Crystal Structure of Germanium Tetrachloride–Trimethylamine, $GeCl_4$,NMe_3

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The title compound has been examined by single-crystal *X*-ray diffraction and crystallises in the space-group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 6{\cdot}53$, $b = 12{\cdot}11$, $c = 12{\cdot}70$, $\beta = 106{\cdot}3°$. The structure was solved from photographically estimated three-dimensional data and refined to R 0·134 (for 583 independent reflections) and consists of discrete $GeCl_4,NMe_3$ molecules. Each molecule may be considered to be based on trigonal-bipyramidal germanium co-ordination with the trimethylamine occupying an axial position.

THE tetrahalides of group IVB (MX_4) are known to react with a variety of donor species and with unidentate ligands (L), to give compounds of the type MX_4,L and MX_4,2L.[1,2] In a few cases with the same donor and acceptor, both stoicheiometries have been observed experimentally, while in other cases either the 1 : 1 or 1 : 2 species, but not both, has been reported. There have been a number of *X*-ray studies on the 1 : 2 species of the tin compounds, and a few for those of silicon and germanium.[3] The literature of the 1 : 1 adducts shows that in tin chemistry a number of species have been structurally characterised on the basis of trigonal-bipyramidal co-ordination geometry whereas with the lighter congeners very little, if any, unambiguous data is to be found.

One of the best characterised 1 : 1 adducts of germanium is $GeCl_4$,NMe_3 [3-5] for which detailed vibrational spectroscopic studies favour a trigonal-bipyramidal molecule with the amine occupying an axial position (C_{3v} point-group symmetry). For trimethylamine with the tetrachlorides of Group IVB we find that silicon gives an unstable 1 : 1, germanium a 1 : 1 and an unstable 1 : 2, and tin both a 1 : 1 and 1 : 2 adduct,[1] the vibrational spectra strongly indicating that the silicon and germanium complexes (1 : 1) are isostructural.[3]

The novelty of five-co-ordination is an exploded myth [6] but there remains the possibility of either monomeric five-co-ordination or chlorine-bridged polymeric species for the compounds of the type MX_4,L. Within the confines of five-co-ordination structures both trigonal-bipyramidal and square-pyramidal shapes may be expected, with, in both cases, the possibility of geometrical isomerism. In order to place the spectroscopic assignments on a firm footing and to establish unambiguously the structure of one of the 1 : 1 adducts, an *X*-ray examination of $GeCl_4$,NMe_3 was undertaken.

Reaction of purified samples of germanium tetrachloride and trimethylamine in a glass vacuum system gave volatile $GeCl_4$,NMe_3. The substance could readily be transferred by low-temperature sublimation but raising the temperature in our early attempts to obtain suitable crystals gave a liquid (decomposition?) product. In the later preparations small quantities of the solid were sublimed *in vacuo* into thin-walled Pyrex capillaries which were sealed off and left at room temperature for several weeks, when crystals of the substance were formed. One crystal of suitable dimensions was deposited in the capillary section of the tube and this was used for the preliminary Weissenberg and precession photographs and for the data collection. It was not found to be possible to handle the compound in our dry-boxes owing to its reactivity and hence D_m was not obtained.

EXPERIMENTAL

Crystal Data.—$C_3H_9Cl_4GeN$, $M = 273{\cdot}6$, Monoclinic, $a = 6{\cdot}53 \pm 0{\cdot}02$, $b = 12{\cdot}11 \pm 0{\cdot}05$, $c = 12{\cdot}70 \pm 0{\cdot}05$ Å, $\beta = 106{\cdot}3 \pm 0{\cdot}2°$, $U = 964{\cdot}5$ Å^3, $Z = 4$, $D_c = 1{\cdot}89$ g cm^{-3}. Space-group $P2_1/c$ (No. 14) from systematic absences: $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 44·2 cm^{-1}. D_c for $Z = 4$ compares with D_m for $GeCl_4$ (1·9) and $GeCl_4$,2pyridine (1·88 g cm^{-3}).[7]

The crystal (*ca.* 0·65 × 0·30 × 0·30 mm) was mounted in a Pyrex capillary about its *a* axis with the longest dimension parallel to *a*. Data were recorded by the multiple-film equi-inclination Weissenberg technique for the layers

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0—5*kl* with zirconium-filtered Mo-K_α radiation; intensities were estimated visually by means of a graduated wedge. 847 independent reflections were measured up to a sin θ (max.) 0·342 from two octants of reciprocal space. Of these, 264 were considered unobserved and were given an intensity equal to one half of the minimum observable. Lorentz and polarization factors were applied in the usual way but no corrections for dispersion or absorption were made.

