The Crystal Structure and Raman Spectrum of $Ge_5Cl_{12}\cdot GeCl_4$ and the Vibrational Spectrum of Ge_2Cl_6

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The Raman spectrum of Ge_2Cl_6 shows close analogies with that of the isoelectronic $[Ga_2Cl_6]^{2-}$. A band at 262 cm^{-1} is assigned as principally a Ge−Ge stretching mode. The compound is very moisture-sensitive and decomposes readily in vacuo to give $GeCl_4$ as one of the products. A sealed sample stored at room temperature gave colorless cuboidal crystals shown by X-ray crystallography to be $Ge_5Cl_{12}\cdot GeCl_4$. The Ge−Ge distance in the neopentyl-like Ge_5 skeleton is 2.420(6) Å, and the Ge−Cl distance in the Ge_5Cl_{12} moiety is 2.119(5) Å whereas in the case of the $GeCl_4$ molecule it is 2.082(7) Å. The symmetric stretching frequency of the Ge_5 tetrahedron is assigned to the band at 224 cm^{-1}.

Introduction

A range of polysilicon halides, notably the chlorides, has been reported.[1] By contrast, the only well-characterized polygermanium halide is Ge_2Cl_6, which has been prepared by three groups.[2−4] In the first synthesis of this compound, elemental germanium was reacted with $GeCl_4$ at ca. 3 Torr and 430 °C, to yield less than 1 mg of product/day.[2] Subsequently a greatly improved method was reported from the passage of $GeCl_4$ at low pressure through a microwave discharge.[3] More recently, germanium vapor co-condensed with tetrahydrofuran at 77 K was allowed to react with $GeCl_4$.[4] Both Ge_2Cl_6 and Ge_3Cl_8 were reported in the mass spectrum from the reaction, but "the yields of products were very low". Si_2Cl_6 is commercially available whereas we could find only one reference[5] to Sn_2Cl_6, which is reputedly stable up to −65 °C when "it disproportionates into $SnCl_2$ and $SnCl_4$". As part of our study of low-valent germanium compounds, we now report our results on two chlorides.

Experimental Section

$GeCl_4$ (99.99%) was degassed and distilled once in vacuo. $GeCl_4$ (ca. 50 mL) was maintained at approximately −60 °C so that a stable discharge could be obtained by passing the vapor through a borosilicate tube held in the specially built microwave discharge cavity of an EMS diathermy unit. The products were initially retained in two U tubes at 77 K. At the end of the experiment, excess $GeCl_4$ was removed by trap-to-trap distillation using $CHCl_3$ and CCl_4 slush baths and finally ice/salt. Ge_2Cl_6 remained as a colorless crystalline material which melted in the range of 40−42 °C. When Ge_2Cl_6 was transferred from one cold bath to another at lower temperature, a small amount of white involatile solid remained. If Ge_2Cl_6 was cautiously warmed, decomposition occurred with the formation of a volatile liquid shown by Raman spectroscopy to be $GeCl_4$. The yield of Ge_2Cl_6 averaged about 50 mg/h, and the crystals were stored in all-glass break-seal ampules held at ca. −20 °C. IR spectra were obtained using vacuum techniques, with the material deposited onto a silicon window at 77 K [Perkin-Elmer 983G (4000−200 cm^{-1})]. Raman spectra were measured using borosilicate ampules at room temperature (J-Y Raman microprobe with 5145 Å radiation).

In one sample of Ge_2Cl_6 left in a sealed ampule at room temperature, cuboidal crystals formed together with a colorless liquid ($GeCl_4$). After removal of the volatiles, the crystals appeared to be stable in vacuo for several weeks. When these extremely moisture-sensitive crystals were transferred from the glass ampule, inside a glovebox, into Na-dried hydrocarbon oil,[6] the crystals were seen to react and "bubble", presumably because of traces of residual moisture.

Crystal Structure Determination. One crystal (0.80 × 0.80 × 0.40 mm) was mounted[6] on a Rigaku AFC7S diffractometer fitted with Mo Kα radiation and an Oxford Cryosystems low-temperature device set at 150 K. The peaks found in the search routine were indexed, and the Delauney reduction strongly indicated a cubic crystal system with an F lattice. However, the intensity checks to confirm this were less than convincing for either of the two cubic Laue groups, and because of the scarcity of crystals and their reactivity, the intensity data (4909 reflections, $2\theta_{max} = 50°$) were collected as a triclinic system as a precaution. Cell constants were refined from 23 reflections (2θ = 46.1−50.2°) and an absorption correction based on ψ scans applied during the data processing [transmission: 1.000 (max), 0.291 (min)]. Inspection of the "triclinic" data using one of the teXsan[7] utilities clearly showed that the diffraction pattern had high symmetry and on transformation to the cubic system the 4-fold symmetry, together with the special absences, became apparent. The data show the eee parity-group reflections more intensely than the ooo group. The systematic absences were consistent with space groups $F\bar{4}3c$ or $Fm3c$. After some initial difficulty which was compounded by the absence of a chemical formula, the structure was solved by direct methods in the noncentrosymmetric space group $F\bar{4}3c$ using the program SHELXS86.[8] Full-

