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Germanium(IV) chloride at 193 K

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Single crystals of germanium(IV) tetrachloride, $GeCl_4$, were grown at 193 K. In the crystal structure, the isolated molecules have very well realised tetrahedral geometry.

Comment

Germanium(IV) chloride is an important intermediate both in the purification of semiconductor-grade germanium (Fisher & Teal, 1951) and in the preparation of organogermanium compounds *via* Li*R* or *R*Mg*X* reagents (Betka & Grobe, 1985). The title compound is a colourless volatile liquid at room temperature and the crystals have a melting point of 223.5 K. The structural chemistry of group IV elements affords abundant illustrations of the trends to be expected from increasing atomic size and electropositivity. In contrast to the homologous compounds silicon(IV) chloride and tin(IV) chloride, the crystal structure of germanium(IV) chloride is unknown. It is of interest whether the so far unknown crystal structure of germanium(IV) chloride is similar to those of silicon(IV) chloride (Zakharov *et al.*, 1986) and tin(IV) chloride (Reuter & Pawlak, 1999). We report here the structure and the crystal packing of the title compound and compare the crystal structures of ECl_4 with E = C, Si, Ge and Sn.

The title molecule is shown in Fig. 1, with the associated dimensions given in Table 1. Solid-state germanium(IV) chloride consists of isolated molecules which are held together by van der Waals interactions. The asymmetric unit consists of one molecule, with bond lengths and angles as expected for tetrahedral symmetry. The mean Ge—Cl distance [2.096 (2) Å] is in good agreement with the value in the cocrystal of Ge_5Cl_{12} with $GeCl_4$ [2.082 (7) Å; Beattie *et al.*, 1998] and can be compared with the r_{GeCl} value determined by electron diffraction for the molecule in the gas state [2.113 (3) Å; Morino *et al.*, 1960]. The crystal structure of germanium(IV) chloride is isostructural with CCl_4 (Piermarini, 1973), $SiCl_4$ (Zakharov *et al.*, 1986) and $SnCl_4$ (Reuter & Pawlak, 1999). For comparison, the cell parameters of these tetrahalides are, CCl_4: a = 9.07 (1) Å, b = 5.764 (3) Å, c = 9.201 (4) Å and β = 104.29 (5)°; $SiCl_4$: a = 9.608 (4) Å, b = 6.356 (2) Å, c = 9.672 (4) Å and β = 102.909 (3)°; $SnCl_4$: a = 9.864 (2) Å, b = 6.680 (1) Å, c = 9.937 (2) Å and β = 102.94 (1)°.

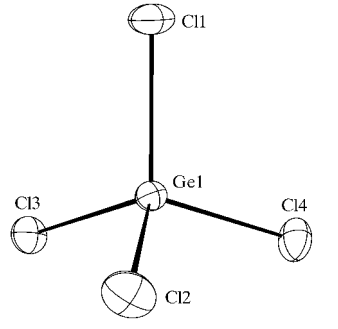

Figure 1
The molecular structure of germanium(IV) chloride, showing 50% probability displacement ellipsoids.

Similarities exist in the unit-cell dimensions, as well as in their ratios, with the differences reflecting the relative size difference in the atoms of the various substances. The crystal packing of germanium(IV) chloride is shown in Fig. 2. An approach to the description of the crystal packing on the basis of the hexagonal close packing for the isostructural compound $SnCl_4$ is given by Reuter & Pawlak (1999). The tetrahedral molecules show intermolecular Cl···Cl distances in the range 3.711 (5)–3.938 (5) Å, significantly longer than the normal van der Waals seperation of 3.6 Å.

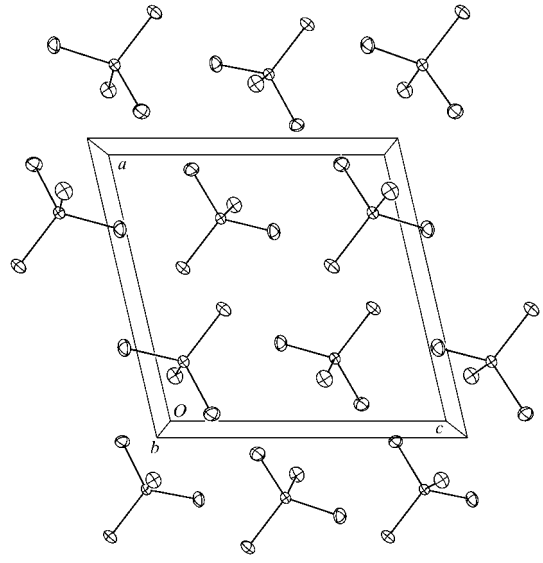

Figure 2
The packing of the germanium(IV) chloride structure.

Experimental

The title compound was first distilled under high vacuum for purification and was then transferred into an attached capillary. The sealed capillary was transferred to the diffractometer, which was fitted with a detachable cooling device. Single crystals suitable for X-ray diffraction were grown along the capillary using the *in situ* method of Boese *et al.* (1999).

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Crystal data

$GeCl_4$	D_x = 2.393 Mg m^{-3}
M_r = 214.39	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 347 reflections
a = 9.690 (3) Å	θ = 3.2–21.3°
b = 6.451 (2) Å	μ = 6.78 mm^{-1}
c = 9.774 (3) Å	T = 193 (2) K
β = 103.075 (6)°	Cylinder, colourless
V = 595.1 (4) Å^3	0.4 × 0.2 × 0.2 mm
Z = 4	

Data collection

Siemens CCD area-detector diffractometer	955 independent reflections
	905 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.018
Absorption correction: multi-scan (Blessing, 1995)	θ_{max} = 25.0°
	$h = -7 \rightarrow 10$
T_{min} = 0.214, T_{max} = 0.258	$k = -3 \rightarrow 7$
1423 measured reflections	$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2 + 0.5556P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F)$ = 0.026	
$wR(F^2)$ = 0.071	
S = 1.27	$(\Delta/\sigma)_{max}$ = 0.001
955 reflections	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
47 parameters	$\Delta\rho_{min}$ = −0.54 e Å^{-3}
	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0293 (19)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1996); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 1
Selected geometric parameters (Å, °).

Ge1—Cl4	2.0930 (12)	Ge1—Cl2	2.0966 (12)
Ge1—Cl1	2.0938 (12)	Ge1—Cl3	2.0984 (12)
Cl4—Ge1—Cl1	109.25 (5)	Cl4—Ge1—Cl3	109.00 (5)
Cl4—Ge1—Cl2	109.49 (5)	Cl1—Ge1—Cl3	109.97 (4)
Cl1—Ge1—Cl2	109.71 (5)	Cl2—Ge1—Cl3	109.42 (5)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1378). Services for accessing these data are described at the back of the journal.

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