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MOLECULAR STRUCTURE OF HETEROCYCLIC DERIVATIVES OF HYPERCOORDINATION SILICON

É. Lukevits and O. A. Pudova

Published data and the authors' own data on the molecular structures of heterocyclic derivatives of hyperconjugation silicon are summarized and classified.

In most of the investigated organosilicon derivatives the silicon atom is tetrahedral. Compounds with a coordination number of less than four are unusual, and study of their structure was commenced in the eighties. On the other hand the silicon atom is capable of increasing its coordination to five, six, and even seven, particularly in cases where it is attached to electron-withdrawing substituents. Compounds of silicon with increased coordination can be subdivided into neutral complexes, formed as a result of intramolecular interactions of the donor–acceptor type, and anionic or cationic complexes. The synthesis and structural aspects of various hypervalent derivatives of silicon have been widely studied [1-12]. The present review is devoted to structural investigations of the heterocyclic derivatives of hyperconjugation silicon.

1. COMPOUNDS OF DONOR—ACCEPTOR TYPE

1.1. Increased Coordination Resulting from the N→Si Bond

The most widely studied in the series of compounds of pentacoordinated silicon are the structures of the organosilicon derivatives of triethanolamine (silatranes) and diethanolamine (siloxanes). X-ray crystallographic analysis was used in most of the investigations, and the structural features of methylsilatranes [13], phenylsilatranes [14], and fluorosilatranes [15-17] were studied by quantum-chemical calculations and conformational analysis. Valuable information on the nature of the N→Si bond and the structure of the silatrane and siloxane molecules is provided by the $^{29}Si—^{15}N$ spin—spin coupling constants [18-21]. Spin—spin coupling through the N→Si bond depends in a complicated manner on the nature of the substituents at the nitrogen and silicon atoms. On the one hand, $^1J_{SiN}$ increases with increase in the strength of the N→Si bond. This is demonstrated by the increase of $^1J_{SiN}$ in the silatranes with a shorter N→Si bond and also with increase in the polarity of the solvent. On the other hand, data obtained for the siloxanes show that the absolute value of $^1J_{SiN}$ through the N→Si coordination bond increases with decrease in the electronegativity of the substituents at the silicon atom. By the analysis of S_N2 substitution a relation between $^1J_{SiN}$ and the length of the N→Si bond (r) was obtained for silatranes in solutions:

$$r_{N-Si} = 2{,}291 - 0{,}084\ (^1J_{SiN})^{0,5}$$

According to x-ray crystallographic analysis, the silicon atom in systems with a silatrane heterocycle **1** has a trigonal-bipyramidal environment with the substituent R and the nitrogen atom in the axial positions. The displacement of the silicon

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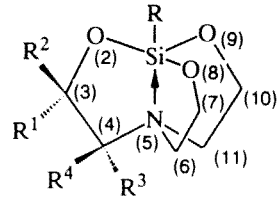
atom from the equatorial plane toward the substituent R (ΔSi) amounts to 0.11-0.12 Å. The nitrogen atom in the silatranes is pyramidal, and like ΔSi its deviation ΔN from the plane formed by the carbon atoms attached to it correlates with the N→Si distance [22]. The three five-membered heterocycles forming the silatrane skeleton are characterized by an envelope conformation, and the oxygen, nitrogen, silicon, and β-carbon atoms lie in one plane. The carbon atom in the α position in relation to the nitrogen atom forms the corner of the envelope. The main geometric parameters of the investigated compounds **1** are given in Table 1, 1a.



1

In papers on the structure of silatranes the greatest attention has been paid to the distance between the silicon and the nitrogen atoms, since this makes it possible to judge the degree of their transannular interaction. In the crystalline state the length of the N→Si bonds for silatranes is in the range of 1.965-2.24 Å, which is significantly less than the sum of the van der Waals radii of the silicon and nitrogen atoms (3.5 Å). A significant increase in the N→Si distance to 2.455 [13] and 2.324 Å [15] is observed for methyl- and fluorosilatranes in the gas phase, and this agrees with the results of *ab initio* and semiempirical calculations [77]. Altogether it is possible to detect a decrease in the interatomic N→Si distance in silatranes with strong electron-donating substituents. The smallest value for the N→Si bond (1.965 Å) is observed for the dimethylsilatranyl oxonium cation [63], and this is followed by chlorosilatrane (2.020 Å). In the molecule of *trans*-bis[(dimethylphenyl)phosphine]-1-silatranylchloroplatinum the N→Si distance is increased to 2.89 Å, and the NC_3 group has an almost planar configuration with the nitrogen atom projecting by only 0.07 Å, while the silicon atom is characterized by a tetrahedral configuration. Such a structure is probably due to the strong positive induction effect and to the large volume of the platinum substituent at the silicon atom. Moreover, all three Si—O—C—C—N rings are characterized by the conformation of an α-envelope and not a β-envelope (as in the usual silatranes).

An investigation was carried out into the effect of such factors as the introduction of methyl [54, 78-81], oxo [74-76, 82, 83], and carboxyl groups [71-73], benzo groups condensed at the C—C bond [80, 84, 85], elongation of one of the three heterocycles by a CH_2 [34, 86] or $SiMe_2$ [87] group, substitution of one [34, 81, 88, 89] or three [90] oxygen atoms by methylene groups, and metallation of the phenyl substituents in phenylsilatrane [56-59] on the structure of the silatrane fragment.

The silicon atom in the molecule of 3,7,10-trimethylsilatrane is characterized by the trigonal-bipyramidal coordination with an N→Si bond length of 2.146 Å normally found in silatranes. However, several special structural features are found: first, the Si—O bond length (1.594 Å) is shorter than in silatranes; second, the five-membered heterocycles have the β-envelope conformation; third, on account of the disordering of the molecule there are several different stereoisomers in the crystal [79]. The lengths of the N→Si coordination bond in phenyl- and 1-(4-tolyl)-3,7,10-trimethylsilatranes are 2.167 Å (2.182 Å for the second independent molecule) and 2.236 Å respectively. As also in 3,7,10-trimethylsilatrane, the five-membered heterocycles in the molecules of these compounds have the β-envelope conformation [54-81].

The presence of the carboxyl group in (3R,4S)-1-chloromethyl-3-methyl-4-carboxysilatrane, (3R,4S)-1-chloropropyl-3-methyl-4-carboxysilatrane, and (3R,4S)-1-vinyl-3-methyl-4-carboxysilatrane does not give rise to substantial changes in the structure of the silatrane heterocycle. In the solid state the molecules of (3R,4S)-1-chloromethyl- and (3R,4S)-1-chloropropyl-3-methyl-4-carboxysilatranes are linked by intermolecular hydrogen bonds through the carboxyl group of one molecule and the oxygen atom in the equatorial position in another molecule [71-73].

According to x-ray crystallographic analysis, the OH group of methylphenyl(silatranylmethyl)silanol [31] also forms a hydrogen bond with the oxygen atom of the silatrane heterocycle, but in this case as a result of intramolecular interaction. The six-membered ring formed as a result of this interaction has the chair conformation.

In methylsilatran-3-one [74] (2.134 Å) and phenylsilatran-3-one (2.216 and 2.111 Å) [75] the N→Si distances are shorter than in the corresponding silatranes. Substitution of the hydrogen atom at the *p* position of the phenyl ring of phenylsilatranone by a fluorine atom (2.129 Å) [76] or trifluoromethyl group (2.106 Å) at the *m* position [76] has little effect on the N→Si bond. The projections of the nitrogen and silicon atoms (ΔSi and ΔN) differ little from those in methyl- and

TABLE 1. Geometric Parameters of the Silatranes **1** ($R^1 = R^2 = R^3 = R^4 = H$)

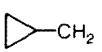
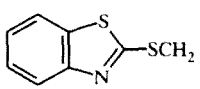
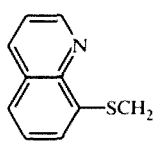
R	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si (Å)	Δ N (Å)	Ref.
1	2	3	4	5	6	7	8	9
Me	2,175(4)	1,870(6)	1,670(4)	179,4(2)	118,4(4)	0,211	0,379	[23]
Me[a]	2,453(47)	1,853(15)	1,656(3)		116,5(9)			[13]
	2,149(4)	1,874(5)	1,659(3)	177,7(2)	118,59(20)	0,2		[24]
$ClCH_2$	2,120(8)	1,912(11)	1,676	176,4(4)	119,1	0,163(3)	0,385(8)	[25]
$I^-Me_2S^+CH_2$	2,046(2)	1,930(3)	1,667(2)	179,1(1)	119,5(1)	0,115	0,396	[26]
$I^-Me_3N^+CH_2$	2,080(13)	1,915(15)	1,662(11)	175,7(6)	119,3(5)	0,13	0,41	[27]
$I^-Ph_3PCH_2$	2,098	1,92		178,3				[28]
	2,100(2)	1,912(2)	1,663(1)	176,7(1)	119,2(1)			[29]
	2,111(3)	1,795(4)	1,667(3)	175,0(2)	119,0(2)	0,18	0,41	[30]
$MePhSi(H)CH_2$[6]	2,208(9) 2,240(9)	1,864(10) 1,869(10)	1,638(8) 1,642(7)		118,2(4) 117,9(4)	0,222(3) 0,241(3)		[31]
$MePhSi(OH)CH_2$	2,214(9)	1,864(16)	1,655(10)		118,3(5)	0,218(3)		[31]
$PhCOOCH_2$	2,122(7)	1,954(5)	1,661(7)	174,0(1)	119,1(1)	0,16	0,36	[32]
CH_2CHO	2,108(6)	1,914(8)	1,660(5)	179,4(3)	119,1(1)			[33]

