

2,2-Dichloro-1,3-bis(trimethylsilyl)- 1,3-diaza-2-silacyclopentane

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In the title compound, $C_8H_{22}Cl_2N_2Si_3$, the central Si atom is tetrahedrally coordinated by two Cl and two N atoms in a molecule that has crystallographically imposed C_2 symmetry. Comparison is made with the isomorphous structure having titanium instead of silicon at the central position in the diazacyclopentane ring [Tinkler, Deeth, Duncalf & McCamley (1996). *Chem. Commun.* pp. 2623–2624].

Comment

Chlorine-containing silicon compounds are useful synthons for the preparation of a variety of organosilanes, higher coordinated silicon derivatives and organopolysilanes (Pawlenko, 1980; Corriu & Young, 1989; West, 1995; Herzog, 2001). Crystallization of the title compound, (I), occurs from a saturated solution in pentane at 248 K. The crystals redissolve when the temperature in the Schlenk tube rises above 273 K.

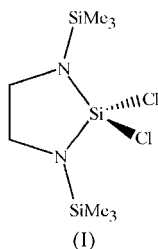


Fig. 1 shows the molecular structure of (I) and the atomic labelling scheme. Selected bond lengths and angles are listed in Table 1. Only half of the molecule is in the asymmetric unit; there is a twofold rotation axis passing through the Si atom and the middle of the C–C bond in the backbone of the diamide substituent. The central Si atom (Si1) is tetrahedrally coordinated by two Cl and two N atoms. Atom Si2 is also tetrahedrally coordinated, by three methyl groups and the N atom. Atom N1 has trigonal–planar geometry coordinated by the two Si atoms and atom C1 (the sum of the bond angles at N1 is 359.25°). The five-membered ring is in a half-chair conformation, in accordance with the crystallographic C_2 symmetry.

There are few reports of compounds containing the 2,2-dichloro-1,3-diaza-2-silacyclopentane fragment (*e.g.* Schlosser *et al.*, 1994), but surprisingly there exists an isomorphous structure with titanium instead of silicon at the central position in the diazacyclopentane ring (Tinkler *et al.*, 1996). Comparison with the titanium compound, (II), shows that the

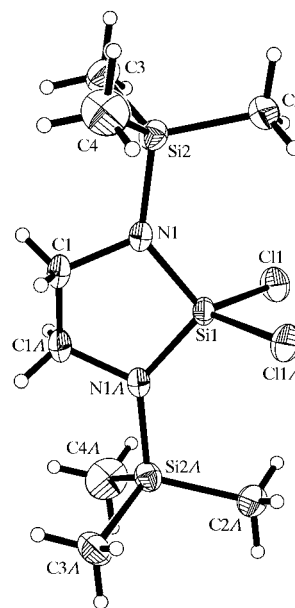


Figure 1

The molecular structure of (I), drawn with 50% probability displacement ellipsoids. Symmetry equivalent atoms with label 'A' are generated by twofold rotation (symmetry code: $-x, y, -z + \frac{1}{2}$).

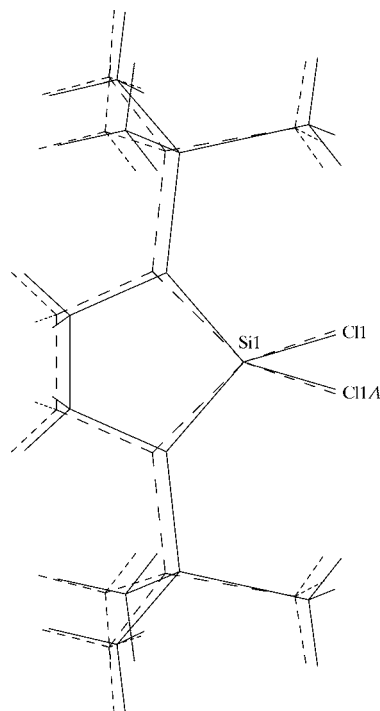


Figure 2

Superposition plot of (I) and the isomorphous titanium compound, (II) (*XP* in *SHELXTL-Plus*; Sheldrick, 1991). The solid line is for (I) and the broken line for (II).

