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Complexes of mixed silicon halides with 4-picoline

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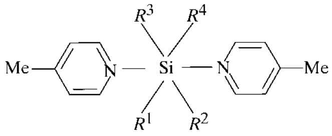
The reaction products of an addition reaction of five different silicon tetrahalides with the aromatic nitrogen base 4-methylpyridine are presented. The following five structures are isomorphous: (I) tetrachlorobis(4-methylpyridine)silicon, $C_{12}H_{14}Cl_4N_2Si$, (II) bromotrichlorobis(4-methylpyridine)silicon, $C_{12}H_{14}BrCl_3N_2Si$, (III) dibromodichlorobis(4-methylpyridine)silicon, $C_{12}H_{14}Br_2Cl_2N_2Si$, (IV) tribromochlorobis(4-methylpyridine)silicon, $C_{12}H_{14}Br_3ClN_2Si$, and (V) tetrabromobis(4-methylpyridine)silicon, $C_{12}H_{14}Br_4N_2Si$. The molecules of (I) and (V), with D_{2h} symmetry, have crystallographic C_{2h} symmetry, while the molecules of (II), (III) and (IV) have a lower molecular symmetry, but as a result of the disorder of the halogen ligands, they appear to be of the same crystallographic symmetry. The environment around the Si atom can be described as a slightly distorted octahedron with the methylpyridine ligands occupying axial positions and the four halogen ligands in the equatorial plane. In spite of the different substitution pattern of the silicon centre, there are only insignificant differences between these five structures.

Comment

In recent years the extension of the coordination sphere of silicon in complexes with organic nitrogen bases has been the subject of numerous studies (Bechstein *et al.*, 1990; Chuit *et al.*, 1993; Kane *et al.*, 1998; Hensen *et al.*, 1998, 2000). Several complexes of silicon halides are already known, but only little is known about adducts of mixed silicon halides, because exchange reactions have to be taken into account. This kind of exchange reaction between silicon tetrahalides at high temperatures and pressures has been described by Forbes & Anderson (1944) and was recently proved (Hensen *et al.*, 2000) at ambient conditions. Furthermore, it was presumed (Wannagat *et al.*, 1954) that pyridine or comparable ligands catalyze halogen exchange reactions of silicon halides. This would mean that during the reaction of mixed silicon halides with nitrogen bases, not only the Lewis acid-base reaction, but also base-catalyzed dismutations have to be taken into account (Hass & Bechstein, 1981; Bassindale *et al.*, 1995; Kost *et al.*, 1995; Herzog *et al.*, 1996; Boudjouk *et al.*, 1998). We present in this work crystal structures of complexes in which the silicon centre carries different halogen ligands.



	R^1	R^2	R^3	R^4
(I)	Cl	Cl	Cl	Cl
(II)	Cl	Cl	Cl	Br
(III)	Cl	Cl	Br	Br
(IV)	Cl	Br	Br	Br
(V)	Br	Br	Br	Br

All five compounds form isomorphous crystals and the cell parameters show only minor differences. However, the following trends are noticeable: in the line from $SiCl_4$ to $SiBr_4$ the *c* axis is shorter, whereas the *a* and the *b* axes are longer.

Compounds (I) and (V) belong to the symmetry point group C_{2h} (deviating only slightly from molecular D_{2h} symmetry). (II), (III) and (IV) are of lower molecular symmetry, but as a result of the disorder of the halogen ligands, they display the same crystallographic symmetry as (I) and (V). The Si atom is located on a special position of site

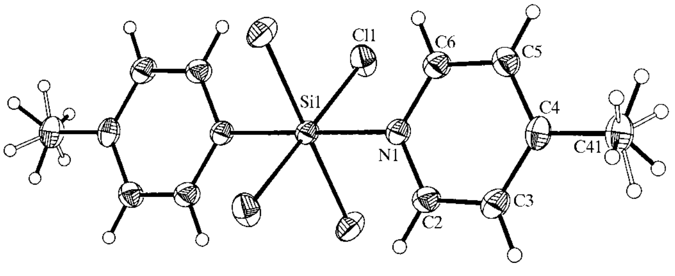


Figure 1
Perspective view of (I) with the atom numbering; only symmetry-independent atoms are labelled; displacement ellipsoids are at the 50% probability level.