Structure Determination.—The structure was solved by conventional heavy-atom methods. Examination of the Harker line $(0,V,\frac{1}{2})$ and Harker section $(U,\frac{1}{2},W)$ of the unsharpened three-dimensional Patterson function gave the germanium position ($x/a = 0{\cdot}724$, $y/b = 0{\cdot}167$, $z/c = 0{\cdot}195$). Scattering factors for the neutral atoms of germanium, chlorine, nitrogen, and carbon were taken from ref. 8. A structure-factor calculation phased on the germanium position followed by an electron-density synthesis gave four large additional peaks corresponding to the four chlorine atoms, fully consistent with the Patterson function. One cycle of full-matrix least-squares refinement of the germanium and chlorine atoms (level-to-level scale-factors, atom positional and isotropic thermal parameters) gave *R* 0·242 and an electron-density synthesis phased on the new parameters gave the position of the nitrogen and three carbon atoms of the trimethylamine ligand from the four largest additional peaks. Two cycles of full-matrix least-squares refinement (42 parameters, all the atoms, scale factors, and atom-positional and isotropic thermal parameters) reduced *R* to 0·155. An analysis of $|\Delta\bar{F}|$ *vs.* $\bar{F}_o$ for various ranges of F_o gave an empirical weighting scheme $[w = 1/(A + BF_o + CF_o^3)$ where $A = 5{\cdot}0$, $B = 3{\cdot}0 \times 10^{-3}$, $C = 8{\cdot}0 \times 10^{-6}]$ and an analysis of $\Sigma\ w\Delta^2$ in terms of F_o and sin θ showed no gross irregularities. Both the observed and unobserved reflections were given weights according to the equation and those unobserved reflections for which $F_c < F_o$ were ignored in computing the parameter shifts in the least-square routines. The introduction of the calculated weights into the refinement reduced *R* to 0·152 and allowing the heavy atoms germanium and chlorine to have anisotropic temperature factors (61 parameters, atom-positional, and thermal parameters) allowed refinement to continue to a final *R* of 0·134, excluding 'less-thans', at which stage refinement was terminated. The decrease in *R* is highly significant when Hamilton's test[9] is applied. An electron-density synthesis phased on the final parameters showed only the expected peaks of the correct magnitude, and a difference synthesis showed no evidence for misplaced atoms. The final residual is higher than one would wish and reflects the poor quality of the data owing to experimental difficulties associated with the very reactive nature of the compound.

No hydrogen atoms were included in the structure-factor calculations. The final positional and thermal parameters and the standard deviations derived from the least-squares refinement are recorded in Tables 1 and 2, and Table 3 shows the intramolecular distances and angles. Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20306 (2 pp., 1 microfiche).*

All calculations were performed on the S.R.C. Atlas Computer, Harwell, using the *X*-ray system of crystallographic programs devised by J. M. Stewart.

TABLE 1

Final positional ($\times 10^4$) and isotropic thermal parameters with standard deviations in parentheses

	x/a	*y/b*	*z/c*	*B* (Å^2)
Ge	7186(06)	1610(03)	1869(03)	
Cl(1)	4406(17)	761(09)	2046(09)	
Cl(2)	8671(18)	990(10)	676(09)	
Cl(3)	9333(18)	587(10)	3198(09)	
Cl(4)	8295(17)	3087(09)	2757(09)	
N	5097(43)	2645(24)	593(22)	3·5(0·6)
C(1)	3543(71)	3230(38)	1035(35)	5·8(1·0)
C(2)	6414(81)	3446(44)	160(40)	6·9(1·2)
C(3)	3961(65)	1939(34)	−406(32)	5·0(0·9)

TABLE 2

Heavy-atom anisotropic temperature factors * ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge	246(13)	56(03)	73(03)	−12(06)	5(5)	0(3)
Cl(1)	246(36)	93(11)	115(10)	−46(16)	86(15)	14(9)
Cl(2)	441(38)	82(11)	89(10)	22(16)	102(16)	−24(8)
Cl(3)	372(37)	77(10)	96(10)	49(16)	61(15)	21(8)
Cl(4)	386(34)	63(10)	78(09)	6(14)	30(13)	−4(8)

