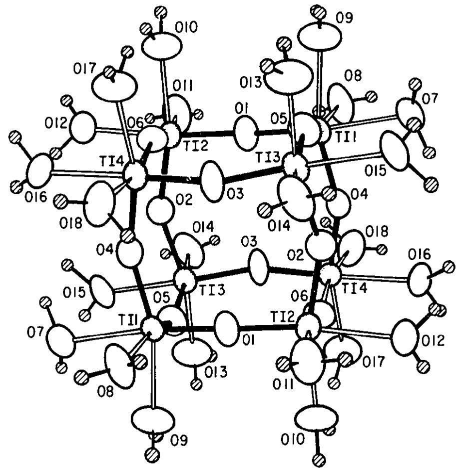

Fig. 1. The octameric cation complex, $[Ti_8O_{12}(H_2O)_{24}]^{8+}$. The ellipsoids are drawn at the 70% probability level.

References

Golub, A. M., Tischenko, A. F. & Kikot, I. F. (1970). *Russ. J. Appl. Chem.* pp. 2159–2163.

Griffith, W. P. (1970). *Coord. Chem. Rev.* **5**, 459–517.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

McCarthy, P. J. & Richardson, M. F. (1983). *Inorg. Chem.* **22**, 2979–2982.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Reichmann, M. G. & Bell, A. T. (1986). *Langmuir*, **3**, 111.

Walter-Levy, L. & Ferey, G. (1966). *Bull. Soc. Chim. Fr.* fasc. 2, p. 482.

Walter-Levy, L. & Ferey, G. (1968). *C.R. Acad. Sci. Sér. C*, **266**, 99–102.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1987). C**43**, 1683–1685

Structure of Germyl Chloride at 97 K

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Abstract. GeH_3Cl, $M_r = 111{\cdot}07$, orthorhombic, $Cmc2_1$, $a = 7{\cdot}146\,(3)$, $b = 5{\cdot}5587\,(21)$, $c = 8{\cdot}383\,(14)$ Å, $V = 333{\cdot}0$ Å^3, $Z = 4$, $D_x = 2{\cdot}215$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 9{\cdot}58$ mm^{-1}, $F(000) = 208$, $T = 97$ K, $R = 0{\cdot}0422$ for 500 observed reflections. The structure contains zigzag chains of molecules formed by close [3·3760 (16) Å] Cl···Ge intermolecular contacts: these chains are approximately linear at Ge and have an angle of 96·85 (5)° at Cl. At 2·2220 (16) Å, the Ge—Cl bond is considerably longer than the value of 2·14947 (5) Å found in the gas phase. Low-temperature X-ray powder diffraction shows SiH_3Cl and GeH_3Cl to be isostructural; it is perhaps more surprising that these compounds are isostructural with CH_3Cl.

Introduction. We have for some time been interested in the structures of the simple silyl halides SiH_3X (X = F, Cl, Br, I) and pseudohalides (*e.g.* SiH_3CN). Part of this interest stems from the observation that in the vibrational spectra large shifts occur in the ν(Si—X) or ν(Si—C) frequencies on going from the gas to the solid phase, suggesting significant intermolecular interactions in the crystal (Ball, Buttler & McKean, 1965; Cradock, personal communication). Single-crystal X-ray studies at low temperature have elucidated the structures of SiH_3CN (Barrow, Ebsworth & Harding, 1987), SiH_3F (Blake, Ebsworth, Henderson & Welch, 1985) and SiH_3I (Blake, Ebsworth, Henderson & Welch, 1987), confirming the presence of important secondary contacts. In the case of SiH_3Cl and SiH_3Br, however, our attempts to grow single crystals have been frustrated by the occurrence of phase transformations below the freezing points of these compounds. We have therefore turned our attention to the analogous germyl series and here we report the crystal structure of GeH_3Cl, where ν(Ge—Cl) drops from 423 to 371 cm^{-1} on going from the vapour to the solid phase (Freeman, Rhee & Wilson, 1963).

Experimental. Colourless cylindrical crystal, 0·04 × 0·04 × 0·05 cm, grown *in situ* on Weissenberg camera

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with low-temperature attachment from sample sealed in Pyrex capillary tube, space group identified by a combination of oscillation and Weissenberg photography, E statistics and successful refinement. D_m not determined, m.p. 221 K. Crystal transferred without melting as described previously (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) to CAD-4 diffractometer, 97 K, 14 reflections ($6{\cdot}5 < \theta < 9{\cdot}7°$) centred, graphite-monochromated Mo $K\alpha$ X-radiation.