TABLE 1. (continued)

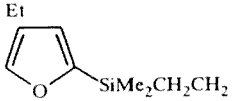
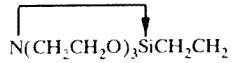
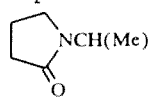
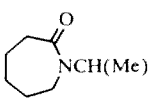
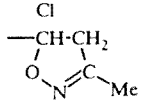
R	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si (Å)	Δ N (Å)	Ref.
1	2	3	4	5	6	7	8	9
Et	2,214(8)	1,881(10)	1,658	178,7(1)	117,8	0,229	0,342	[34]
	2,230(7)	1,874(7)	1.654	178,9(3)	118,0	0.233	0,362	[35,36]
	2,230(5)	1,870(6)	1.650(5)	177,5(2)	117,9(3)	0,24		[37]
$HOCH_2CHBr$	2,123(9)	1,928(7)	1,655(11)	177,6(9)	119,0(9)			[38]
	2,126(9)	1,94(1)	1,674(8)	178,5(4)	119,0(4)	0,169	0,380	[39]
	2,122(2)	1,909(3)	1,665(2)	177,3(1)		0,176	0,386	[40]
$HO(CH_2)_3$	2,173(2)	1,869(2)	1,665(1)	179,4(2)	118,4(1)	0,21(1)	0,372(3)	[41]
$HS(CH_2)_3$	2,177(4)	1,872(4)	1,652(4)	178,6(5)	118,4(5)	0,21	0,37	[42]
$Cl(CH_2)_3$	2,181(7)	1.875(8)	1,662	178,2(6)	118,6	0,199	0,368	[43]
$NC(CH_2)_3$	2,164(4)	1,884(5)	1,659(5)	178,9(4)	118,6			[44]
$NCS(CH_2)_3$	2,209(4)							[45]
	2.228(9)	1,94(1)	1,664(8)	176,0(7)	117,9(5)	0,24	0,35	[46]
	2,150(3)	1,877(4)	1,664(3)	178,7(2)	118,7(2)			[47]
	2,118(2)	1,897(3)	1,657(2)	176,1(1)	119,(1)	0,168(8)	0,386(2)	[48]

TABLE 1. (continued)

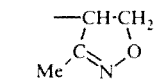
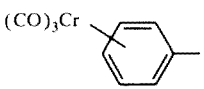
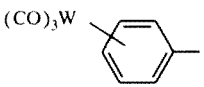
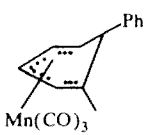
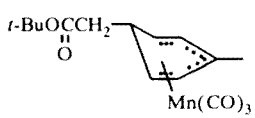
R	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si (Å)	Δ N (Å)	Ref.
1	2	3	4	5	6	7	8	9
	2,119(2)	1,920(8)	1,644(7)	177,5(4)	119,0(3)	0,170(6)	0,363(6)	[48]
CH_2=CH	2,150(6)	1,880(8)	1,664(5)	178,72(25)	118,60(52)	0,20	0,40	[49]
Ph(α)	2,193(5)	1,882(6)	1,656(5)	177,90(22)	118,51(28)	0,204	0,34	[50]
Ph(β)	2,156(4)	1,908(5)	1,657(5)	177,04(29)	118,64(30)	0,195	0,379	[51, 52]
Ph(γ)	2,132(4)	1,894(5)	1,656(4)	179,0(2)	118,8(2)	0,183	0,39	[51, 53]
p-MeC_6H_4[6]	2,171(1) 2,167(1)	1,887(1) 1,892(2)	1,556 1,557	178,8(1) 179,1(1)	118,5 118,5	0,204	0,366	[54]
m-$NO_2C_6H_4$	2,116(8)	1,904(9)	1,656(6)	177,4(3)	118,94(35)	0,17	0,39	[55]
	2,108(5)	1,907(6)	1,656(5)	176,4(3)	119,2(3)			[56]
	2,102(18)	1,902(7)	1,667(9)	176,6(4)	119,1(5)	0,15		[57]
	2,170(3)	1,896(3)	1,653(3)	177,7(2)	118,5(2)			[58]
	2,127(6)	1,898(6)		176,9(3)				[59]

TABLE 1. (continued)

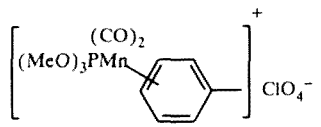
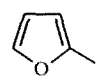
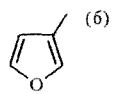
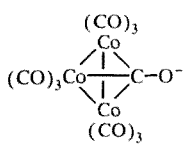
R	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si (Å)	Δ N (Å)	Ref.
1	2	3	4	5	6	7	8	9
	2,064(3)	1,921(4)	1,657(3)	179,2(1)	119,5(1)	0,13		[60]
	2,112(5)	1,894(6)	1,656(6)	177,2(2)	119,1	0,144	0,387	[35, 36]
(б) 	2,130(9) 2,168(9)	1,892(11) 1,859(11)	1,675 1,661	177,7(4) 178,7(4)	118,9 118,6	0,175 0,197	0,384 0,378	[35, 36]
	2,133(9)	1,905(11)	1,666	177,2(4)	119,1	0,162	0,360	[36]
F	2,042(1)	1,622(1)	1,645(2)	179,7(1)	119,5(2)	0,117	0,390	[61]
F[a]	2,324							[15]
Cl	2,022(9)	2,153(4)	1,649	179,8(3)	119,7	0,095	0,396	[62]
EtO	2,152	1,658	1,648		118,9	0,179		[63]
t-BuO	2,189(4)	1,659(4)	1,650(4)	179,4(2)		0,201(2)	0,371(4)	[64]
$BF_4^-Me_2O^+$ –	1,965	1,830	1,642		120	0,017		[63]
EtO— ⋮ CF_3COOH	2,050	1,710	1,652		119,5	0,102		[63]

TABLE 1. (continued)

R	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si (Å)	Δ N (Å)	Ref.
1	2	3	4	5	6	7	8	9
p-MeC_6H_4O	2,107(2)	1,677(2)	1,649(2)	174,7(2)	119,1(2)	0,154	0,372	[65]
m-ClC_6H_4O	2,079(2)	1,690(2)	1,656	176,5(2)	119,2	0,14	0,40	[66]
$Ph_2P(S)O$	2,060(3)	1,934(1)	1,649(3)	178,9(2)	118,6(1)			[67]
	2,010(5)	1,707(4)	1,644(7)	177,2(4)	119,6(4)			[68]
$(PhMe_2P)_2PtCl$	2,89(1)	2,292(4)	1,649(9)	176,7	110(5)	0,53	0,07	[69, 70]

a) Electron-diffraction data.

b) For two independent molecules.

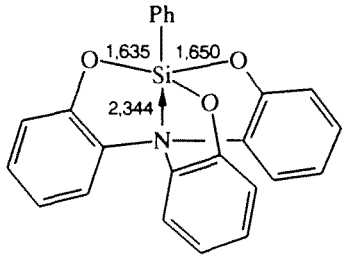
TABLE 1a. Geometric Parameters of the Silatranes **1**

R	R^1	R^2	R^3	R^4	r(N→Si) (Å)	r(Si-R) (Å)	r(Si-O) (Å)	N-Si-R (°)	O-Si-O (°)	Δ Si(Å)	Δ N (Å)	Ref.
$ClCH_2$	Me	H	H	COOH	2,136(3)	1,895(4)	1,661(3)	178,7(2)	118,9(2)			[71]
$Cl(CH_2)_3$	Me	H	H	COOH	2,244(3)	1,884(4)	1,663(3)	179,6(2)	119,4(2)			[71]
$H_2O \cdot Cl(CH_2)_3$	H	H	H	COOH	2,176(4)	1,873(5)	1,667(4)	178,5(2)	118,4(2)			[72]
CH_2=CH	Me	H	H	COOH	2,169(3)	1,878(5)	1,666(3)	178,4(2)	118,5(2)			[73]
Me	-O		H	H	2,134(1)	1,861(2)		177,4(1)		0,209(1)	0,384(1)	[74]
Ph[a]	-O		H	H	2,126(3) 2,111(3)	1,859(3) 1,886(3)		177,7(2) 177,5(2)		0,198(1) 0,182(1)	0,386(3) 0,388(3)	[75]
p-FC_6H_4	-O		H	H	2,129(3)	1,885(3)		176,2(2)		0,196(1)	0,386(2)	[76]
m-$CF_3C_6H_4$	-O		H	H	2,106(3)	1,884(4)		174,6(3)		0,186(1)	0,385(4)	[76]

a) For two independent molecules.

phenylsilatranes. The length of the N→Si donor—acceptor bond in methylsilatrane-3,7-dione (2.146 Å) [82] is only 0.03 Å shorter than the corresponding length in methylsilatrane. The Si—O bond in the five-membered heterocycles $SiOC(O)CH_2N$ of silatranones and silatranedione (~ 1.720 Å) is longer than in the heterocycles $SiOCH_2CH_2N$ (~ 1.658 Å) and in silatranes.

In phenyltribenzosilatrane **2** [84] the N→Si distance is increased (2.344 Å) compared with phenylsilatrane.