* In the form

$$T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

TABLE 3

Intramolecular distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances			
Ge–Cl(1)	2·15(01)	Ge–N	2·19(03)
Ge–Cl(2)	2·15(01)	N–C(1)	1·47(06)
Ge–Cl(3)	2·24(01)	N–C(2)	1·50(06)
Ge–Cl(4)	2·13(01)	N–C(3)	1·54(05)
(*b*) Angles			
Cl(1)–Ge–Cl(2)	117·8(0·5)	N–Ge–Cl(1)	89·0(0·8)
Cl(1)–Ge–Cl(3)	91·4(0·4)	N–Ge–Cl(2)	89·4(0·9)
Cl(1)–Ge–Cl(4)	121·1(0·5)	N–Ge–Cl(3)	178·7(0·8)
Cl(2)–Ge–Cl(3)	91·5(0·5)	N–Ge–Cl(4)	87·7(0·8)
Cl(2)–Ge–Cl(4)	120·9(0·5)		
Cl(3)–Ge–Cl(4)	91·0(0·4)		
Ge–N–C(1)	110·2(2·2)	C(1)–N–C(2)	110·8(3·4)
Ge–N–C(2)	109·8(2·2)	C(1)–N–C(3)	111·0(2·8)
Ge–N–C(3)	110·3(2·1)	C(2)–N–C(3)	104·5(3·1)

DISCUSSION

The structure consists of discrete $GeCl_4,NMe_3$ molecules which are not required by the crystallographic analysis to have any symmetry. Table 3 and Figure 1 show, however, that to a good approximation the molecule has C_{3v} symmetry and that the co-ordination geometry around the germanium atom can very satisfactorily be described as a trigonal bipyramidal with N and Cl(3) occupying the axial positions. The Ge–Cl(ax) bond (2·24) is significantly longer than the Ge–Cl(eq) bonds (2·15, 2·15, and 2·13 Å). These bond lengths may be compared with values of 2·08(3) Å obtained from early electron diffraction studies[10] on $GeCl_4$ and 2·114(1) Å from microwave spectroscopy[11] on $GeHCl_3$. The

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies).

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trimethylamine geometry is consistent with that obtained from previous studies on similar molecules;[12] presumably to minimise steric interactions with the chlorine atoms it adopts a staggered rotameric configuration with respect to the Ge, Cl(1), Cl(2), Cl(4) grouping. All C ··· Cl contact distances are approximately the same [minimum 3·21(05), maximum value 3·36(04), mean (of six) 3·26 Å]. Figure 1 shows the isolated molecule and Figure 2 the molecular packing arrangement. The structure shows interesting similarities with $AsCl_3,NMe_3$ in which a formal lone-pair may be thought of as replacing Cl(4).[12]

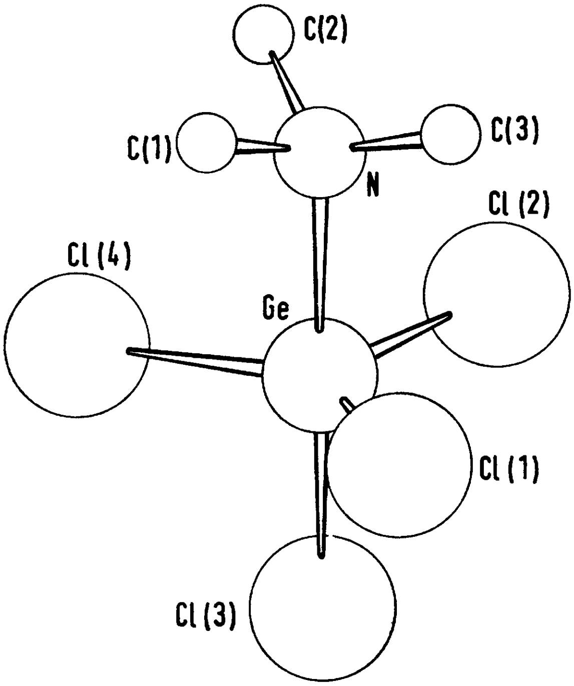

FIGURE 1 An isolated molecule

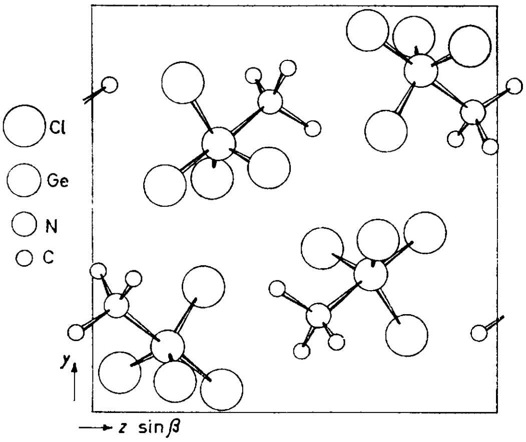

FIGURE 2 The unit cell showing the molecular packing arrangement looking in the +*x* direction

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