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trans-Dichlorotetrakis(4-methylpyridine)silicon bis(triiodide) chloroform solvate

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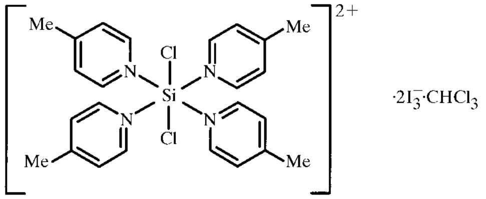
At 173 K, the dication of the title compound, $C_{24}H_{28}Cl_2N_4Si^{2+}\cdot 2I_3^{-}\cdot CHCl_3$, is located on a crystallographic fourfold rotation axis. The chloro ligands occupy axial positions and the four 4-methylpyridine ligands lie in the equatorial plane. The almost linear I_3^{-} ion is located on a crystallographic mirror plane and displays two significantly different I—I bond lengths. Furthermore, chloroform molecules, which are disordered about a centre of inversion, fill the remaining gaps in the crystal structure.

Comment

The extension of silicon's coordination sphere in compounds formed from silicon halides and organic nitrogen bases has been of scientific interest over a long period of time (Hensen *et al.*, 1983; Bechstein *et al.*, 1990; Chuit *et al.*, 1993; Kane *et al.*, 1998; Hensen *et al.*, 1998; Hensen, Mayr-Stein, Stumpf *et al.*, 2000). Neutral adducts as well as cationic complexes have been characterized. Silylium ions have played an important part in recent research efforts in the area of silicon chemistry (Belzner, 1997; Reed, 1998). Most known ionic complexes contain charge-stabilizing alkyl ligands bound to the silicon centre. Only recently, the first ligand-stabilized SiH_2^{2+} dications (Fleischer *et al.*, 1996; Hensen *et al.*, 1998) and $SiCl_2^{2+}$ dications (Hensen, Mayr-Stein, Stumpf *et al.*, 2000) were found. These were prepared using the strong nitrogen base *N*-methylimidazole as a stabilizing ligand. In the work presented in this paper, we have prepared a ligand-stabilized $SiCl_2^{2+}$ dication by introducing iodine as a suitable leaving group which enabled the use of a common pyridine derivative as a ligand. The title compound, (I), was synthesized from $SiCl_2I_2$ and the unidentate ligand 4-methylpyridine.



(I)

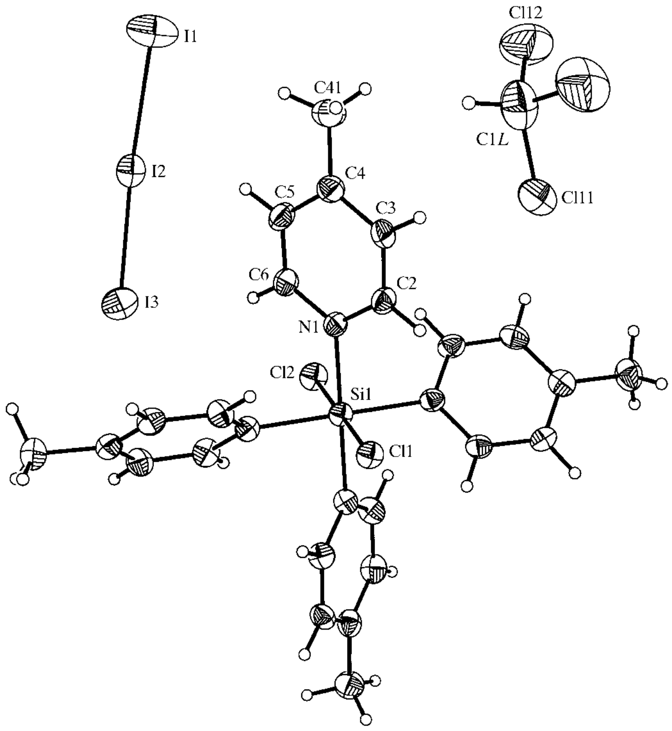


Figure 1
Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Compound (I) shows a sixfold coordinated silicon centre, with only insignificant deviations from ideal octahedral symmetry (Fig. 1). The four 4-methylpyridine ligands are located in the equatorial plane and two chloro ligands occupy axial positions. The $SiCl_2$ moiety is located on a crystallographic fourfold rotation axis, with the result that only a quarter of the molecule is in the asymmetric unit. The two Si—Cl bonds are of equal length. The I_3^{-} ion is located on a crystallographic mirror plane; it is nearly linear, but the two I—I bonds are significantly different. A search in the Cambridge Structural Database (CSD, Version 5.18, October 1999; Allen & Kennard, 1993) revealed that the two I—I bond lengths in I_3^{-} anions are usually equal, but different bond lengths are not uncommon. The resulting gaps in the crystal structure, located around the sites with crystallographic $2/m$ symmetry, are filled with chloroform molecules (see experimental section).

