

Coordinative Interactions in Chelated Complexes of Silicon, Part III Crystal and Molecular Structure of 1-Trichlorosilyl-1,2,3,4-tetrahydro-1,10-phenanthroline

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The crystal structure of $C_{12}H_{11}N_2SiCl_3$ (monoclinic, $P2_1/m$, $Z = 2$, with $a: 9.284(4)$, $b: 7.226(2)$, $c: 10.832(5)$ Å, $\beta = 115.14(3)^\circ$) was refined to $R(F) = 0.035$ from 1228 independent reflections. A trigonal bipyramidal, pentacoordinate silicon is observed. The chelated complex shows two different Si–N bonds, a coordinative bond (1.984(2) Å) between Si and N on the axial position and a Si–N single bond (1.737(3) Å, equatorial plane), introduced by chemical reaction. The coordinative bond is 14.2% longer than the Si–N single bond. The lengthening of the coordinative bond in the present case is compared with distances in other extracoordinated silicon compounds.

Introduction

Silicon is found in tetrahedral coordination in the great majority of its compounds. In contrast to carbon it shows only little tendency to form multiple covalent bonds. At room temperature stable molecules with coordination numbers less than four at silicon are rather unusual [3, 4]. On the other hand, silicon is able to expand its valence shell to penta- and hexa-coordination, especially when bonded to electronegative substituents.

The compounds with coordination numbers higher than four can be subdivided into neutral Lewis-acid-base adducts (Table IV) and cationic or anionic complexes, in which Si is formally iso-electronic with its neighbouring elements in the third row.

As crystal structure analysis shows, a trigonal-bipyramidal arrangement is usually found for Si in neutral penta-coordinated adducts [5–8], whereas pronounced distortions towards a square pyramidal geometry is detected in some anionic complexes [9–11]. Hexa-coordinated silicon is normally surrounded octahedrally by ligands [12–17].

In the present study, the structure of the penta-coordinated silicon compound 1-trichlorosilyl-1,2,3,4-tetrahydro-1,10-phenanthroline (1) which is

characterized by an intramolecular Lewis-acid-base interaction, is described.

Experimental

The compound was prepared as described by Hensen and Klebe [1]. Orange coloured crystals were obtained by sublimation *in vacuo* (ca. 0.01 Torr) at 140 °C with a temperature gradient of 3 °C. Due to their pronounced sensitivity to moisture, the crystals were selected in an argon atmosphere and sealed in glass capillaries. The space group was determined by film methods to be $P2_1$ or $P2_1/m$ and the lattice parameters were refined from 15 reflections on a Syntex $P2_1$ diffractometer: $a: 9.284(4)$, $b: 7.226(2)$, $c: 10.832(5)$ Å, $\beta = 115.14(3)^\circ$, $V = 657.8(9)$ Å³.

Data were collected in four quadrants of reciprocal space with Nb-filtered MoK α -radiation by $\theta/2\theta$ scans up to $\sin \theta/\lambda = 0.596$ Å⁻¹, resulting in 5351 observations. Background corrections were applied by profile analysis [18]. Three standard reflections, observed after every 60 reflections, showed no significant fluctuations. A weight was assigned to every observations according to $w(I) = 1/[\sigma^2(I) + (0.03 I)^2]$.

Data were not corrected for absorption ($\mu = 7.65$ cm⁻¹). The equivalent reflections were averaged and a set of 1228 independent observations were used for structure determination. The structure was determined by direct methods using MULTAN [19] and difference Fourier synthesis. A statistical test of the normalized structure factors indicated the space group to be centrosymmetric. The structure was refined with the X-RAY-system [20] in both

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For Parts I and II see ref. [1] and [2].

space groups $P2_1$ and $P2_1/m$ to the same final $R(F) = 0.035$ ($R_w(F) = 0.036$). In the centrosymmetric group the major part of the ring system, the silicon and the axial chlorine atom are restricted to special positions on m . The scattering factors for Cl, Si, N, and C were taken from Cromer and Mann [21], those for H from Stewart, Davidson and Simpson [22]. All non-hydrogen atoms were refined anisotropically. The H-atoms were included in the positional refinement and a fixed overall temperature factor was assigned*.

Discussion

Interatomic distances (in Å) and bond angles are given in Tables II and III, using the numbering scheme of Fig. 1. The penta-coordinated silicon is

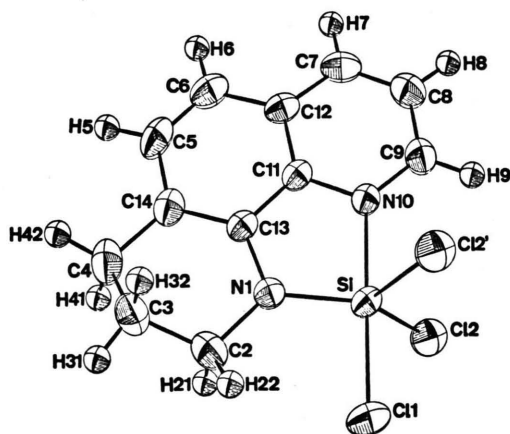


Fig. 1. Molecular structure of 1-trichlorosilyl-1,2,3,4-tetrahydro-1,10-phenanthroline, the thermal ellipsoids are the 50% probability surfaces.

