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cis-Bis(2,2′-bipyridyl-*N*,*N*′)dichlorosilicon diiodide

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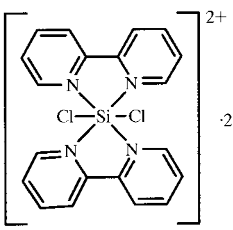
The crystal and molecular structure of the title compound, $C_{20}H_{16}Cl_2N_4Si^{2+}\cdot 2I^-$, has been determined at 173 K. To our knowledge, this is the first crystal structure of a silicon tetrahalide complex with a bidentate base as a ligand. The two chloro ligands are *cis* relative to each other. The Si—N bonds *trans* to a chloro ligand are longer than the Si—N bonds *trans* to an Si—N bond. This feature is observed for the majority of M(bipy)$_2$Cl$_2$ (M = metal and bipy = 2,2′-bipyridyl) complexes, but it does not hold for all structures retrieved from the Cambridge Structural Database. The two pyridyl rings of each bipyridyl unit are nearly coplanar, whereas the bipyridyl units are almost perpendicular to each other. The two I$^-$ ions are more than 5 Å from the silicon centre. As a result, the compound can definitely be described as ionic. The crystal packing is stabilized by short C—H···I contacts.

Comment

In recent years coordination compounds of silicon have been the subject of many structural (Hensen *et al.*, 1983; Tandura *et al.*, 1986), spectroscopic (Helmer *et al.*, 1983; Bassindale & Stout, 1984), reactivity (Chuit *et al.*, 1993) and *ab initio* studies (Damrauer *et al.*, 1988; Arshadi *et al.*, 1996). A subset of that class of compounds, the complexes between silicon halides and tertiary aromatic nitrogen bases, are of fundamental interest concerning Lewis acid–base interactions. However, little information is available about the molecular structure of complexes containing a bidentate nitrogen base. Cationic bis(2,2′-bipyridyl)silicon complexes have been described by Kummer & Seshadri (1977), Kummer *et al.* (1977) and Sawitzki *et al.* (1978). The cation has been characterized spectroscopically with IR and NMR techniques and an octahedral structure was proposed for the complex with the chlorine ligands *cis* to each other.

In order to determine unambiguously the nature of the silicon complex and its precise geometry we have synthesized the title compound, (I), and present here the first crystal structure of a silicon tetrahalide complex containing a bidentate nitrogen base.

The Si atom in (I) is in fact virtually octahedrally coordinated (Table 1). The two chloro ligands are arranged *cis* with respect to each other. The two Si—Cl bonds are rather short compared with similar ionic complexes (Hensen *et al.*, 2000), where these bonds are in the range 2.184 (1)–2.207 (1) Å. The Si—N bond lengths are in the usual range, but they are significantly different from each other. The Si—N bonds *trans* to an Si—Cl bond are longer than the Si—N bonds *trans* to an Si—N bond. This feature could also be observed when the central atom of the complex is replaced by Ga (Restivo & Palenik, 1972), Al (Bellavance *et al.*, 1977), Mo (Hey *et al.*, 1983), Fe (Figgis *et al.*, 1983; Figgis, Patrick *et al.*, 1983), Ni (Hipler *et al.*, 1998) and Mn (Lumme & Lindell, 1988; McCann *et al.*, 1998). In the Re complex (Helberg *et al.*, 1996), all four Si—N bonds are of equal length. In the Co complex (Krämer & Strähle, 1986) in one bipyridyl unit the Si—N bond *trans* to a Cl ligand is longer than the Si—N bond *trans* to an Si—N bond, but in the other bipyridyl unit the inverse situation is found. In the Rh complex (Lahuerta *et al.*, 1991), the Si—N bonds *trans* to a Cl ligand are shorter than the Si—N bonds *trans* to an Si—N bond. In the Ru^{III} complex, the Si—N bonds show the same relation as in the title compound, but in the Ru^{II} complex the situation is the inverse (Eggleston *et al.*, 1985). As a result, there is a strong tendency of the Si—N bond *trans* to the chloro ligand to be longer than the Si—N bond



(I)

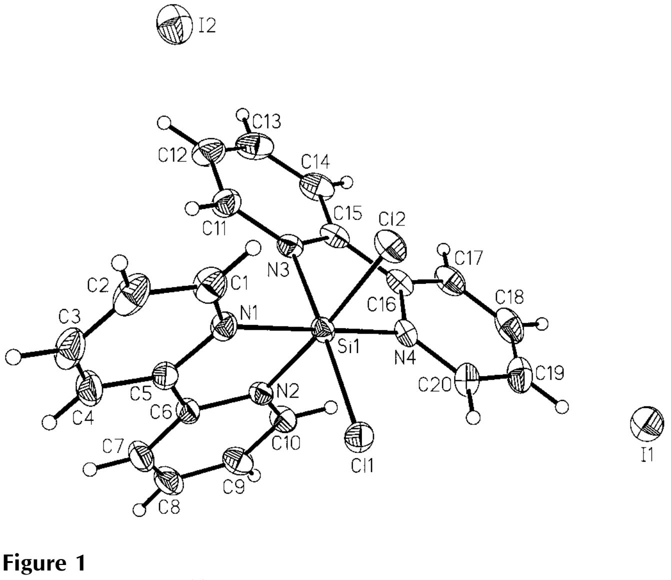


Figure 1
Perspective view of (I) with the atom numbering; displacement ellipsoids are at the 50% probability level.