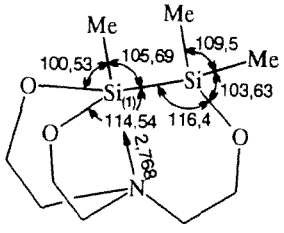
2

π-Complexation of the phenyl group in phenylsilatrane with transition metals [$(MeO)_3PMn(CO)_2^+$, $Cr(CO)_3$, $W(CO)_3$] does not have a significant effect on the geometry of the silatrane heterocycle. It is only possible to detect an extremely small degree of shortening in the N→Si bond (2.064-2.108 Å) and lengthening of the Si—C bond (1.902-1.921 Å) [56, 57, 60].

Substitution of one oxygen atom of the silatrane heterocycle in methyl-, phenyl-, and *p*-tolylsilatranes by the less electronegative methylene group weakens the electron-withdrawing action of the silicon and increases the length of the N→Si bond to 2.336 Å [88], 2.291 Å [89], and 2.290 Å [81] respectively. In addition, the five-membered heterocycle of methylcarbasilatrane, not containing an oxygen atom, is characterized by the β-envelope conformation. Changes in the heterocycle without change in the environment of the silicon atom, do not lead to such substantial changes in the N→Si distance; this distance in methoxy-2-carbasilatrane [34] is 2.22 Å. Even greater elongation of the N→Si bond (2.477 Å) is observed for the tricarbasilatrane $[N(CH_2CH_2CH_2)_3Si]_2O$. The silicon atom in this compound has a coordination intermediate between a trigonal bipyramid and a tetrahedron [90].

In chloromethyl-3-homosilatrane — a silatrane analog with one six-membered heterocycle $SiOCH_2CH_2CH_2N$ — the five-membered rings have a disordered structure, while the six-membered ring is almost planar. The N→Si distance is 0.13 Å longer than the distance in chloromethylsilatrane as a result of the steric effect of the CH_2 group [86].

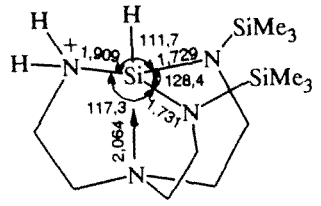
In atrane compounds **3** with two silicon atoms [87] considerable angular disordering is observed at $Si_{(1)}$, and the substituents are in a coordination intermediate between tetrahedral and trigonal-bipyramidal. The $Si_{(1)}\cdots N$ distance of 2.768 Å is considerably longer than in silatranes.



3

According to x-ray crystallographic analysis, the replacement of the three equatorial oxygen atoms by nitrogen atoms, i.e., the transition from silatranes to 2,8,9-triazasilatranes does not lead to substantial changes in the structure of the atrane heterocycle. In phenyl-2,3,9-triazasilatrane [91] and 1-fluoro-2,3,9-trimethyltriazasilatrane [92, 93] the silicon atom is almost trigonal-bipyramidal, and the transannular N→Si bond is 2.132 and 2.034 Å respectively.

The protonation of one of the nitrogen atoms in the equatorial position of the azasilatranes has a strong effect on the length of the $Si—N_{eq}^+$ bond and on the values of the $N_{eq}SiN_{eq}$ angles [94, 95]. In the cations of compounds **4** and **5** the $Si—N_{eq}^+$ bond is 10% longer than the other two $Si—N_{eq}$ bonds; the $N_{eq}SiN_{eq}$ angle (128.4 Å), opposite the protonated nitrogen, is significantly larger than the adjacent $N_{eq}^+SiN_{eq}$ angles. It should be noted that compound **5** represents a mixture of the protonated and the initial unprotonated azasilatrane.



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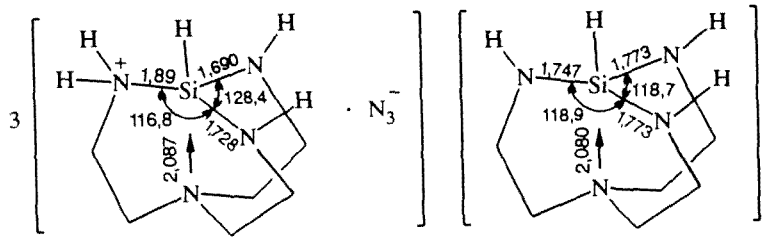
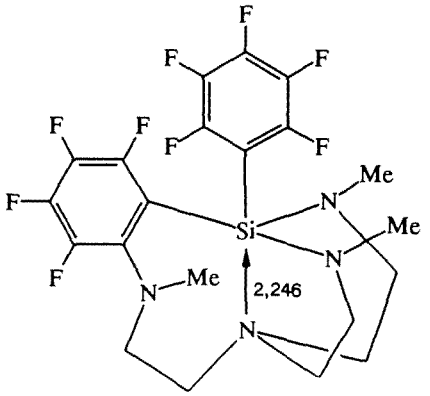


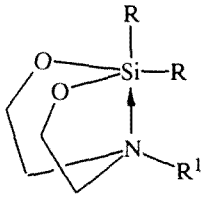
5

The insertion of a tetrafluorobenzene group at the Si—N_{eq} bond of 1-pentafluorophenyl-2,8,9-trimethyltriazasilatrane (**6**) leads to elongation of the N→Si bond (2.246 Å). The average values of the Si—C and Si—N_{eq} bonds are 1.960 and 1.733 Å respectively [92, 93].



6

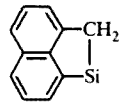
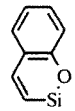
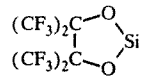
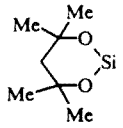
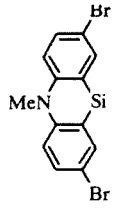
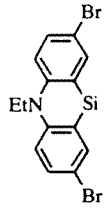
The effect of various substituents at the silicon and nitrogen atoms on the interatomic N→Si distances was investigated for a series of cyclic derivatives of diethanolamine **7** (Table 2). The coordination polyhedron of this type of silicon atom represents a distorted trigonal bipyramid, the base of which is formed by the two oxygen atoms of the 1,3-dioxa-6-aza-2-silacyclooctane ring and the substituent R, and the vertices are the nitrogen atom and the second substituent R.



7

The transannular interaction between the nitrogen and silicon atoms, which shows up in broad fluctuations of the N→Si interatomic separations from 2.004 [100] to 3.19 Å [97], varies considerably, depending on the electronic and steric nature of the groups R and R^1. In the series of 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclanes this value increases in the order H < Me < Ph < *t*-Bu (R^1). Electron-withdrawing cyclic ether groups at the silicon atom increase the positive charge at the silicon and substantially shorten the N→Si distance.

TABLE 2. Geometric Parameters of the Siloxanes **7**

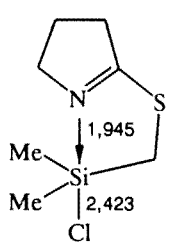
R_2Si	R^1	r(N — Si) (Å)	r(Si-O) (Å)	O-Si-O (°)	Δsi (Å)	Ref.
Ph_2Si	H	2,301(6)	1,657(5)	121,8(3)	0,25	[96]
Ph_2Si	Me	2,68(1)	1,63(1)	118(1)	0,38	[97]
Ph_2Si	*t*-Bu	3,16(2)	1,64(2)	115(1)	0,49	[97]
Ph_2Si	Ph	3,08(1)	1,64(1)	115(1)		[97]
Me_2Si	Ph	3,19(1)	1,63(3)	111(1)		[97]
	Me	2,263(6)	1,652(5)	118,9(3)	0,16	[98]
	Me	2,297(6)	1,639(6)	119,4		[99]
	H	2,004(3)	1,666(3)	118,9(2)	0,101	[100]
	Me	2,032(7)	1,636(6)	119,4(3)	0,088	[101]
	Me	2,247(5)	1,649(4)	119,9(2)	0,219	[102]
	Me	2,968	1,64(1)	114,7(5)		[103]
	Me	2,986	1,626(6)	114,8(3)		[103]

The Si···C(6) distance in the test molecule of 2,2-diphenyl-1,3-dioxa-2-silacyclooctane (3.576 Å) indicates the absence of any intramolecular interactions between the silicon and the C(6) carbon atom [104].

It was established by x-ray crystallographic analysis that the silicon atom in certain organosilicon derivatives of nitrogen-containing heterocycles **8-14** is pentacoordinated.

In 2-(dimethylchlorosilylmethylthio)-1-pyrroline **8** [105] the silicon atom has a disordered trigonal-bipyramidal environment with the nitrogen atom of the heterocycle and the chlorine atom in the axial positions (<N—Si—Cl = 172.5°). A special feature of this compound is the strong shortening of the N→Si bond (1.945 Å) and the elongation of the Si—Cl bond (2.423 Å) [105].