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Table 1. Crystallographic Data for $Ge_5Cl_{12}{\cdot}GeCl_4$

mol formula	$Cl_{16}Ge_6$
fw	1002.74
cryst syst	cubic
space group	$F\bar{4}3c$ (No. 219)
a, Å	17.437(9)
V, Å^3	5302(9)
Z	8
ρ_{calcd}, g cm^{-3}	2.512
μ(Mo Kα), cm^{-1}	83.3
λ, Å	0.71073
temp, °C	−123
R1[a] ($F > 4\sigma(F)$)	0.053
wR2[b] (all reflns)	0.1170

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (0.068P)^2$, where $P = [F_o^2 + 2F_c^2]/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $Ge_5Cl_{12}{\cdot}GeCl_4$

atom	x	y	z	U_{eq}[a]
Ge(1)	0.500 0	0.500 0	1.000 0	29.0(7)
Ge(2)	0.750 0	0.750 0	0.750 0	25.8(6)
Ge(3)	0.830 17(4)	0.669 83(4)	0.830 17(4)	26.2(5)
Cl(1)	0.568 96(16)	0.568 96(16)	0.931 04(16)	79.8(17)
Cl(2)	0.767 73(10)	0.631 48(11)	0.927 15(9)	43.2(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

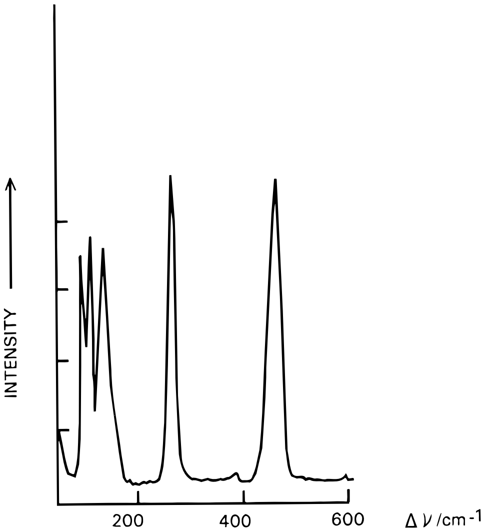

Figure 1. Raman spectrum of crystalline Ge_2Cl_6 at ambient temperature.

matrix least-squares refinement on F^2 using SHELXL97[9] converged to a final R1 of 0.053 (402 unique reflections, 18 parameters, all atoms anisotropic) with the residual electron density in the range of +0.75 to −2.02 e Å^{-3}. The absolute configuration of the crystal examined was established,[10] and the possibility of the $GeCl_4$ residue having only a partial occupancy because of the sample being pumped to remove volatiles was excluded when refinement was carried out using variable site occupation factors. Crystallographic details are given in Table 1 and atomic coordinates in Table 2.

Results and Discussion

Figure 1 shows the Raman spectrum of Ge_2Cl_6. If the molecule has a 3-fold axis of symmetry, then for the purposes of this account, it is not important whether the point group is D_3, D_{3d}, or D_{3h}. We shall adopt a D_{3d} model as was done for Si_2Cl_6.[11] The band at 434 cm^{-1} can be assigned to the in-phase Ge−Cl stretching mode of the two $-GeCl_3$ residues and is of a_{1g} symmetry. The Ge−Ge stretch (also a_{1g}) is assigned at 262 cm^{-1} by analogy with Ge_2Me_6,[12] $[Ge_4]$,[4−13] and $[Ge_5]$,[2−14] which have Ge−Ge stretches in the range of 229−279 cm^{-1}. These two a_{1g} modes can interact so that their description as Ge−Ge or Ge−Cl bond stretching is only approximate. A normal coordinate analysis using SOTONVIB[15] gave the following potential energy contributions. 434 cm^{-1}: 64% Ge−Cl; 21% Ge−Ge. 262 cm^{-1}: 54% Ge−Ge; 31% Ge−Cl.