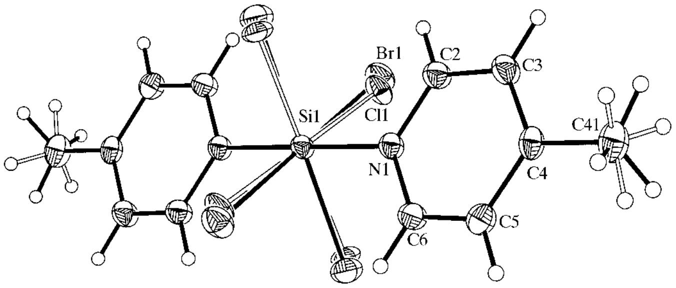


Figure 2
Perspective view of (II) with the atom numbering; only symmetry-independent atoms are labelled; displacement ellipsoids are at the 50% probability level. The crystallographic symmetry imposes Br/Cl disorder at the site of each halogen ligand. This figure is also representative of the structures of (III) and (IV).

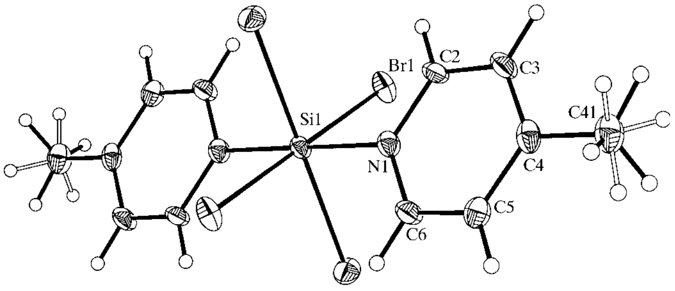


Figure 3
Perspective view of (V) with the atom numbering; only symmetry-independent atoms are labelled; displacement ellipsoids are at the 50% probability level.

symmetry $2/m$ and the picoline moieties lie on a crystallographic mirror plane. Only the halogen ligands and two H atoms of each methyl group occupy a general position. The silicon centre appears in a nearly ideal octahedral environment, where the two picoline ligands occupy axial positions and the four halogen ligands lie in the equatorial plane. There are only minor deviations from the perfect octahedral coordination. The planes of the methylpyridine rings bisect the Hal—Si—Hal angle almost exactly. As a result of the crystallographic symmetry, the N—Si—N bond angles and the Hal—Si—Hal bond angles of opposite halogen atoms are exactly 180°. The remaining bond angles at Si differ only insignificantly from 90°. In spite of the different substitution pattern of the silicon centre, comparable geometric parameters are nearly identical in all five structures: the mean value of the Si—N bond length is 1.980 (4) Å. The C—N—C angle [mean value is 117.6 (1)°] is not affected by the different substitution pattern of the silicon centre, either. The crystallographic symmetry requires that there is only a quarter of the molecule in the asymmetric unit. As a result of that, the halogen atoms in (II), (III) and (IV) are disordered and they cannot be distinguished (see experimental section).

The molecules crystallize in planes perpendicular to the crystallographic *a* axis. The distance between these planes is *a*/2. A view (Fig. 4) of these planes shows that the aromatic residues are nearly perfectly stacked and the Si—Hal$_4$ moieties fill the remaining gaps.

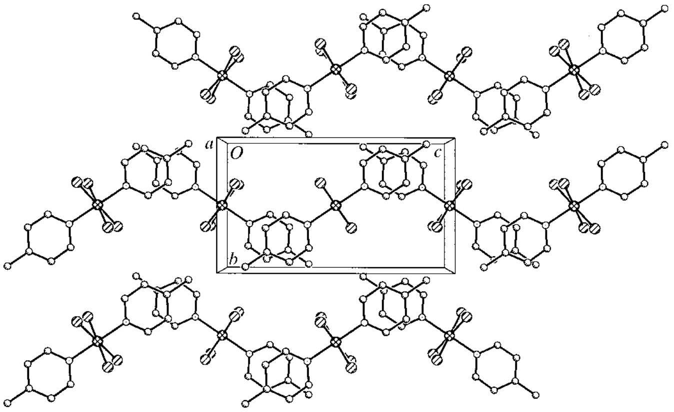


Figure 4
Packing diagram of (I) representative for all five structures; view perpendicular to the *b*/*c* plane.

The structures presented in this paper are isostructural with *trans*-tetrachlorobis(4-methylpyridine)titanium (Hensen *et al.*, 1999). The presence of an aromatic base during the reaction to synthesize these compounds did not considerably stimulate the halogen exchange, a fact that has already been observed (Hensen *et al.*, 2000). As a result of that, no dismutation could be detected and each of the reaction products could be recrystallized. This result could also be attributed to the high dilution of the substance in the solvent and the fact that the complexes are extremely poorly soluble.