in the center of a slightly distorted trigonal-bipyramid. The distance of the equatorial Si–N1 bond is in agreement with many typical Si–N1 single bonds (1.69–1.81 Å). The “pyridine”-nitrogen N10 occupies one of the apical positions, and the distance to silicon is 14.2% longer as compared with the intramolecular Si–N1 “single” bond. The other two equatorial positions and the site opposite to the “pyridine”-nitrogen are occupied by chlorine atoms. The Si–Cl bonds are remarkably elongated in comparison with Si–Cl distances in tetravalent silicon

* Lists of structure factors, positional and thermal parameters can be obtained through the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, under the deposit number CSD 50186, G. Klebe, Dissertation (Frankfurt/Main, 1982).

Table I. Atomic positions and the arithmetic mean of the thermal ellipsoids projected on the principal axis, standard deviations in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq}
Cl1	.39365(9)	.25000(0)	.01704(7)	.0488(4)
Cl2	.46821(6)	.49005(8)	.27000(5)	.0417(4)
Si	.56466(9)	.25000(0)	.22691(8)	.0284(4)
N1	.7324(3)	.2500(0)	.1944(2)	.030(1)
N10	.7208(3)	.2500(0)	.4211(2)	.028(1)
C13	.8807(3)	.2500(0)	.3074(3)	.027(1)
C11	.8713(3)	.2500(0)	.4327(3)	.027(1)
C2	.7410(5)	.2500(0)	.0609(3)	.040(2)
C3	.8877(6)	.3342(7)	.0637(5)	.039(2)*
C4	1.0403(5)	.2500(0)	.1722(4)	.042(2)
C5	1.1636(4)	.2500(0)	.4334(4)	.043(2)
C6	1.1565(4)	.2500(0)	.5555(4)	.046(2)
C7	.9757(4)	.2500(0)	.6753(3)	.044(2)
C8	.8228(4)	.2500(0)	.6617(3)	.040(2)
C9	.6966(4)	.2500(0)	.5335(3)	.037(2)
C12	1.0060(3)	.2500(0)	.5592(3)	.034(2)
C14	1.0281(4)	.2500(0)	.3057(3)	.032(2)
H9	0.583(4)	0.250(0)	0.524(3)	
H8	0.800(3)	0.250(0)	0.742(3)	
H7	1.066(4)	0.250(0)	0.761(3)	
H6	1.252(4)	0.250(0)	0.638(3)	
H5	1.264(4)	0.250(0)	0.429(3)	
H21	0.739(5)	0.119(7)	0.037(4)	*
H22	0.637(5)	0.322(6)	−0.008(4)	*
H31	0.879(4)	0.319(5)	−0.028(4)	*
H32	0.877(5)	0.469(7)	0.085(4)	*
H41	1.046(5)	0.120(7)	0.140(4)	*
H42	1.134(5)	0.326(6)	0.175(4)	*

* Half populated

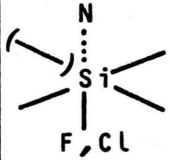
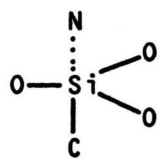
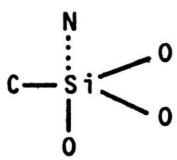
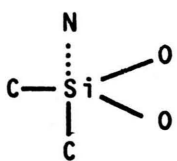
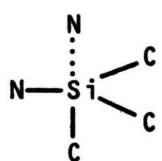
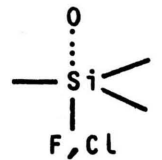
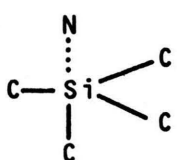
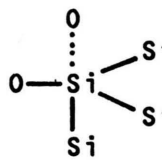
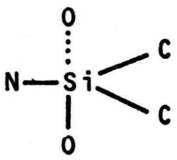
Table II. Interatomic distances (in Å), standard deviations in parentheses.

Atom 1	Atom 2	Distance [Å]	
Cl1	—	Cl2	3.063(1)
Si	—	Cl1	2.150(2)
Si	—	Cl2	2.0936(9)
Si	—	N1	1.737(3)
Si	—	N10	1.984(2)
N1	—	C13	1.401(3)
N1	—	C2	1.482(5)
N10	—	C11	1.349(4)
N10	—	C9	1.328(5)
C13	—	C11	1.397(5)
C13	—	C14	1.376(5)
C11	—	C12	1.409(3)
C2	—	C3	1.480(7)
C3	—	C4	1.530(5)
C4	—	C14	1.498(6)
C5	—	C6	1.352(6)
C5	—	C14	1.420(4)
C6	—	C12	1.415(5)
C7	—	C8	1.364(6)
C7	—	C12	1.400(5)
C8	—	C9	1.386(4)

compounds ($\text{Si-Cl}_{\text{mean}}$: 2.04 Å). The axial distance is 2.8% longer than the equatorial ones. The N10-Si-Cl1 axis is almost linear and nearly perpendicular to the plane formed by N1 and the two equatorial Cl atoms. The silicon atom is slightly shifted out of the trigonal-base plane in the direc-

tion towards Cl1. The two benzoid rings of the ligand, C4, N1, C2, silicon, and Cl1 are situated in the mirror plane of space group $P2_1/m$. C3 occupies a general position and is equally populated in the two symmetry-related sites below and above the mirror plane.