This may be contrasted with Si_2Cl_6[11] where a similar analysis gave the *highest* frequency Raman band as 64% Si−Si; 21% Si−Cl. A close (isoelectronic) analogue of Ge_2Cl_6 is $Ga_2Cl_6^{2-}$. Ignoring two of the weak bands in $Ga_2Cl_6^{2-}$ (314 and 59 cm^{-1}) and multiplying the remaining Raman frequencies[16] by the ratio of ν_1 for $GeCl_4$ to ν_1 for $GaCl_4^-$ gives a set of predicted frequencies for Ge_2Cl_6 which may be compared with those observed. (Predicted: 430, 267, 167, 133, 122. Observed: 434, 262, 151, 126, 106 cm^{-1}.) The greatest difference is 16 cm^{-1}. We were not able to obtain depolarization ratios because of the decomposition of Ge_2Cl_6. However, as both the high-frequency modes are certainly totally symmetric and depolarization data on deformations are frequently not clear-cut (vide $Ga_2Cl_6^{2-}$), this is not a serious loss. The corresponding main IR bands at 448 (vs) and 392 (m) cm^{-1} can be assigned as e_u and a_{2u} modes by analogy with $Ga_2Cl_6^{2-}$. There was also a weak band at 243 cm^{-1} which we do not assign. There was no sign of a band at 743 cm^{-1}, which is reputedly characteristic of Ge_2OCl_6.[17]

An in-situ Raman spectrum of the small quantity of cuboidal crystals arising from the decomposition of Ge_2Cl_6 gave a series of sharp lines (Figure 2). We initially thought this might be $GeCl_2$, although a strong band at 424 cm^{-1} suggested the presence of germanium in an oxidation state higher than 2+ (the highest frequency of monomeric $GeCl_2$ is at 399 cm^{-1} in the gas phase[18]). An X-ray structure determination of these crystals (see below) demonstrated that the formulation should be $Ge_5Cl_{12}{\cdot}GeCl_4$ with the Ge_5Cl_{12} moiety containing a neopentyl-like Ge_5 skeleton. With hindsight it is rather easy to interpret the main features of the Raman spectrum (Figure 2). The intense bands at 424, 224, and 99 cm^{-1} are respectively the symmetric stretching vibration of the four $-GeCl_3$ residues, the breathing frequency of the Ge_5 tetrahedronm, and the symmetric deformation of the four $-GeCl_3$ residues. The band at 398 cm^{-1} is assigned to ν_1 of the "independent" $GeCl_4$ molecule in the structure.

Crystal Structure of $Ge_5Cl_{12}{\cdot}GeCl_4$. The structure consists of discrete Ge_5Cl_{12} and $GeCl_4$ molecules, and these are shown in Figure 3 with bond distances and angles given in Table 3. The Ge−Ge bond hitherto unknown in binary halides of Ge is

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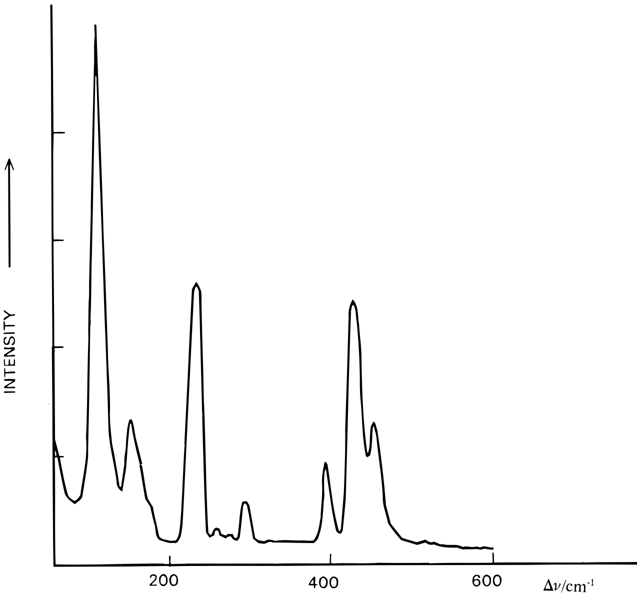

Figure 2. Raman spectrum of crystalline Ge_5Cl_{12}·$GeCl_4$ at ambient temperature.