Experimental

To the respective silicon halide (5 mmol) in chloroform (25 ml) 4-picoline was added and the reaction was monitored by measuring the temperature. After approximately 3 h, the precipitated solid was isolated, washed and dried. Crystals of (V) were obtained by heating the powder in an evacuated glass ampoule for 2 h to 500 K, then for 5 h to 445 K and cooling down the sample to room temperature within 4 h. (I) to (IV) were dissolved in hot chloroform and crystals appeared within 10 to 15 h at room temperature. Elemental analyses: (II), $C_{12}H_{14}BrCl_3Si$: calculated: C 36.0, H 3.5, Br 19.9, Cl 26.5, N 7.0%; found: C 36.3, H 3.7, Br 18.9, Cl 25.7, N 7.0%; (III), $C_{12}H_{14}Br_2Cl_2Si$: calculated: C 32.4, H 3.2, Br 35.9, Cl 15.9, N 6.3%; found: C 33.0, H 3.3, Br 36.3, Cl 16.1, N 6.3%; (IV), $C_{12}H_{14}Br_3ClSi$: calculated: C 30.9, H 3.4, Br 47.5, Cl 7.0, N 5.6%; found: C 30.1, H 3.4, Br 48.8, Cl 6.1, N 5.8%.

Compound (I)

Crystal data

$C_{12}H_{14}Cl_4N_2Si$
$M_r = 356.14$
Orthorhombic, *Pmna*
$a = 7.1766 (1)$ Å
$b = 7.8911 (1)$ Å
$c = 13.7036 (1)$ Å
$V = 776.052 (16)$ Å^3
$Z = 2$
$D_x = 1.524$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1$–$25°$
$\mu = 0.827$ mm^{-1}
$T = 173 (2)$ K
Block, colourless
0.60 × 0.40 × 0.40 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.637$, $T_{\max} = 0.733$
10 172 measured reflections
853 independent reflections
815 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\max} = 26.27°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
211 standard reflections
frequency: 1080 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.058$
$S = 1.148$
853 reflections
56 parameters
H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.2249P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Si1—N1	1.9835 (13)	N1—C2	1.357 (2)
Si1—Cl1	2.2030 (3)	N1—C6	1.359 (2)
N1—Si1—Cl1	89.88 (3)	C2—N1—C6	117.47 (14)
Cl1—Si1—N1—C6	45.452 (9)		

Compound (II)

Crystal data

$C_{12}H_{14}BrCl_3N_2Si$
$M_r = 400.60$
Orthorhombic, *Pmna*
$a = 7.177$ (1) Å
$b = 7.962$ (1) Å
$c = 13.557$ (1) Å
$V = 774.69$ (16) Å^3
$Z = 2$
$D_x = 1.717$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 8192 reflections
$\theta = 1$–25°
$\mu = 3.235$ mm^{-1}
$T = 173$ (2) K
Plate, colourless
0.40 × 0.30 × 0.10 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.358$, $T_{\max} = 0.738$
24 114 measured reflections
1278 independent reflections
1051 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 30.49°$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$
162 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.111$
$S = 1.123$
1278 reflections
65 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.7835P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = < 0.001$
$\Delta\rho_{\max} = 0.65$ e Å^{-3}
$\Delta\rho_{\min} = -1.14$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Br1—Si1	2.3695 (11)	Si1—N1	1.973 (3)
Cl1—Si1	2.1856 (10)		
N1—Si1—Cl1	89.5 (2)	C2—N1—C6	117.7 (3)
N1—Si1—Br1	90.9 (2)		
Cl1—Si1—N1—C2	47.09 (19)	Br1—Si1—N1—C2	43.4 (2)

Compound (III)

Crystal data

$C_{12}H_{14}Br_2Cl_2N_2Si$
$M_r = 445.06$
Orthorhombic, *Pmna*
$a = 7.252$ (2) Å
$b = 8.120$ (2) Å
$c = 13.540$ (3) Å
$V = 797.3$ (3) Å^3
$Z = 2$
$D_x = 1.854$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7725 reflections
$\theta = 1$–25°
$\mu = 5.481$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.35 × 0.30 × 0.12 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.162$, $T_{\max} = 0.520$
14 499 measured reflections
1110 independent reflections
969 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 28.68°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 18$
183 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.063$
$S = 1.119$
1110 reflections
66 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 0.6549P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0048 (9)

Table 3
Selected geometric parameters (Å, °) for (III).

