncomplexed acceptor molecules.

The experimental result of 107 ± 5° for ∠Cl—Ge—Cl in $GeCl_2$ is in conformity with the observed structural variations if its large error limit is taken into consideration. We have also to note that the uncertainties for most of the data used in the above comparison are also relatively very large.

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