trans to an Si—N bond, but this feature is not encountered in all the structures retrieved from the Cambridge Structural Database (Version 5.18, October 1999; Allen & Kennard, 1983), a fact which might be attributed to the different electronic configuration of the central atom. It is interesting to note that in all but one of the $M(\text{bipy})_2\text{Hal}_2$ complexes retrieved from the database the halogen ligands are Cl atoms. The only exception is bis(2,2′-bipyridine)-*cis*-diiodocalcium (Skelton *et al.*, 1996).

The N—Si—N bond angles between two N atoms of the same bipyridyl unit are rather small due to steric strain. This fact is also observed in the previously mentioned bis(bipyridyl) complexes.

Both N—C—C—N torsion angles of the bipyridyl units are very small [3.0 (3)°] indicating that the two pyridyl rings of each bipyridyl unit are nearly coplanar. The dihedral angle between the two bipyridyl units is 85.47 (5)°. The distances between Si1 and the two iodine ions [Si1···I1($2-x, 1-y, 1-z$) 5.130 (1) and Si1···I2($x-1, y, z$) 5.677 (1) Å] demonstrate the ionic character of the title compound. Both iodine ions show short contacts to aromatic H atoms (Table 2).

Experimental

The title compound was prepared according to Kummer *et al.* (1977) from $SiCl_2I_2$ with 2,2′-bipyridine in chloroform and dried *in vacuo*. An elemental analysis revealed that the red–brown powder still contained one equivalent of chloroform. The crystal structure analysis, however, clearly showed that there is no solvent in the crystal. A ^{29}Si NMR spectrum of (I) in deuterated methanol showed one single signal at −161.0 p.p.m. Kummer & Seshadri (1977) had found a value of −161.1 p.p.m. for $[SiCl_2(bipy_2)]Cl_2$. Thus, the different anions do not show any effect on the chemical shift of the Si atom. Recrystallization of (I) in warm methanol yielded dark red crystals, which seemed not to be very susceptible to hydrolysis.

Crystal data

$C_{20}H_{16}Cl_2N_4Si^{2+}\cdot 2I^-$
$M_r = 665.16$
Monoclinic, $P2_1/c$
$a = 11.831$ (2) Å
$b = 14.927$ (3) Å
$c = 12.929$ (3) Å
$\beta = 98.63$ (3)°
$V = 2257.4$ (8) Å^3
$Z = 4$
$D_x = 1.957$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 0$–25°
$\mu = 3.091$ mm^{-1}
$T = 173$ (2) K
Block, dark red
0.50 × 0.45 × 0.40 mm

Table 1
Selected geometric parameters (Å, °).

Si1—N4	1.9155 (19)	Si1—N2	1.9411 (19)
Si1—N1	1.9209 (19)	Si1—Cl1	2.1450 (9)
Si1—N3	1.9359 (19)	Si1—Cl2	2.1502 (9)

N4—Si1—N1	172.65 (9)	N3—Si1—Cl1	174.93 (6)
N4—Si1—N3	83.05 (9)	N2—Si1—Cl1	89.98 (6)
N1—Si1—N3	92.13 (9)	N4—Si1—Cl2	90.28 (6)
N4—Si1—N2	90.95 (8)	N1—Si1—Cl2	95.33 (7)
N1—Si1—N2	83.10 (8)	N3—Si1—Cl2	90.54 (6)
N3—Si1—N2	85.27 (8)	N2—Si1—Cl2	175.46 (6)
N4—Si1—Cl1	95.27 (7)	Cl1—Si1—Cl2	94.26 (3)
N1—Si1—Cl1	89.06 (7)		

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.240$, $T_{\max} = 0.290$
47312 measured reflections
6809 independent reflections
5513 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.031$
$\theta_{\max} = 31.89°$
$h = -15 \rightarrow 16$
$k = -20 \rightarrow 22$
$l = -17 \rightarrow 17$
619 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.060$
$S = 1.071$
6809 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 2.5510P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.82$ e Å^{-3}

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···I1^{i}	0.95	3.00	3.938 (3)	170.9
C13—H13···I1^{ii}	0.95	3.01	3.829 (3)	145.1
C8—H8···I1^{iii}	0.95	2.99	3.693 (3)	132.0
C11—H11···I2^{iv}	0.95	3.33	3.745 (3)	108.9
C18—H18···I2^{v}	0.95	3.17	4.093 (3)	165.2

Symmetry codes: (i) $x, y, 1+z$; (ii) $1-x, 1-y, 1-z$; (iii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $x-1, y, z$; (v) $2-x, 1-y, 1-z$.

All H atoms were located by difference Fourier synthesis refined with fixed individual displacement parameters $[U(\text{H}) = 1.2U_{\text{eq}}(\text{C})]$ using a riding model with C—H = 0.95 Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); 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: SK1363). Services for accessing these data are described at the back of the journal.

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