Br1—Si1	2.3734 (8)	Si1—N1	1.983 (2)
Cl1—Si1	2.1994 (11)		
N1—Si1—Cl1	89.1 (3)	C2—N1—C6	117.7 (2)
N1—Si1—Br1	90.46 (15)		
Cl1—Si1—N1—C2	47.5 (4)	Br1—Si1—N1—C2	44.60 (14)

Compound (IV)

Crystal data

$C_{12}H_{14}Br_3ClN_2Si$
$M_r = 489.52$
Orthorhombic, *Pmna*
$a = 7.296$ (1) Å
$b = 8.211$ (1) Å
$c = 13.472$ (1) Å
$V = 807.07$ (16) Å^3
$Z = 2$
$D_x = 2.014$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 4418 reflections
$\theta = 1$–25°
$\mu = 7.725$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.25 × 0.15 × 0.10 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.224$, $T_{\max} = 0.462$
11 697 measured reflections
1005 independent reflections
823 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 27.48°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 17$
137 standard reflections
frequency: 900 min
intensity decay: none

Table 4
Selected geometric parameters (Å, °) for (IV).

Br1—Si1	2.3758 (6)	Si1—N1	1.981 (2)
Cl1—Si1	2.2021 (11)		
N1—Si1—Cl1	88.3 (6)	C2—N1—C6	117.4 (3)
N1—Si1—Br1	90.32 (9)		
Cl1—Si1—N1—C2	47.4 (5)	Br1—Si1—N1—C2	45.24 (5)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.052$
$S = 1.161$
1005 reflections
66 parameters
H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.3546P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0044 (6)

Compound (V)

Crystal data

$C_{12}H_{14}Br_4N_2Si$
$M_r = 533.98$
Orthorhombic, *Pmna*
$a = 7.3298$ (2) Å
$b = 8.2819$ (3) Å
$c = 13.4126$ (3) Å
$V = 814.21$ (4) Å^3
$Z = 2$
$D_x = 2.178$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7725 reflections
$\theta = 1$–$25°$
$\mu = 9.947$ mm^{-1}
$T = 143$ (2) K
Block, colourless
0.30 × 0.20 × 0.05 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.105$, $T_{\max} = 0.609$
7079 measured reflections
907 independent reflections
728 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.045$
$\theta_{\max} = 26.38°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 16$
183 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.041$
907 reflections
56 parameters
H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.9192P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (V).

Br1—Si1	2.3835 (3)	Si1—N1	1.979 (4)
N1—Si1—Br1	90.11 (8)	C6—N1—C2	117.6 (4)
Br1—Si1—N1—C2	45.660 (9)		

All H atoms were initially located by difference Fourier synthesis. Subsequently their positions were idealized and constrained to ride on their parent atoms with C—H$_{\rm aromatic}$ = 0.95 and C—H$_{\rm methyl}$ = 0.98 Å, and fixed individual displacement parameters [U(H) = $1.2U_{\rm eq}$(C$_{\rm aromatic}$) or U(H) = $1.5U_{\rm eq}$(C$_{\rm methyl}$)]. The H atoms of the methyl groups are disordered. Two orientations differing by a 60° rotation about the C$_{\rm aromatic}$—C$_{\rm methyl}$ bond could be identified.

Due to the crystallographic symmetry of these structures, the halogen atoms of (II), (III) and (IV) are disordered. The resolution of the data did not allow for distinguishing two distinct positions for Cl and Br. Only one peak was found in the respective difference maps. Thus, Br and Cl were refined with a site occupation factor fixed to the appropriate value (according to the elemental analyses) and a restrained bond length of 2.383 (1) and 2.203 (1) Å for Si—Br and Si—Cl, respectively. A search in the Cambridge Structural Database (Version 5.18, October 1999; Allen & Kennard, 1993) for the fragment SiN_2X_4 (X = any group 7A element) yielded only one comparable structure: tetrachlorodipyridylsilane (Bechstein *et al.*, 1990) which was measured at room temperature. Thus, we employed the values found in (I) and (V) as restraints for the Si—Cl and Si—Br lengths. For (II), the anisotropic displacement parameters of Cl and Br were restrained to have the same $U_{\rm ij}$ components with an effective standard deviation of 0.001.

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1098). Perspective views of compounds (III) and (IV) and a packing diagram of (I) have also been deposited. Services for accessing these data are described at the back of the journal.

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