molecular geometry is very similar (Fig. 2). Differences between the two molecules arise from the different atomic radii of silicon and titanium. We observed differences of 0.204 (1) (for $M\text{—Cl}$) and 0.157 (2) Å (for $M\text{—N}$) compared with the usual radii difference value (Pauling, 1962) of 0.19 Å. Thus, the Ti—Cl1 [2.2603 (6) Å] and Ti—N1 [1.844 (2) Å] bonds are longer than the Si1—Cl1 and Si1—N1 bonds by 9.9 and 9.4%, respectively. These different bond lengths also lead to different bond angles at the central atom. The N—M—N angle is 91.0 (1)° in (II) compared with a value of 99.77 (6)° in (I) (Table 1). This deformation allows the diamide ligand to retain its geometric features. The deformation of the five-membered ring from the titanium to the isomorphous silicon compound is shown in Fig. 2 in a superposition plot of both molecules. By contrast, the other angle in the coordination tetrahedron is compressed here from 110.73 (4)° (Cl1—Ti—Cl1A) by 8.86 (4)°. The molecules of the titanium and silicon compounds are arranged in the cell in an antiparallel orientation along the b axis. There are no intermolecular interactions within the sum of the van der Waals radii.

The structure of (I) is an example that titanium can be replaced by silicon with the formation of isomorphous compounds. Compound (I) might serve as a useful synthon for the preparation of organosilanes.

Experimental

Triethylamine (5 ml, 0.036 mol) was added to a solution of silicon tetrachloride (2 ml, 0.017 mol) in 100 ml of tetrahydrofuran. 1,3-Bis-(trimethylsilyl)ethylenediamine (3.27 g, 0.016 mol) was dissolved in tetrahydrofuran and added dropwise to the reaction mixture. A white precipitate of triethylammonium chloride was formed. The suspension was stirred for 6 h at reflux temperature. The solid triethylammonium chloride was removed by filtration. The solvent and the excess of triethylamine were then distilled off at reduced pressure. The product was distilled at 0.013 Torr and 303–323 K. The viscous liquid that was obtained after distillation solidified on standing overnight at room temperature (yield 3.3 g, 68%; m.p. 356 K). Crystals suitable for X-ray structure analysis were obtained by recrystallization from pentane and storage in a freezer at 248 K for several weeks. NMR (CDCl_3 , 298 K, TMS): ^1H δ 0.19 (s, SiMe_3), 3.16 (s, $-\text{CH}_2-$); ^{13}C δ -0.5 (SiMe_3), 45.2 ($-\text{CH}_2-$); ^{29}Si δ -18.6 (SiCl_2), 6.2 (SiMe_3).

Crystal data

$\text{C}_8\text{H}_{22}\text{Cl}_2\text{N}_2\text{Si}_3$	$V = 1605.52$ (8) Å ³
$M_r = 301.45$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 6.8227$ (2) Å	$\mu = 0.61$ mm ⁻¹
$b = 13.4226$ (4) Å	$T = 153$ (2) K
$c = 17.5317$ (5) Å	$0.50 \times 0.45 \times 0.35$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	18751 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2488 independent reflections
$T_{\min} = 0.752$, $T_{\max} = 0.816$	2143 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.068$	$\Delta\rho_{\text{max}} = 0.38$ e Å ⁻³
$S = 0.97$	$\Delta\rho_{\text{min}} = -0.18$ e Å ⁻³
2488 reflections	
80 parameters	

Table 1

Selected geometric parameters (Å, °).

Si1—N1	1.6866 (9)	N1—C1	1.4912 (14)
Si1—Cl1	2.0562 (3)	C1—C1^i	1.524 (2)
Si2—N1	1.7413 (10)		
$\text{N1}^i\text{—Si1—N1}$	99.77 (6)	C1—N1—Si2	118.23 (7)
Cl1—Si1—Cl1^i	101.87 (2)	Si1—N1—Si2	133.73 (5)
Cl1—N1—Si1	107.29 (7)		

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

Atoms H1 and H2 on C1 were located by difference Fourier synthesis and refined without constraints. The positions of the H atoms of the methyl groups were idealized and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 1991); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3074). Services for accessing these data are described at the back of the journal.

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