Table IV. Percentage of coordinative Si...N or Si...O bond lengthening as compared with "normal" single bonds in different extracoordinated silicon compounds. In presence of an intramolecular Si-N or Si-O bond, the value refers to this distance, otherwise to the mean value of 1.75 Å for Si-N or 1.64 Å for Si-O bonds (all distances in Å).

	Si N % Lit.					Si N % Lit.			
	F	1.857	7.0	5		2.106	20.3	27	
		1.982	13.3	13		2.116	20.9	28	
		1.972	12.7	13		2.12	21.1	29	
		1.984	14.2	+))		2.129	21.7	27	
	Cl	2.023	15.6	26		2.132	21.8	30	
	Si N % Lit.				2.156	23.2	30		
		2.223	27.0	36	2.175	24.3	31		
		2.29	30.9	36	2.18	24.6	32		
	Si N % Lit.				Si N % Lit.				
		2.301	31.5		37	2.741	54.9	39	
	2.336	33.5	38		Si O % Lit.				
	Si N % Lit.				F	1.94	18.3	8	
		2.951	68.6	40	Cl	1.918	17.0	7	
	3.021	72.6	41		Si O % Lit.				
	Si O % Lit.					2.92	67.6	43	
		2.613	56.5	42					

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Table III. Bond angles (in °), standard deviations in parentheses.

Atom 1	Atom 2	Atom 3	Angle [degree]
Cl1	— Si	— Cl2	92.41(3)
Cl1	— Si	— N1	96.24(9)
Cl1	— Si	— N10	179.44(9)
Cl2	— Si	— N1	123.41(3)
Cl2	— Si	— N10	87.28(6)
Cl2	— Si	— Cl2	111.88(5)
N1	— Si	— N10	84.3 (1)
Si	— N1	— C13	117.1 (2)
Si	— N1	— C2	128.5 (2)
C13	— N1	— C2	114.4 (3)
Si	— N10	— C9	129.8 (2)
Si	— N10	— C11	111.1 (2)
C11	— N10	— C9	119.1 (2)
N1	— C13	— C11	113.9 (3)
N1	— C13	— C14	127.0 (3)
C11	— C13	— C14	119.1 (2)
N10	— C11	— C13	113.6 (2)
N10	— C11	— C12	123.2 (3)
C13	— C11	— C12	123.3 (3)
N1	— C2	— C3	114.2 (3)
C2	— C3	— C4	113.3 (4)
C14	— C4	— C3	108.5 (4)
C6	— C5	— C14	124.2 (4)
C5	— C6	— C12	119.2 (3)
C8	— C7	— C12	120.0 (3)
C7	— C8	— C9	120.4 (4)
N10	— C9	— C8	121.2 (3)
C11	— C12	— C6	116.8 (3)
C11	— C12	— C7	116.0 (3)
C6	— C12	— C7	127.1 (3)
C13	— C14	— C4	119.7 (3)
C13	— C14	— C5	117.5 (3)
C4	— C14	— C5	122.8 (3)

The coordinative Si–N10 bond has to be classified as an interatomic contact longer than “normal” single bonds (Si–N_{mean}: 1.75 Å) and shorter than

van der Waals interactions (Si···N 3.65 Å [23], 3.55 Å [24]). The elongation of the coordinative bond by 14.2% is in agreement with the distances between Si and N found in other halogeno-silanes with extracoordinated silicon. In all examples of penta- and hexa-coordinated Si with halogen atoms opposite the coordinating nitrogen atom (Table IV), the “coordinative” bond is about 13–15% longer as compared with a “single” bond. It shows only little dependence on additional substitution on silicon. If Si is bonded to less polarizable atoms such as O, N, or C, the lengthening of the coordinative bond is larger and it varies much more with a change of substituents on silicon. With an increasing number of electronegative atoms bonded to silicon, the coordinative interaction is also found to increase (Table IV).

A difference of only 7%, as observed in a trifluorosilylphosphinimine [5], is the lowest reported in the literature. A whole range of distances for coordinative interactions above this value up to pure van der Waals interactions were observed in the solid state. Even in the region above the limit of 2.7 Å, termed “minimal nonbonding distance” by Glidewell [25] and Dräger [24], geometrical distortions of the coordination sphere of silicon indicates the presence of coordinative interactions.

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