Table 1. *Selected geometric parameters (Å, °)*

Ni—S6	2.1517 (9)	S7—C5	1.721 (3)
Ni—S1	2.1602 (8)	S8—C6	1.731 (3)
Ni—S7	2.1628 (8)	S8—C4	1.749 (3)
Ni—S2	2.1651 (8)	S9—C6	1.727 (3)
S1—C1	1.718 (3)	S9—C5	1.746 (3)
S2—C2	1.714 (3)	S10—C6	1.652 (3)
S3—C1	1.739 (3)	C1—C2	1.360 (4)
S3—C3	1.740 (3)	C4—C5	1.352 (4)
S4—C3	1.733 (3)	Cu—N1	2.065 (2)
S4—C2	1.750 (3)	Cu—N2	2.083 (2)
S5—C3	1.640 (3)	Cu—N3	2.088 (2)
S6—C4	1.719 (3)		
S6—Ni—S1	174.37 (4)	N1—Cu—N2^i	98.42 (9)
S6—Ni—S7	93.14 (3)	N2—Cu—N2^i	175.72 (13)
S1—Ni—S7	87.14 (3)	N1—Cu—N3^i	94.07 (9)
S6—Ni—S2	87.43 (3)	N2—Cu—N3^i	90.63 (9)
S1—Ni—S2	92.93 (3)	N1—Cu—N3	168.92 (9)
S7—Ni—S2	173.52 (4)	N2—Cu—N3	92.67 (9)
N1—Cu—N1^i	93.97 (13)	N3^i—Cu—N3	79.06 (14)
N1—Cu—N2	78.62 (9)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2. *Intermolecular S$\cdots$S contacts (Å) shorter than 3.70 Å*

S2$\cdots$S2^i	3.3959 (15)	S4$\cdots$S6^i	3.3904 (12)
S2$\cdots$S6^i	3.4936 (11)	S4$\cdots$S8^i	3.6581 (11)
S3$\cdots$S8^{ii}	3.4032 (13)	S7$\cdots$S9^{iii}	3.4657 (11)
S3$\cdots$S10^{ii}	3.6705 (13)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iii) $-x, y, \frac{1}{2} - z$.

H atoms were placed geometrically at a distance of 0.95 Å from and riding on their adjacent C atom, with an isotropic displacement parameter 20% higher than that of the parent atom. Although it would have been experimentally possible to locate the area detector 70 mm from the crystal (this would have allowed measurement up to $\theta_{max} = 26.2°$), it was deliberately placed 80 mm from the crystal ($\theta_{max} = 24.2°$). The reasons for this are: (i) a previous data collection on a four-circle diffractometer had shown that no significant diffraction occurred above 21°, showing that the diffracting power of the crystal was low, and (ii) because of this poor diffracting power, recorded reflections are mainly concentrated in the central part of the area detector. Overlapping reflections that may have occurred at a distance of 70 mm would have been eliminated during the integration process. This may have led to a low reflection-to-parameter ratio.

Data collection: *IPDS Software* (Stoe & Cie, 1996a). Cell refinement: *IPDS Software*. Data reduction: *X-RED* (Stoe & Cie, 1996b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *CAMERON* (Watkin *et al.*, 1996). Software used to prepare material for publication: *SHELXL97*.

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Redetermination of the Germanium Dichloride Complex with 1,4-Dioxane at 173 K

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Abstract

The structure of germanium dichloride–1,4-dioxane (1/1), $GeCl_2.C_4H_8O_2$, (1), has been redetermined at 173 K and refined in space group $C2/c$, rather than Cc which was used in the original determination by Kulishov *et al.* [*Zh. Strukt. Khim.* (1970), **11**, 61–64]. The data from the original determination have already been used to redetermine the structure of (1) in the revised space group $C2/c$ [Marsh (1997). *Acta Cryst.*

B53, 317–322], but we present here a more accurate structure determination using new data. The Ge—Cl bond length is 2.2813 (5) Å. The structure consists of infinite chains of alternating $GeCl_2$ and $C_4H_8O_2$ molecules, with a Ge···O distance of 2.399 (1) Å.