The analogous effect shows up even more clearly in compound **9** [106]. As a result the N→Si bond (1.852 Å) approximates in value to a covalent bond, while the very long Si—Cl bond (2.679 Å) indicates increased ionic character. The N—Si distances in 2-{[methyl(trifluorosilyl)amino]methyl}pyridine **10** [107] are nonequivalent; the N_1—Si coordination bond is increased significantly compared with the normal $N_{(2)}$—Si bond. The silicon atom is trigonal-bipyramidal with the nitrogen



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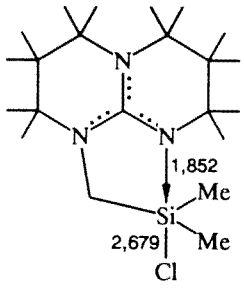

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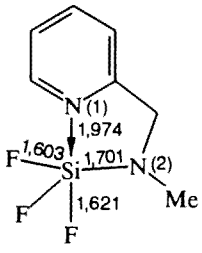

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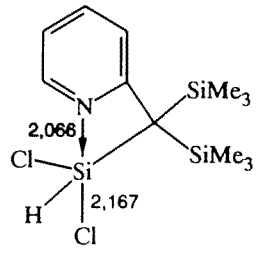

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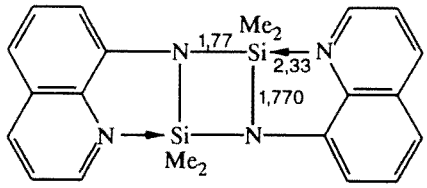

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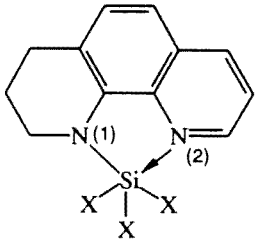

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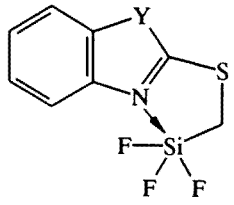


14

atom of the pyridine ring and the fluorine atom in the axial positions ($N_{(1)}SiF_{ax}$ = 178.0°), and the Si—F_{ax} bond (1.621 Å) is longer than Si—F_{eq} (1.603 Å).

The coordination of the silicon atom in 2-[diphenyl(methyldichlorosilyl)methyl]pyridine is close to tetrahedral, whereas the silicon atom of the dichlorosilyl group in 2-[bis(trimethylsilyl)(dichlorosilyl)methyl]pyridine **11** [108] is trigonal-bipyramidal, and the N→Si bond is 2.066 Å. The N→Si distance in the cyclosilazane **12** [109] (2.33 Å) with 8-quinolyl substituents at the nitrogen atoms is greater than the N→Si distance in compounds **8-11**.

According to the data from x-ray crystallographic analysis [110, 111] and neutron diffraction [112], the length of the $N_{(2)}$→Si coordination bond is considerably greater than that of Si—$N_{(1)}$ (1.732 and 1.737 Å) both in the trifluorosilyl derivative (1.969 Å) and in the trichlorosilyl (1.984 Å) derivative of 1,2,3,4-tetrahydro-1,10-phenanthroline **13**. The substitution of one (2.027 Å) or two (2.028 Å) chlorine atoms by a methyl group leads to a slight increase in the $N_{(2)}$→Si distance [113]. At the same time, the $N_{(2)}$→Si bond is significantly longer (2.689 Å) for the trimethylsilyl derivative of 1,2,3,4-tetrahydro-1,10-phenanthroline. In this compound the coordination at the silicon atom can be characterized as a strongly disordered tetrahedron, in contrast to the compounds with X = F, Cl, where the silicon has a trigonal-bipyramidal configuration [114] (Table 3).

The structure of compounds **14** with Y = S and O is similar in many respects. The silicon atom of both molecules is trigonal-bipyramidal with a donor—acceptor bond of 1.988 and 1.967 Å respectively. Elongation of the axial Si—F bond (1.632 and 1.624 Å) compared with the equatorial bond (1.589-1.594 Å) was also observed [115].

Expansion of the coordination at the silicon atom is typical of phenylsilanes containing one (compounds **15** and **16**) [116-120] or two (compounds **17-18**) [121, 122] dimethylaminomethyl groups and also one trimethylhydrazine substituent (compounds **19** and **20**) [123] at the *o* positions of the phenyl ring and for 1-silylnaphthalenes **21-25** with the Me_2N group [119,

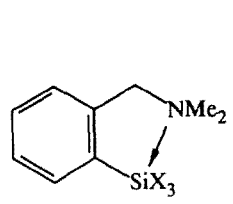
TABLE 3. Geometric Parameters of N-Silyl-1,2,3,4-tetrahydro-1,10-phenanthrolines **13**

X_3Si	$r(Si-N_{(2)})$ (Å)	$r(N_{(1)}-Si)$ (Å)	$N_{(1)}$-Si-X (°)	$N_{(1)}$-Si-$N_{(2)}$ (°)	Ref.
F_3Si	1,732(4)	1,969(4)	178,2(1)	83,9(2)	[110]
Cl_3Si	1,737(3)	1,984(2)	179,44(9)	84,3(1)	[111]
Cl_3Si[a]	1,746(2)	1,979(2)	179,71(7)	84,23(5)	[112]
$MeCl_2Si$	1,739	2,027(4)			[113]
Me_2ClSi	1,770(6)	2,028(7)	176,8(2)	81,8(3)	[113]
Me_3Si	1,746(8)	2,689(8)	177,0(4)	70,3(3)	[114]

*Neutron-diffraction data.

124-129] or Me_2NCH_2 group (compound **26**) [124] at position 8 of the naphthalene ring. As a rule, coordination results in the formation of five-membered 1-sila-2-azapentanes or 1-sila-2,3-diazapentanes and, only in the case of the naphthalene derivative **26**, a six-membered heterocycle.

The silicon atom in compound **15** with SiX_3 = $SiMeF_2$ [116], $SiH_2(\alpha\text{-}C_{10}H_7)$ [117], and Si(H)Ph(OSO_2CF_3) [118] has various geometric parameters. In the first two molecules the silicon polyhedron can be described as intermediate between a tetrahedron and a trigonal bipyramid with very long N→Si distances (2.356 and 2.44 Å). For these two compounds, the lengths of the Si—F_{ax} (1.627 Å) and Si—C_{ax} (Np) (1.92 Å) bonds are increased compared with Si—F_{eq} (1.627 Å) and Si—C_{eq} (1.86 Å). In the triflate the silicon atom is trigonal-bipyramidal with the nitrogen and oxygen atoms in the axial positions. The N→Si bond (2.052 Å) is short, but the Si—O bond (1.951 Å) is considerably longer than usual covalent Si—O bonds. The structure of the triflate can therefore be described as an ion pair between the intramolecularly coordinated silyl cation and the triflate anion, in which some degree of covalent interaction is retained.



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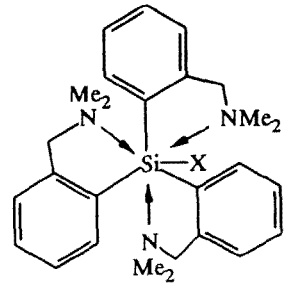

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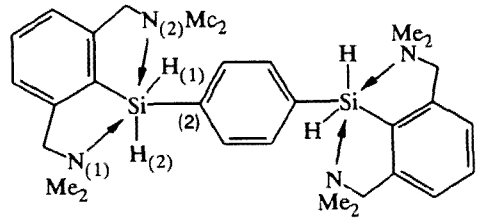

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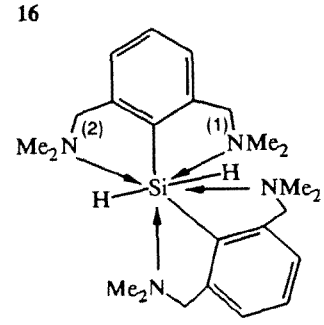

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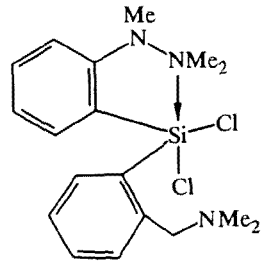

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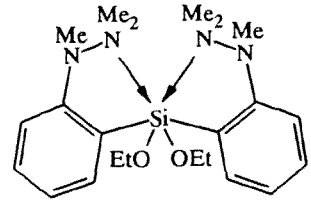

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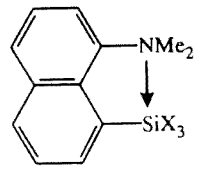
The conclusion about the seven-coordinated silicon was reached on the basis of x-ray crystallographic analysis of tris[2-(dimethylaminomethyl)phenyl]silane **16** (X = H) [120], in which the three weak N→Si interactions lead to the [3 + 4] tetrahedral configuration of the silicon atom. However, accurate data were not obtained for the hydrosilane **16** on account of the unsatisfactory quality of the crystals. The main feature of the fluorosilane **16** (X = F) [119] is the presence of three inequal N→Si interactions (3.004, 3.307, and 3.489 Å). On the basis of the minimum value of 3.004 Å it could be supposed that the silicon atom is not seven-coordinated but only five-coordinated. However, the general geometry of the silicon differs from the trigonal bipyramid characteristic of pentacoordinated silicon on account of the fact that the closest NMe_2 group is not in the *trans* position in relation to the fluorine atom. Together the four σ-bonded substituents form a tetrahedron at the silicon atom, while the three N→Si interactions are weak on account of steric hindrances and are insufficient to increase the coordination number [119].

In the centrosymmetric molecule of 1,4-bis{2,6-bis[(dimethylaminomethyl)phenyl]silyl}benzene **17** the nitrogen atoms and the two NMe_2 groups are coordinated unsymmetrically with the silicon, and the $N_{(2)}Me_2$ group is closer to the Si on the side opposite the $Si—H_{(2)}$ bond ($N_{(2)}—Si—H_{(2)}$ = 169.4°), whereas the $N_{(1)}Me_2$ group is in the *trans* position in relation to the $Si—C_{(2)}$ bond ($N_{(1)}—Si—C_{(2)}$ = 166.8°). In addition, the $N_{(2)}$→Si distance (3.008 Å) is greater than $N_{(1)}$→Si (2.681 Å), while the silicon atoms in compound **17** remain tetrahedral with [4 + 2) coordination [121].