For data collection $\theta_{\max} = 30°$, ω–2θ scans in 96 steps, ω scan width $1{\cdot}0 + 0{\cdot}5\tan\theta$, rapid pre-scan after which reflections with $I \geq 0{\cdot}5\sigma(I)$ remeasured to give final net $I > 33\sigma(I)$ subject to a maximum measuring time of 75 s, crystal orientation checked every 30 reflections and reset if necessary, two standards, no significant crystal movement or decay, two octants of data (519 unique reflections, h 0→7, k 0→10, l −11→11) in 8 X-ray hours.

For structure solution and refinement 500 reflections [$F \geq 6\sigma(F)$], Patterson and successive Fourier syntheses (Sheldrick, 1976), full-matrix least squares (F), at isotropic convergence data corrected for absorption, max. and min. corrections 1·031 and 0·697 respectively (Walker & Stuart, 1983), $w^{-1} = [\sigma^2(F) + 0{\cdot}000689F^2]$, H atoms included in calculated positions with r(Ge—H) = 1·33 Å and ∠HGeH = 109·47°, anisotropic thermal parameters for Ge and Cl, $U_{\rm iso} = 0{\cdot}08$ Å^2 for H. Alternative polarity gave R, wR 0·0463, 0·0649, polarity chosen gave R, wR 0·0422, 0·0574 and lower e.s.d.'s on all Ge and Cl parameters, S 1·19, data:variable ratio 24:1, $(\Delta/\sigma)_{\max}$ in final cycle <0·22, max. peak and min. trough in final ΔF synthesis 2·16 and −1·13 e Å^{-3} respectively. No correction for secondary extinction. Neutral scattering factors for Cl and H (Sheldrick, 1976) and Ge (Cromer & Mann, 1968), computer programs *SHELX76* (Sheldrick, 1976), *CALC* (Gould & Taylor, 1986), *PLUTO* (Motherwell, 1976).

Discussion. Table 1 lists the atomic fractional coordinates.* Fig. 1(a) is a view of the structure along the crystallographic a axis, onto the mirror planes which bisect the GeH_3Cl molecules; Fig. 1(b) is the same view for the published CH_3Cl structure (Burbank, 1953). Germyl chloride crystallizes as infinite zigzag in-phase chains of molecules running parallel to the c axis with, on average, Cl→Ge vectors parallel to +**c**. Chains are formed by short [3·3760 (16) Å] Cl···Ge contacts between molecules related by 2_1 screw axes and are characterized by Cl···Ge—Cl and Ge—Cl···Ge angles of 179·41 (6) and 96·85 (5)° respectively. The 4 + 1 coordination observed at Ge in the crystal is associated with a marked lengthening of the Ge—Cl bond in the crystal [2·2220 (16) Å] as compared with the gas-phase value of 2·14947 (5) Å (Cradock, McKean & MacKenzie, 1981).

Table 1. *Fractional coordinates of atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$(Å^2)
Ge	0·0	0·43303 (12)	0·44737 (24)	0·0282 (3)
Cl	0·0	0·1662 (3)	0·25	0·0374 (9)
H(1)	0·0	0·6535	0·3868	0·0800
H(2)	0·1516	0·4026	0·5365	0·0800

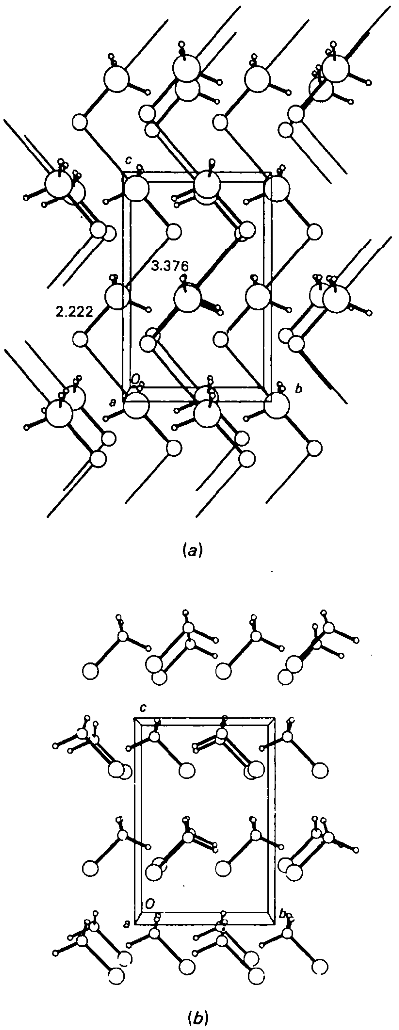

Fig. 1. Views of the packing of (a) GeH_3Cl and (b) CH_3Cl molecules along the a axis: the molecules lie on mirror planes normal to the direction of view. Bond lengths in (a) are in Å; e.s.d.'s are 0·0016 Å.