Comment

The title compound, (1), can be prepared by reduction of $GeCl_4$ with triethylsilane (Denk & Herrmann, 1993). The adduct of germanium dichloride with 1,4-dioxane is a stabilized form of the unstable (Neumann, 1991; Mironov, 1989) dichlorogermylene $GeCl_2$. The adduct is stable indefinitely under exclusion of air and moisture and is the preferred starting material for the synthesis of other divalent germanium compounds (Neumann, 1991; Mironov, 1989; Denk & Herrmann, 1993; Jutzi *et al.*, 1996). The original high-temperature synthesis from metallic germanium and HCl gas is quite cumbersome but the compound is now easily accessible by reduction of $GeCl_4$ with triethylsilane (Denk & Herrmann, 1993). In marked contrast to dicoordinate germylenes which are very air and moisture sensitive (Neumann, 1991; Mironov, 1989; Denk & Herrmann, 1993; Jutzi *et al.*, 1996), $GeCl_2$(1,4-dioxane) can be handled in air for brief periods of time. $GeCl_2$(1,4-dioxane) contains germanium with the coordination number 4 (two covalent bonds to chlorine and two dative bonds from the dioxane lone pair). The structure of the compound was described as a polymer by Kulishov and co-workers in 1970. We were intrigued by the high solubility of $GeCl_2$(1,4-dioxane) in ethers such as tetrahydrofuran, Et_2O and 1,4-dioxane. This high solubility is not usually associated with polymeric compounds. It implies either weak bonding between the germanium and the oxygen lone pairs in Kulishov's structure or the existence of a different modification composed of discrete units.

Cl—Ge—Cl

(1)
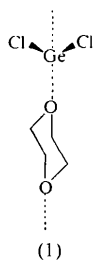
The crystal structure of (1) was originally determined by Kulishov and co-workers in 1970 using eye-estimated X-ray intensities which were measured from equi-inclination Weissenberg photographs exposed using Cu $K\alpha$ radiation. We have redetermined the structure of (1) at low temperature, using four-circle diffractometer data rather than using the original data collected by Kulishov *et al.* (1970) and reinterpreted by Marsh (1997).

As in the earlier determination, this structure consists of discrete molecules of $GeCl_2$ complexed with 1,4-dioxane molecules. In the space group $C2/c$, with $Z = 4$, molecules must lie on special positions. In the structure of (1), the Ge atom of the $GeCl_2$ molecules and the midpoints of both of the C—C bonds of the 1,4-dioxane molecules lie on twofold axes. The Ge—Cl bond length is 2.2813 (5) Å, which is longer than the average value of 2.163 (5) Å for Ge—Cl bonds in compounds which contain four-coordinate sp^3-hybridized Ge atoms [from a sample of 51 from the Cambridge Structural Database (Allen *et al.*, 1979)]. Fig. 1 shows the environment of a Ge atom in the unit cell. The closest distances between a Ge atom and O atoms of two different dioxane molecules is 2.399 (1) Å, which gives rise to infinite ···$O(C_4H_8)O$···$Ge(Cl_2)$···$O(C_4H_8)O$··· chains in the x direction. The Cl—Ge—Cl$(-x, y, \frac{1}{2} - z)$ angle is 94.30 (2)°, the O1···Ge···O1$(-x, y, \frac{1}{2} - z)$ angle is 173.15 (6)° and the Cl—Ge···O1 angle is 85.83 (3)°. In the vicinity of the Ge atom, there are two Cl atoms related by symmetry $(-x, -y, 1-z$ and $x, -y, -\frac{1}{2} + z)$ which give two Ge···Cl non-bonded distances of 3.463 (1) Å. The closest six atoms to Ge are two bonded Cl atoms, two non-bonded Cl atoms, and two O atoms from two different 1,4-dioxane molecules. These six atoms form a pseudo-octahedral environment around germanium, as shown in Fig. 1.

Two other compounds which are structurally similar to (1) are those formed between 1,4-dioxane and $HgCl_2$
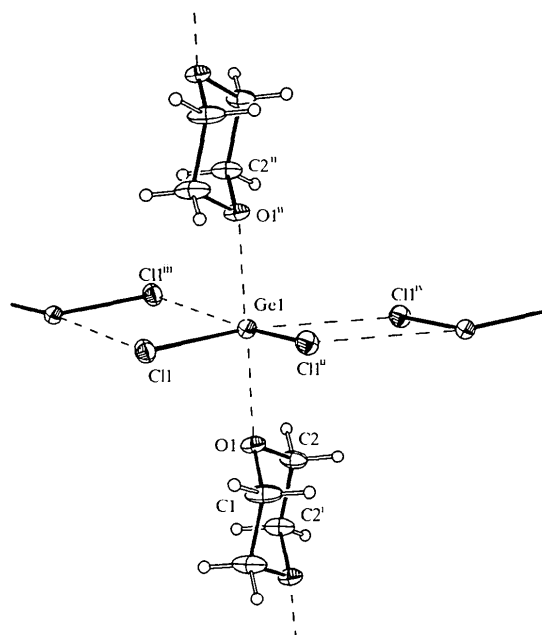

Fig. 1. View of the Ge-atom environment in the crystal structure of (1). Displacement ellipsoids are drawn at the 50% probability level. Symmetry-related atoms are as follows: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $-x, y, \frac{1}{2} - z$; (iii) $-x, -y, 1 - z$; (iv) $x, -y, -\frac{1}{2} + z$.