The introduction of a second 2,6-bis(dimethylaminomethyl)phenyl substituent at the silicon (compound **18**) leads to [4 + 4] coordination of the silicon. The $N_{(1)}—Si$ distance, in the *trans* position to the Si—H bond, is 3.117 Å, and the $N_{(1)}—Si—H$ angle amounts to 177.5°, whereas the $N_{(2)}$→Si bond (*trans* to the Si—C bond) is shorter (2.895 Å) and the $N_{(2)}—Si—C$ angle is smaller (168.5°). All the indicated bond lengths and bond angles in compound **18** exceed the analogous values in compound **17** [122].

In compound **19** with (2-trimethylhydrazino)phenyl and 2-dimethylaminomethyl substituents, the silicon atom is pentacoordinated, and the additional coordination arises on account of the terminal nitrogen atom of the hydrazine group (2.564 Å). The N→Si distances in di[(2-trimethylhydrazino)phenyl]diethoxysilane **20** amount to 2.689 and 2.772 Å [123].



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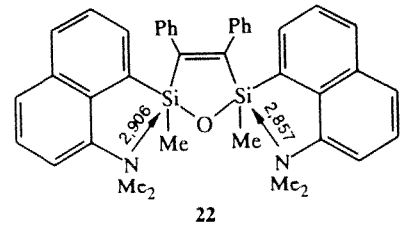

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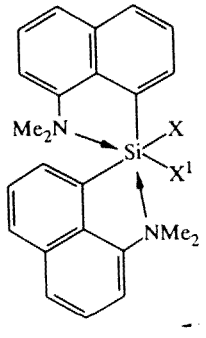

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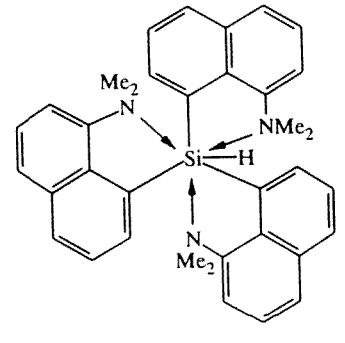

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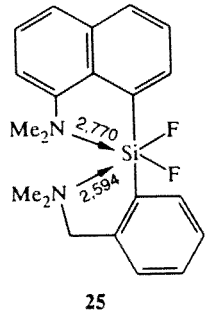

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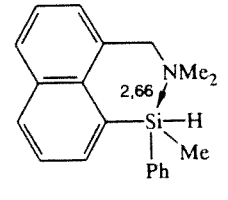

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For compounds **21** the N→Si distance and the coordination polyhedron are determined by the substituents X at the silicon atom. The structures of the two independent molecules of 8-dimethylamino-1-trifluorosilylnaphthalene **21** (X = F) are similar. In both cases the naphthalene ring, the silicon atom, and the nitrogen atom lie almost in one plane. The geometry of the silicon atom is trigonal-bipyramidal, and the average length of the N→Si coordination bond is relatively large (2.303 Å) [125] but smaller than in the molecule of 8-dimethylamino-1-phenylsilylnaphthalene **21** (SiX_3 = SiH_2Ph) (2.584 Å) [124]. An even longer N→Si distance is characteristic of the molecule of 8-dimethylamino-1-[methylbis(methyltriphenylsilyl)silyl]naphthalene **21** [SiX_3 = $SiMe(SiMePh_2)_2$] [129]. On account of the weak interaction it amounts to 3.159 Å.

According to the data from x-ray crystallographic analysis, the two silicon atoms in compound **22** [129] have geometry intermediate between tetrahedral and trigonal-bipyramidal, which is confirmed by the long N→Si distances (2.906 and 2.857 Å) and the N—Si—C angles (173.49 and 175.50°). It should be mentioned that in this case the nitrogen atom and the carbon atom of the central 1,3-disila-2-oxacyclopentene heterocycle occupy the axial position, displacing the electronegative oxygen atom to the equatorial position.

In compound **23** [$SiXX^1$ = SiH_2, SiHF, $Si(C{\equiv}CH)_2$] the nitrogen atoms of the two 8-dimethylaminomethyl groups are directed toward the silicon, creating a formal hexacoordinated [4 + 2] configuration at the silicon atom. The molecular structure of the dihydro- and hydrofluorosilanes is similar. A special feature of the dihydrosilane is the nonequivalence of the two Si—H bonds (1.44 and 1.54 Å) and the two N→Si distances (2.610 and 2.800 Å); the shorter N→Si bond is located on the side opposite the C_{Ar} carbon atom, while the longer bond is opposite the hydrogen atom. The N→Si distances in hydrofluorosilane are almost identical (2.680 and 2.646 Å) [127]. The two nitrogen atoms in diethynyl(8-dimethylamino-1-naphthyl)silane **23** [$SiXX^1$ = $Si(C{\equiv}CH)_2$] are in the *trans* position in relation to the ethynyl groups. At the same time, in dihydrosilane one nitrogen is in the *trans* position in relation to one Si—H bond and *cis* to the other, while the second nitrogen is in the *cis* position in relation to both hydrogen atoms. The N→Si distances in the diethynyl derivative **23** are 2.836 and 2.789 Å [128].

In the molecule of tris[1-(8-dimethylamino)naphthyl]silane **24** [118], in addition to the four σ-bonds, the silicon atom forms three very weak N→Si donor—acceptor bonds with an average length of 2.895 Å, and none of the NMe_2 groups approaches the silicon on the side opposite the Si—H bond.

The structure of 8-dimethylamino-1-naphthyl[2-(dimethylaminomethyl)phenyl]difluorosilane **25** was studied in order to compare the effectiveness of the N→Si interaction of the 8-dimethylamino-1-naphthyl and 2-dimethylaminomethylphenyl groups. The N→Si distance for the 8-dimethylaminonaphthyl substituent is longer (2.770 Å) than for 2-dimethylaminomethylphenyl (2.594 Å). In the molecule of (8-dimethylaminomethyl-1-naphthyl)methylphenylsilane **26** [124] as a result of N→Si donor—acceptor interaction, a six-membered heterocycle is formed with an N→Si distance of 2.66 Å, which is longer than in (8-dimethylamino-1-naphthyl)phenylsilane **21** (SiX_3 = SiH_2Ph).

A major feature of the silanol **27** [130] is the extremely short bonds of the pentacoordinated silicon atom. Although the axial Si—N bond is 0.19 Å longer than the equatorial bond, it is considerably shorter than the N→Si bonds in other pentacoordinated derivatives of silicon.

In the silyl ethers of acetoxime — methylchloro(isopropylideneaminoxy)silane [131], tetra(isopropylideneaminoxy)silane [132], and phenyltri(isopropylideneaminoxy)silane [133] — the coordination at the silicon atom differs significantly from tetrahedral; the oxygen atoms approach each other so that the O—Si—O angle is 98°. The Si—O—N=C fragments have a planar *trans* configuration; the distances between the silicon and nitrogen atoms of the oxime groups (2.50-2.53 Å) are less than the sum of the van der Waals radii but substantially greater than in silatranes.

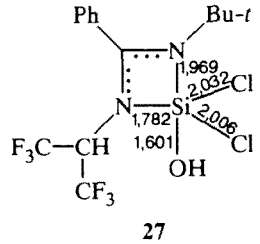

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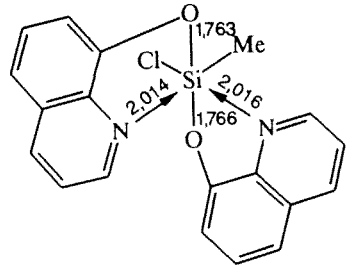
TABLE 4. Geometric Parameters of the Bipyridine Complexes **32**

X	X^1	X2	X^3	N → Si (Å)	Si-X (Å)	Si-X^1 (Å)	Si-X^2 (Å)	Si-X^3 (Å)	X-Si-X^3 (°)	N-Si-N (°)	Ref.
F	F	F	F	1,982(4) 1,972(4)	1,654(3)	1,629(3)	1,632(3)	1,659(3)	170,5(2)	79,7(2)	[140]
Cl	Cl	Cl	$CHCl_2$	1,959(3) 1,967(3)	2,207(2)	2,184(2)	2,180(2)	1,983(5)	179,1(2)	80,7(1)	[141]
Cl	Cl	Cl	CCl_3	1,966(6)	2,184(4)	2,165(3)		2,067(12)	177,6(3)	80,4(4)	[141]
Cl	Cl	Cl	CCl_2SiCl_3	1,955(4) 1,967(4)	2,237(2)	2,155(2)	2,172(2)	2,071(5)	173,3(2)	81,7(2)	[141]
Cl	Cl	$OSiCl_3$	Cl	1,969(6) 1,967(6)	2,175(10)	2,153(3)	1,685(5)	2,180(9)	171,6(1)	80,9(3)	[142]
$SiCl_2Me$	Cl	Cl	Me	2,029(12) 2,007(11)	2,367(5)	2,392(10)	2,274(8)	1,888(12)	170,7	79,9	[143]

A series of compounds with a hexacoordinated silicon atom in which the coordination is also increased on account of N→Si interaction are known. The two bidentate ligands of compound **28** [134] are almost perpendicular to each other and are in the *cis* position, and the silicon atom is therefore a chiral center. The Si—O bond forms an angle of 168.7°, and the NSiN angle is nearly a right angle (85.3°). The length of the N→Si bonds is significantly increased in comparison with the usual covalent bond but is comparable with the value in the penta- and hexacoordinated complexes. For compounds **28** and **29** [135] with an identical configuration at the silicon atom, the lengths of the N→Si and Si—O bonds are very close in value. The silicon in compounds **28-31** [134-137] and also in the phthalocyanine polymer $(PcSiO)_n$ [138, 139] is octahedral.