The only comparable compound published so far in the CSD is *trans*-dichlorotetrakis(*N*-methylimidazolyl)silicon, of which three different crystal structures were obtained (Hensen, Mayr-Stein, Stumpf *et al.*, 2000): one with chloride as counterion and chloroform as solvent, and two with bromide as counterion, but with chloroform and acetonitrile, respectively, as solvent. Whereas the mean Si—N bond in these structures [1.90 (1) Å] is a little bit shorter than in the title compound, the mean Si—Cl bond [2.19 (1) Å] is slightly longer.

A comparison of the title compound with the related hydride structures dihydridotetrakis(3-picoline)silicon dichloride (Fleischer *et al.*, 1996), dichlorodihydrodipyridylsilane, dichlorodihydrobis(3-picoline)silane and dihydrotetrapyridylsilane (Hensen *et al.*, 1998) revealed that the Si—N bond length is nearly independent of the kind of the nitrogen base ligand, but the Si—Cl bond is considerably longer [2.2881 (4) and 2.2922 (4) Å] when the central Si atom is bonded to two H atoms instead of two nitrogen bases.

Experimental

Due to the silicon halides' extreme susceptibility to hydrolysis, all operations were carried out under an inert gas atmosphere. Also, exposure of $SiCl_2I_2$ to light was minimized. 4-Methylpyridine (5.0 mmol) was added dropwise to $SiCl_2I_2$ (1 mmol) in *n*-pentane (20 ml). The yellow precipitate was separated. Elemental analysis of the substance as well as thermochemical observations revealed that less than the expected four equivalents of the nitrogen base reacted to form a complex. Dismutation of $SiCl_2I_2$ (Hass *et al.*, 1989) occurred during the preparation of the complex leading to a mixture of product complexes with varying stoichiometry with respect to halide distribution and silicon halide/methylpyridine ratio. We were able to crystallize two component complexes from the moderately soluble product powder: $SiCl_4$(4-methylpyridine)$_2$ (Hensen, Mayr-Stein, Spangenberg & Bolte, 2000) and the title compound from a hot chloroform solution that was allowed to evaporate at room temperature under vacuum over two weeks. The unexpected presence of I_3^- indicates side reactions with air.

Crystal data

$C_{24}H_{28}Cl_2N_4Si^{2+}\cdot 2I_3^-\cdot CHCl_3$
$M_r = 1352.26$
Tetragonal, I_4/m
$a = 16.241$ (2) Å
$c = 15.210$ (3) Å
$V = 4011.8$ (11) Å^3
$Z = 4$
$D_x = 2.239$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8014 reflections
$\theta = 0$–25°
$\mu = 5.032$ mm^{-1}
$T = 173$ (2) K
Block, dark red
0.30 × 0.25 × 0.25 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.244$, $T_{\max} = 0.284$
47624 measured reflections
2392 independent reflections
1957 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 27.48°$
$h = -21 \rightarrow 21$
$k = -21 \rightarrow 21$
$l = -19 \rightarrow 19$
398 standard reflections
frequency: 1200 min
intensity decay: none

Table 1

Selected geometric parameters (Å, °).

I1—I2	2.9327 (10)	Si1—Cl1	2.140 (3)
I2—I3	2.8944 (10)	Si1—Cl2	2.142 (3)
Si1—N1	1.967 (4)		
I3—I2—I1	175.98 (3)	N1—Si1—Cl2	90.08 (13)
N1—Si1—Cl1	89.92 (13)	C6—N1—C2	117.3 (4)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 1.047$
2392 reflections
113 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 56.0581P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 3.21$ e Å^{-3} (0.87 Å from I1)
$\Delta\rho_{\min} = -3.36$ e Å^{-3}

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(aromatic) = 0.95 and C—H(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 methyl group was allowed to rotate about its local threefold axis.

The C atom, the H atom and one Cl atom of the chloroform are located on a crystallographic mirror plane, one Cl atom occupies a general position. Due to the chloroform's position so close to a crystallographic inversion centre, another chloroform molecule is generated by the symmetry operation $-x, 1 - y, 1 - z$. Since the existence of both chloroform molecules is mutually exclusive, the chloroform site was refined as half occupied.

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: LN1099). A packing diagram of compound (I) has also been deposited. Services for accessing these data are described at the back of the journal.

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