nevertheless well-established in organo−germanium compounds. The present Ge−Ge distance [2.420(6) Å] may be compared with those in $PhCl_2GeGeCl_2Ph$ [2.413(1) Å][19] and $Ph_3GeGePh_3$ [2.446(1) Å].[20] The value in elemental germanium is 2.450 Å, and thus, it appears that the bond length in the present study is typical. The angles at Ge(1) and Ge(2) are 109.5° imposed by the crystallographic symmetry, and that at Ge(3) is close to this value (Table 3). The Cl(2)−Ge(3)−Ge(2)−Ge(3a) torsion angle is 38.68(5)° (symmetry operation a: *y*, *z*, *x*), giving a staggered conformation but some 21° from the idealized angle (60°). The tetrahedral $GeCl_4$ shows only normal Cl···Cl contacts [3.663(10) Å] to the other residue, and the Ge−Cl distance [2.082(7) Å] may be compared with the r_g determined by electron diffraction on the gaseous molecule [2.113(3) Å].[21] The corresponding and isomorphous silicon analogue Si_5Cl_{12}·$SiCl_4$ has been reported[22] [Si−Cl 1.955(12) Å ($SiCl_4$), 1.994(7) Å ($-SiCl_3$); Si−Si 2.332(9) Å]. We also note that Ge_5F_{12} is not isostructural with Ge_5Cl_{12} but is a mixture of Ge^{IV} and Ge^{II} species[23] formally containing 1 mol of GeF_4/formula unit.

Conclusions

These results suggest that, despite the apparent instability of Ge_2Cl_6, there is no inherent instability in the polygermanium chlorides and that it should be possible to obtain a range of compounds analogous to those found with silicon.

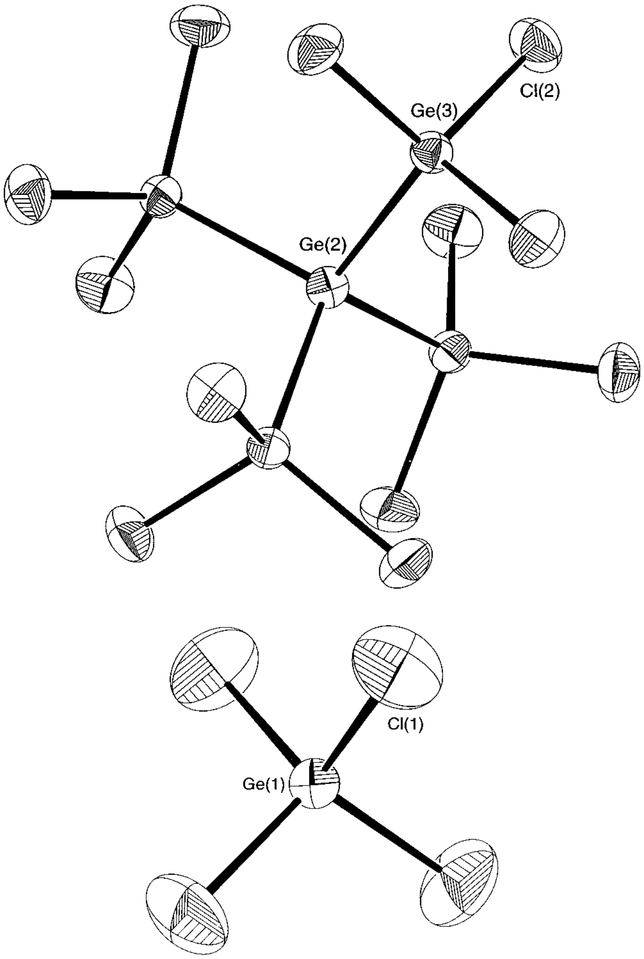

Figure 3. Crystal structure of Ge_5Cl_{12}·$GeCl_4$ showing the atom numbering scheme for (a) Ge_5Cl_{12} and (b) $GeCl_4$. Displacement ellipsoids are drawn at the 50% probability level.

Table 3. Bond Distances (Å) and Angles (deg) for Ge_5Cl_{12}·$GeCl_4$[a]

Ge(1)−Cl(1)	2.082(7)	Cl(1)#1−Ge(1)−Cl(1)	109.5
Ge(2)−Ge(3)	2.420(6)	Ge(3)#2−Ge(2)−Ge(3)	109.5
Ge(3)−Cl(2)	2.119(5)	Cl(2)#3−Ge(3)−Cl(2)	108.67(6)
		Cl(2)−Ge(3)−Ge(2)	110.26(6)

[a] Symmetry transformations used to generate equivalent atoms: #1, $z - {}^1/_2, -x + 1, -y + {}^3/_2$; #2, $y, -z + {}^3/_2, -x + {}^3/_2$; #3, $-y + {}^3/_2, -z + {}^3/_2, x$.

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Supporting Information Available: Listings of final positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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