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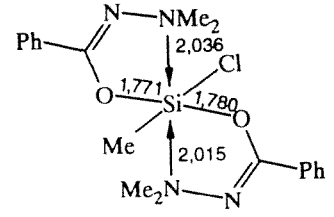

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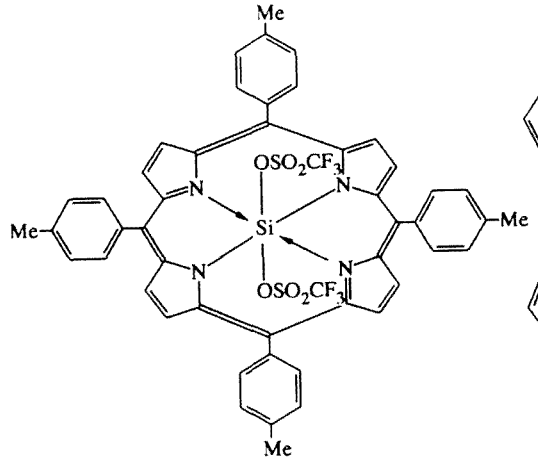

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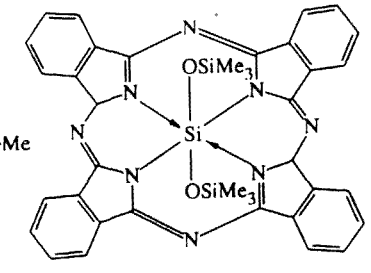

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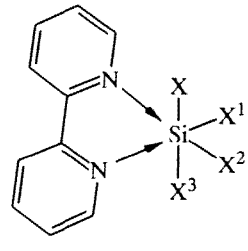
Additional coordination appears in the derivatives of 2,2'-bipyridine **32** (Table 4) and 1,10-phenanthroline **33** [144] on account of the N→Si coordination bonds of the two nitrogen atoms. The N→Si distance in compounds **32** varies between 1.955 and 2.029 Å.



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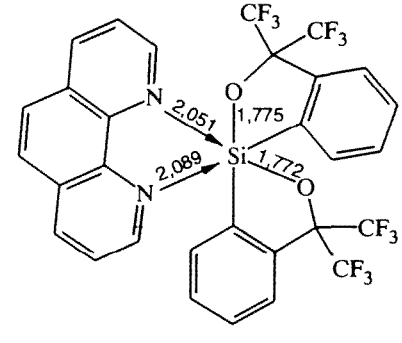

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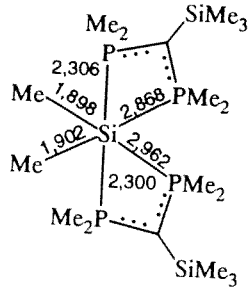
1.2. Increased Coordination Resulting from the P→Si Bond

In the dimethylsilyl derivative **34** with two diphosphamethanide ligands, the silicon atom has distorted octahedral geometry with the two methyl groups and the two Me_2P groups forming the equatorial plane and lying in the *cis* position. The

length of the Si—P_{ax} bonds (2.306 and 2.300 Å) is only slightly greater than in the tetrahedral derivatives. The equatorial Si—P bonds are 26.6% longer than the axial bonds. The four-membered chelate heterocycles formed as a result of coordination are planar, and the carbon atoms in them also have a planar coordination [145].



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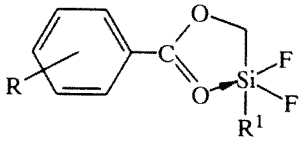
1.3. Increased Coordination Resulting from the O→Si Bond

According to data from x-ray crystallographic analysis, the silicon atom is pentacoordinated in such compounds as aroyloxymethylfluorosilanes, N-silylmethyllactams, N-trifluorosilylmethylacetamides, and N-methylsilyltri-methylamido-phosphates, and the additional coordination appears on account of O→Si interaction of the donor—acceptor type. In aroyloxymethyltrifluorosilanes **35** (Table 5) the O→Si distance varies in the range of 1.94-2.08 Å, depending on the substituent R, and this is less than the sum of the van der Waals radii (3.6 Å). The substitution of one fluorine atom by a methyl group leads to substantial elongation of the O→Si bond, and this distance in methyl(benzoyloxymethyl)difluorosilane is 2.216 Å. In the molecules of the investigated compounds the silicon atom has a slightly distorted trigonal-bipyramidal coordination. The oxygen and fluorine atoms are at the axial vertices. The dihedral angle between the mean plane of the five-membered heterocycle and the plane of the benzene ring in (2-chlorobenzoyloxymethyl)trifluorosilane is increased to 17.5° on account of the repulsion of the chlorine atom and the oxygen, whereas the five-membered ring and the benzene ring in the 4-halogen derivative are practically coplanar.



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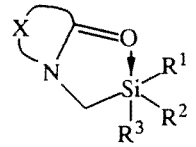

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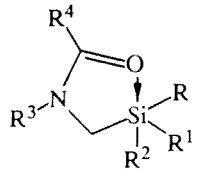

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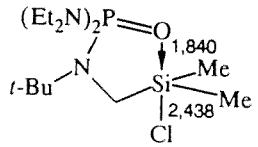

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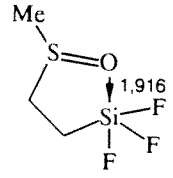

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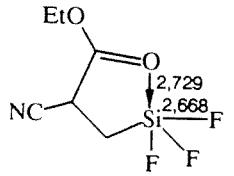

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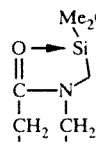
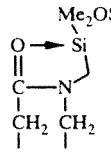
TABLE 5. Geometric Parameters of Aroyloxymethylfluorosilanes **35**

R	R^1	r(O—Si) (Å)	r(Si-F_{ax}) (Å)	r(Si-F_{eq}) (Å)	r(Si-C) (Å)	O-Si-F_{ax} (°)	Ref.
H	F	2,006(8)	1,610(7)	1,578(9)	1,855(13)	176,0	[146]
H	Me	2,216(3)	1,629(2)	1,588(3)	1,848(4)	171,0(1)	[147]
4-F	F	2,029(2)	1,606(2)	1,583(2)	1,869(3)		[148]
4-Cl	F	2,08(2)	1,56(2)	1,60(2)	1,84(3)		[148]
4-Br	F	1,94(2)	1,61(2)	1,68(2)	1,81(2)	176,5(4)	[148, 149]
2-Cl	F	2,040(9)	1,620(9)	1,578(9)	1,810(13)		[150]

TABLE 6. Geometric Parameters of N-Silylmethyllactams **36**

X	R	R^1	R^2	r(O—Si) (Å)	r(Si-R^3) Å	O-Si-R^3	Ref.
$(CH_2)_3$	Me	Me	F	2,395(8)	1,652(7)		[151]
$(CH_2)_3$	Me	Me	OPh	2,367	1,711		[152]
$(CH_2)_3$	Me	Me	OCOPh	2,228	1,711		[152]
$CH_2CHPhCH_2$	Me	Me	Cl	2,050(2)	2,284(1)	172,2(1)	[153]
CMe_2OCHMe	Me	Me	Cl	2,450(2)	2,154(2)	170,3(1)	[153]
$(CH_2)_4$	Me	Me	Cl	1,954(1)	2,307(2)	171,16(5)	[154]
$(CH_2)_4$	Me	Me	Br	1,800(4)	3,122(2)	162,6(3)	[155]
$(CH_2)_4$	Me	Me	I	1,749(2)	3,734(1)	161,90(7)	[15,157]
$(CH_2)_4$	Me	Me	OSO_2CF_3	1,753	2,785		[152]
$(CH_2)_4$	Cl	Cl	Cl	1,852(4)	2,207(2)	175,3(1)	[158]
$(CH_2)_2OCHEt$	Me	Me	Cl	2,021	2,282(1)	170,7(1)	[159]
-*o*-$Me_2COC_6H_4$-	Me	Me	Cl	1,988(2)	2,312(1)	172,0(1)	[151, 153]
$(CH_2)_5$	Me	Me	Cl	1,950(1)	2,315(1)	171,7(7)	[151, 160]
$(CH_2)_5$	Me	Me	OC_6F_5	2,078	1,787		[152]
$(CH_2)_5$	Me	Cl	Cl	1,907(2)	2,256(1)	173,3(1)	[158]
$(CH_2)_5$	Cl	Cl	Cl	1,865(2)	2,213(1)	175,3(1)	[158]
$(CH_2)_5$	Cl	Cl	OMe	1,885(2)	2,236(1)	173,8(1)	[158]
$(CH_2)_5$	Me	1-$C_{10}H_8$	Cl	1,933(2)	2,327(1)	171,0(1)	[161]
	Me	Me	Cl	2,050(1)	2,271(1)	170,5(1)	[162]
	Me	Me	OSO_2CF_3	1,843(2)	2,241(2)	170,3(1)	[162]

The effect of various structural changes on the length of the O→Si bond in compounds **36** was investigated (Table 6). In the transition from the chlorine to the bromine, triflate, and iodine derivatives of N-[dimethyl(R^3)silylmethyl]piperid-2-one **36** [X = $(CH_2)_4$] the length of the O→Si coordination bond decreases from 1.954 to 1.747 Å. Analysis of the Si—R^3 bonds showed that the Si—Cl bond is increased by ~0.27 Å compared with the normal covalent bond, the Si—Br bond by 0.95 Å, the Si—O bond by 1.12 Å, and the Si—I bond by 1.27 Å, while the Si—I bond (3.734 Å) is only slightly less than the sum of the van der Waals radii. The obtained data confirm that the ionic character of the Si—R^3 bond increases in the order Cl < Br < $NOSO_2CF_3$ < I. The coordination at the silicon atom in N-(dimethylhalogenosilylmethyl)piperid-2-ones **36** also varies. In contrast to 1-(dimethylchlorosilylmethyl)piperid-2-one, in which the silicon is trigonal-bipyramidal, the silicon atom in the bromine and iodine derivatives has a highly disordered trigonal-bipyramidal coordination. The five-membered heterocycle in compounds **36** is an envelope; in the chlorine and iodine derivatives the silicon atom projects from the plane of the other four atoms by 0.15 and 0.058 Å respectively, and in N-(dimethylbromosilylmethyl)piperid-2-one the corner of the envelope is formed by the carbonyl carbon atom, which is deflected by 0.20 Å.