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* Lists of structure factors and anisotropic thermal parameters for Ge and Cl have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44009 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Unit-cell dimensions* (Å) *and space-group data*

	a	*b*	*c*	Space group	Reference
Cl_2	6·29	4·50	8·21	*Cmca*	Collin (1952)
CH_3Cl	6·495 (10)	5·139 (10)	7·523 (10)	$Cmc2_1$	Burbank (1953)
SiH_3Cl	7·119 (15)	5·568 (9)	8·453 (11)	$Cmc2_1$	This work
GeH_3Cl	7·146 (3)	5·5587 (21)	8·383 (14)	$Cmc2_1$	This work

From Guinier powder films of SiH_3Cl recorded at 148 K, we have established that it is isostructural with GeH_3Cl, and the close structural similarities between methyl chloride and elementary chlorine have been noted previously (Burbank, 1953): selected crystallographic data for these four compounds are listed in Table 2. Whereas the similarities between CH_3Cl and Cl_2 may be explained in terms of the similar sizes of Cl and CH_3 (van der Waals radii 1·8 and 2·0 Å respectively) and those between silyl and germyl chlorides in terms of the similar sizes of the silyl and germyl groups and the analogous Cl(3*p*)→Si(3*d*) and Cl(3*p*)→Ge(4*d*) supplementary bonding involved in the intermolecular interactions, the reasons for the similarity between the former and latter pair of compounds are less obvious. We believe this can be explained as follows: although the angles at C (~180°) and Cl (~90°) in solid CH_3Cl are similar to those at Ge and Cl in GeH_3Cl, the C···Cl non-bonded distance is 3·51 Å, well outside the sum of the van der Waals radii for C and Cl (3·3 Å) and indicative of essentially isolated molecules.

In the larger GeH_3Cl molecules, the existence of strong Ge···Cl intermolecular interactions allows a closer approach than would be possible for non-interacting molecules. The combination of these factors – increasing molecular size compensated by closer approach of molecules – has the result that the CH_3Cl structure is retained in GeH_3Cl and SiH_3Cl.

New studies of the vibrational spectra of solid GeH_3Cl and other silyl and germyl halides, using both IR and Raman spectroscopy, are under way in this Department and will be reported independently (Cradock & Gillespie, 1987).

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References

Ball, D. F., Buttler, M. J. & McKean, D. C. (1965). *Spectrochim. Acta*, **21**, 451–464.

Barrow, M. J., Ebsworth, E. A. V. & Harding, M. M. (1987). In preparation.

Blake, A. J., Cradock, S., Ebsworth, E. A. V., Rankin, D. W. H. R. & Welch, A. J. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2029–2033.

Blake, A. J., Ebsworth, E. A. V., Henderson, S. G. D. & Welch, A. J. (1985). *Acta Cryst.* C**41**, 1141–1144.

Blake, A. J., Ebsworth, E. A. V., Henderson, S. G. D. & Welch, A. J. (1987). In preparation.

Burbank, R. D. (1953). *J. Am. Chem. Soc.* **75**, 1211–1214.

Collin, R. L. (1952). *Acta Cryst.* **5**, 431–432.

Cradock, S. & Gillespie, G. (1987). In preparation.

Cradock, S., McKean, D. C. & MacKenzie, M. W. (1981). *J. Mol. Struct.* **74**, 265–276.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Freeman, D. E., Rhee, K. H. & Wilson, M. K. (1963). *J. Chem. Phys.* **39**, 2908–2922.

Gould, R. O. & Taylor, P. (1986). *CALC*. Program for molecular geometry calculations, Fortran77 version. Univ. of Edinburgh, Scotland.

Motherwell, W. D. S. (1976). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Structures of the Isomorphous Compounds Dimeric Tris[2(1*H*)-pyridine-2-thione]copper(I) Chloride and Tris[2(1*H*)-pyridine-2-thione]copper(I) Bromide

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Abstract. $[Cu(C_5H_5NS)_3]_2^{2+}.2Cl^-$, $M_r = 865{\cdot}0$, monoclinic, $P2_1/n$, $a = 7{\cdot}593\ (1)$, $b = 18{\cdot}995\ (2)$, $c = 13{\cdot}038\ (2)$ Å, $\beta = 102{\cdot}13\ (2)°$, $Z = 2$, $V = 1838{\cdot}5$ Å^3, $D_x = 1{\cdot}562$, $D_m = 1{\cdot}556$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}70$ mm^{-1}, $F(000) = 880$, $T = 295$ K, final $R = 0{\cdot}050$ for 1243 unique observed reflections.

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