(Hassel & Hvoslef, 1954) and 1,4-dioxane and $GeBr_2$ (Gar et al., 1987). In the $HgCl_2$ complex, the Hg—Cl bond length is given as 2.34 Å and the Hg···O distance is 2.66 Å. The corresponding Ge—Br bond length in the $GeBr_2$ compound is 2.451 (1) Å and the Ge···O distance 2.43 Å.

The 1,4-dioxane molecule has crystallographic two-fold symmetry and is in the chair conformation. The bond lengths and angles are not statistically different from those in the structure of uncomplexed 1,4-dioxane at 153 K (Buschmann et al., 1986). 1,4-Dioxane forms an extensive series of adducts with element chlorides (MX_2). In these adducts, 1,4-dioxane always retains the chair conformation and acts as a monodentate or bridging ligand. The stoichiometries 1:1, 3:2 and 1:2 have been observed for transition metal chlorides of 1,4-dioxane (denHeijer & Driessen, 1980).

Experimental

$GeCl_2$(1,4-dioxane) was obtained according to the method of Denk & Herrmann (1993). Crystals were grown by slow cooling of a saturated hot solution of $GeCl_2$ in 1,4-dioxane (2 g in 100 ml of solvent) under inert gas.

Crystal data

$GeCl_2.C_4H_8O_2$	Mo $K\alpha$ radiation
$M_r = 231.59$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 40
$C2/c$	reflections
$a = 7.5811$ (6) Å	$\theta = 5.42–12.62°$
$b = 11.6974$ (8) Å	$\mu = 4.583$ mm^{-1}
$c = 8.7800$ (6) Å	$T = 173$ (2) K
$\beta = 97.129$ (7)°	Needle
$V = 772.58$ (10) Å^3	$0.36 \times 0.23 \times 0.18$ mm
$Z = 4$	Colourless
$D_x = 1.991$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.019$
ω scans	$\theta_{max} = 30°$
Absorption correction:	$h = -3 \rightarrow 10$
semi-empirical using ψ	$k = -1 \rightarrow 16$
scan (Sheldrick, 1995)	$l = -12 \rightarrow 12$
$T_{min} = 0.296$, $T_{max} = 0.438$	3 standard reflections
1491 measured reflections	every 97 reflections
1131 independent reflections	intensity decay: 6.96%
1059 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{max} = 0.392$ e Å^{-3}
$wR(F^2) = 0.053$	$\Delta\rho_{min} = -0.586$ e Å^{-3}
$S = 1.075$	Extinction correction:
1131 reflections	SHELXTL/PC
42 parameters	Extinction coefficient:
H atoms riding	0.0024 (5)

$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.5905P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ge1	0	0.02481 (2)	1/4	0.01527 (8)
Cl1	0.01998 (6)	0.15744 (4)	0.44186 (5)	0.02160 (10)
C1	0.4027 (2)	0.1376 (2)	0.2203 (3)	0.0293 (4)
C2	0.4026 (2)	-0.0634 (2)	0.2199 (2)	0.0232 (4)
O1	0.3180 (2)	0.03707 (10)	0.2715 (2)	0.0187 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ge1—Cl1	2.2813 (5)	C1—C1^i	1.503 (4)
Ge1—O1	2.3989 (12)	C2—O1	1.439 (2)
C1—O1	1.439 (2)	C2—C2^i	1.505 (3)
Cl1—Ge1—Cl1^{ii}	94.30 (2)	O1—C2—C2^i	110.24 (12)
Cl1—Ge1—O1	85.83 (3)	C1—O1—C2	109.59 (14)
Cl1^{ii}—Ge1—O1	89.51 (3)	C1—O1—Ge1	120.49 (10)
O1—Ge1—O1^{ii}	173.15 (6)	C2—O1—Ge1	114.18 (9)
O1—C1—C1^i	110.40 (14)		

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $-x, y, \frac{1}{2} - z$.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1995). Program(s) used to refine structure: SHELXTL/PC. Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

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