TABLE 7. Geometric Parameters of N-Silylmethylacetamides **37**

R	R^1	R^2	R^3	R^4	r(O→Si) (Å)	r(Si-R^2) (Å)	O-Si-R^3 (°)	Ref.
F	F	F	Me	Me	1,879(1)	1,635(1)	177,4(1)	[163]
F	F	F	Me	CF_3	1,943(2)	1,620(2)	172,2(1)	[163]
Me	F	F	Me	Me	1,985(4)	1,651(4)	172,6(5)	[164]
Me	Me	Cl	COMe	Me	2,077(6) 2,027(6)	2,229(4) 2,259(4)	170,0(2) 171,6(2)	[165]
Me	Me	Cl	CH_2SiMe_2Cl	Me	1,918	2,348		[166]

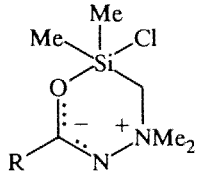
The substitution of one or two methyl groups at the silicon atom in N-(dimethylchlorosilylmethyl)perhydroazepin-2-one by chlorine is accompanied by a decrease of 0.043 and 0.085 Å in the O→Si distance and 0.059 and 0.102 Å in the Si—Cl_{ax} bond. The overall effect of the size of the nitrogen-containing heterocycle shows up in the elongation of the O→Si bond in compounds with five-membered rings, e.g., in N-[dimethyl(R^3)silylmethyl]pyrrolid-2-ones and particularly in 2,2,5-trimethyl-N-(dimethylchlorosilylmethyl)oxazolidin-4-one compared with N-silylmethylpiperid-2-ones and N-silylmethylperhydroazepin-2-ones.

The five-membered heterocycles of silylmethylacetamides **37** are almost planar. The shortest length of the O→Si bond (1.879 Å) for compounds of this type is found in N-methyl-N-trifluorosilylmethylacetamide. The substitution of one fluorine atom by a methyl group and the transition to N-methyl-N-trifluorosilylmethyltrifluoroacetamide is accompanied by an increase in the O→Si distance to 1.985 and 1.943 Å respectively (Table 7).

The silicon atom in the molecule of N,N,N′,N′-tetraethyl-N″-*tert*-butyl-N″-[(dimethylchloro-silyl)methyl]-triamidophosphate **38** [167] is trigonal-bipyramidal with short O→Si (1.840 Å) and long Si—Cl (2.438 Å) bonds. It is also necessary to note that the P=O distance (1.528 Å) is only slightly shorter (0.05 Å) than an ordinary P—O bond in compounds with a tetracoordinated phosphorus atom.

In contrast to the previously examined aroyloxymethyltrifluorosilanes **35**, N-silylmethyllactams **36**, N-silylmethyl-acetamides **37**, the amidophosphate **38**, and (2-methylsulfinylethyl)trifluorosilane **39** [168], in which the O→Si distances lie in the range of 1.840-2.450 Å, the O→Si interaction in ethyl 3-(trifluorosilyl)-2-cyanopropionate **40** [163] is weak, and the O→Si distances for the two independent molecules amount to 2.729 and 2.668 Å.

In the silylmethyl derivatives of hydrazine **41** (R = CF_3, 4-$MeOC_6H_4$) [169-171] the O→Si coordination leads to the formation of a six-membered heterocycle. As in compounds **36-38** with chlorosilyl substituents, a characteristic feature of the hydrazines **41** is the elongation of the Si—Cl bond (2.432 and 2.624 Å) and shortening of the O→Si bond (1.879 and 1.788 Å). The electron density distribution in the trifluoromethyl derivative **41** (R = CF_3) was investigated by precision x-ray crystallographic analysis at 163 K [171].



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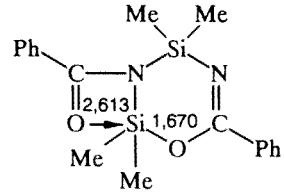

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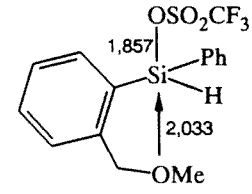


43

The O→Si distance in 2,2,4,4-tetramethyl-6-phenyl-3-benzoyl-2,4-disila-1,3,5-oxadiazine **42** [172, 173] is less than the sum of the van der Waals radii but significantly exceeds (2.613 Å) the corresponding values in compounds **35-39** and **41**. The O→Si interaction is also demonstrated by the disordering of the angles at the silicon atom from tetrahedral to trigonal-bipyramidal (OSiO angle = 161°).

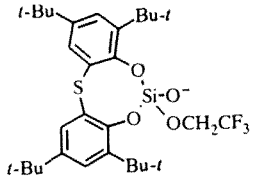
The oxygen atom of the ether group in phenyl[2-(methoxymethyl)phenyl]silyl triflate **43** [174] interacts extremely effectively with the silicon. As a result the latter becomes trigonal-bipyramidal with the two nitrogen atoms in the axial positions (O—Si—O angle 174.6°). The O→Si distance (2.033 Å) is fairly short, and the Si—OSO_2CF_3 distance (1.857 Å) is significantly longer than the normal covalent Si—O bonds. On the whole the structures of the triflate **43** and phenyl[2-(dimethylaminomethyl)phenyl]silyl triflate **15** [SiX_3 = Si(H)Ph(OSO_2CF_3)] [118] are similar in many respects.

TABLE 8. Geometric Parameters of Dioxathiasilocins **47**

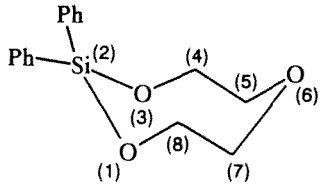
R	R^1	R^2	R^3	r(S—Si) (Å)	r(Si-O) (Å)	S-Si-R (°)	Ref.
Me[a]	Me	Me	Me	3,2800(13) 3,2917(14)	1,639(2) 1,639(2)	166,78(14) 164,07(14)	[181]
Me	Me	Me	*t*-Bu	3,074(1)	1,644(2)		[181]
-$CH_2CH_2CH_2CH_2$-		*t*-Bu	*t*-Bu	2,977(4)	1,638(7)	179,7(4)	[181]
Ph	Me	*t*-Bu	*t*-Bu	3,061(2)	1,639(5)	169,8(3)	[182]
Ph	Ph	Me	Me	3,630(2)	1,634(4)	125,3(2)	[182]
Ph	Ph	*t*-Bu	*t*-Bu	2,996(2)	1,637(4)	173,4(2)	[182]
Ph	CH_2=CH	Me	*t*-Bu	3,0737(14)	1,640(3)	166,50(14)	[182]
R**	OCH_2CF_3	*t*-Bu	*t*-Bu	3,04(1) 3,11(1)	1,63(2) 1,61(2)		[183]

a) For two independent molecules.

R** =

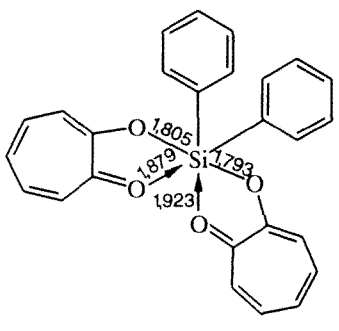


In the structural analog of the siloxanes 2,2-diphenyl-1,3,6-trioxa-2-silacyclooctane **44**, the eight-membered heterocycle has a distorted crown conformation. The $O_{(1)}$, $O_{(3)}$, $C_{(5)}$, and $C_{(7)}$ atoms lie in one plane, from which all the others are deflected to one side. The crown conformation is stabilized by very weak additional O→Si interaction (2.976 Å) [175, 176].



44

In the neutral complexes **45** [177] and **46** [178] the silicon atom is hexacoordinated with octahedral geometry. Additional coordination in compound **45** arises as a result of O→Si interaction of the silicon with two oxygen atoms of the tropolone rings, the planes of which are almost perpendicular to each other (dihedral angle 81.1°). The two phenyl groups are in the *cis* position. The length of the Si—O bond lies in the range of 1.793-1.923 Å. The coordination number of six in the complex **46** is achieved on account of the interaction of the silicon with the oxygen atoms of two molecules of tetrahydrofuran. The Si—O distances are nonequivalent, and the Si—O_{THF} bond is longer (1.9307 Å) than the Si—O bonds of the pyrocatechol fragments (1.7234 Å).



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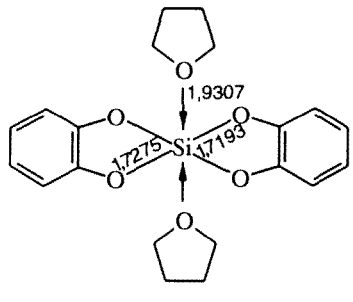


46

According to data from electron diffraction [179, 180] and x-ray crystallographic analysis [179], weak interaction is observed in the silyl esters of formic [180] and acetic [179] acids. In these compounds the O→Si distance is 2.865 and 2.795

TABLE 9. Geometric Parameters of the Anions in the Silicates **49**

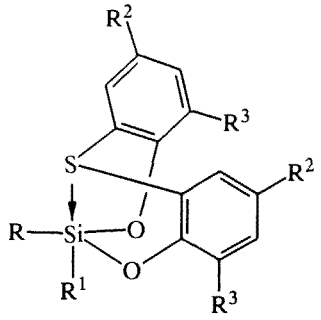
R	M^+	Solvate	X	r(Si-R) (Å)	r(Si-O) (Å)	$O_{(1)}$-Si-$O_{(3)}$, $O_{(2)}$-Si-$O_{(4)}$ (°)	$O_{(1)}$-Si-$O_{(4)}$, $O_{(2)}$-Si-$O_{(3)}$, (°)	$O_{(1)}$-Si-$O_{(2)}$ $O_{(2)}$-Si-$O_{(4)}$, (°)	Change from TBP to SP, %	Ref.
Me	$0,5H_3N^+(CH_2)_6N^+H_3$		H	1,876(3)	1,741(2)	161,7(1) 136,1(1)	86,5(1) 83,7(1)	88,3(1) 87,9(1)	25,7	[186]
Ph	$0,5H_3N^+(CH_2)_6N^+H_3$		H	1,883(3)	1,726(2)	159,2(1) 143,6(1)	85,4(1) 85,1(1)	88,2(1) 88,5(1)	72	[187]
$HOCH_2CH_2O$	Na^+	0,25MeCN	H	1,669(2)	1,735(2)	173,76(10) 128,13(10)	87,73(9) 88,40(9)	89,89(9) 88,61(9)	27	[188]
$HOCH_2CH_2O$	K^+		H							[189]
i-Pr	K^+(18-краун-6)		Me	1,667(3)	1,701(3)	171,7(2) 130,8(2)	86,9(1) 89,4(1)	88,4(1) 88,5(1)	29,4	[190]
t-Bu	K^+(18-краун-6)		Me						24,1	[191]
MeO	BuN^+H_3	MeOH	Me						71,2	[191]
EtO	BuN^+H_3		Me						38,9	[191]
F[a]	Me_4N^+	CH_2Cl_2	Me	1,642(8)	1,705(12)	163,7(5) 146,4(5)	87,5(4) 88,5(4)	87,5(5) 88,5(4)	69,1 52,3	[192]

a) For two independent molecules.

Å respectively, which is substantially longer than in the previously examined organosilicon derivatives. The silicon atom projects from the plane of the heavy atoms and is turned from the planar *cis* conformation by 21° in the formate and by 10° in the acetate. In the crystalline state at 150 K, the skeleton of the silyl acetate molecule is almost planar. It should be noted that the intramolecular O→Si distance (2.832 Å) is greater than the intermolecular O→Si contact (2.721 Å).

1.4. Increased Coordination Resulting from the S→Si Bond

According to the data from x-ray crystallographic analysis, in compounds **47** (Table 8) with 1,3-dioxa-6-thia-2-silocin heterocycles the sulfur atom is coordinated with the silicon, and the S→Si distance varies from 2.977 to 3.630 Å. In derivatives with a long S→Si bond of 3.00-3.11 Å, the eight-membered heterocycle adopts the boat conformation (the syn conformation). In the cyclic silane **47** with R = R^1 = Ph and R^2 = R^3 = Me and with weak S→Si interaction, the heterocycle is in the chair (anti) conformation.



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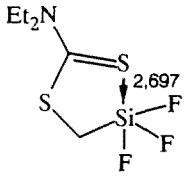


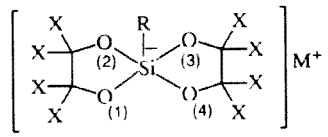
48

Additional coordination of the silicon in N,N-diethyldithiocarbamoylmethylfluorosilane **48** [184] arises as a result of S→Si interaction. The silicon atom is trigonal-bipyramidal with the sulfur and fluorine atoms in the axial positions (S—Si—F angle 177.8°). The S→Si bond in compound **48** (2.697 Å) is approximately 25% longer than in the compounds of tetrahedral silicon but shorter than in 1,3-dioxa-6-thia-2-silocins **47**.

For the silyl monothioacetate $MeC(S)OSiH_3$, the intramolecular S→Si distance in the gas (3.143 Å) and the solid (3.185 Å) is also less than the sum of the van der Waals radii of silicon and sulfur [185].

2. COMPOUNDS OF IONIC TYPE

Among the compounds with a penta- and hexacoordinated silicon atom the most widely studied are the structures of the bis(1,2-ethylenedithiolato)silicates **49** (Table 9), bis(glycolato)-, bis(lactato)-, and bis(citrato)-λ^5Si-silicates **50** (Table 10), bis(1,2-phenylenediolato)-λ^5Si-silicates **51** (Table 11), and bis(2,3-naphthalenediolato)-λ^5Si-silicates **52** (Table 12). In addition, the structures of the bis(tartrato)-λ^5Si,λ^5Si′-disilicate **53** [214], monooxalato-λ^5Si-silicate **54** [195], and the zwitterionic silicate **55** [195], in which the diolate ligand is formed by hydroxamic acid, were also investigated.



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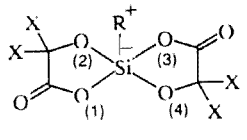

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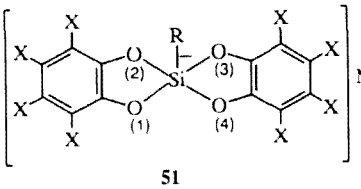

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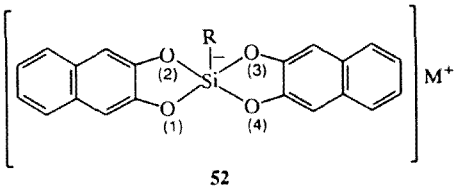

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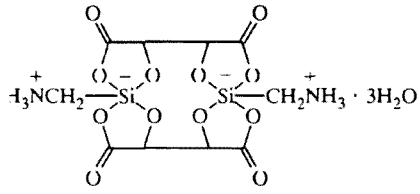

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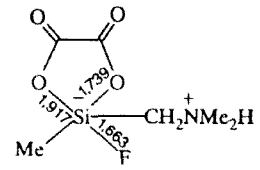

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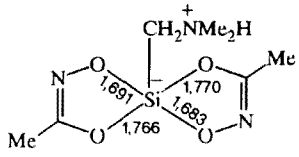

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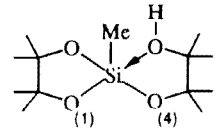


56

In the series of silicates **49-52**, the coordination center (the polyhedron of the silicon atom) changes from almost trigonal-bipyramidal to square-pyramidal. Numerous factors (the structure of the substituent R, the nature of the counterion, the formation of solvates, etc.) determine the change of the silicon geometry from trigonal-bipyramidal to square-pyramidal. In the anion of the bis(ethylenediolato)-λ^5Si-silicate **49** [X = H, M^+ = 0.5 $H_3N^+(CH_2)_6N^+H_3$] substitution of the methyl group at the silicon by phenyl is accompanied by a shift of the coordination toward the square pyramid from 25.7% to 72%. The silicon atom in the derivatives of pinacone **49** (X = Me, M^+ = *n*-BuN^+H_3) with R = MeO and EtO has the coordination of a distorted square pyramid and a trigonal bipyramid respectively. For the zwitterionic 2-(dimethylammonio)phenylsilicates **50** the change from the trigonal-bipyramidal to the square-pyramidal form decreases depending on the substituents X in the order H > Me > Ph.

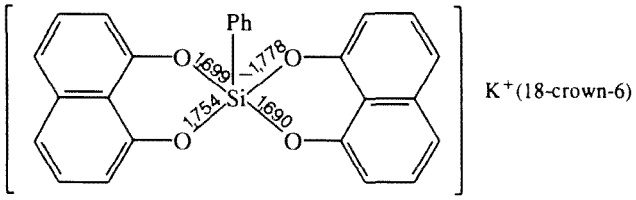
The spirosilicate **56** has an extremely unusual structure. Unlike the derivatives of pinacone **49**, compound **56** is neutral and one of the oxygen atoms of the spirocyclic system is attached to a hydrogen atom, which could not be removed by the action of triethylamine. The silicate **56** is characterized by three short Si—O bonds (1.61-1.66 Å) and one very long bond (2.74 Å).

In the tetraethylammonium salts $[RSi(O_2C_6H_4)_2]^-[Et_4N]^+$ the fraction of the trigonal-bipyramidal structure decreases with the substituents in the order Np > F ≈ Bu > *t*-Bu. The structure of the ammonium cation has a significant effect on the coordination of the substituents at the silicon atom. Cations of the $R^1{}_3N^+H$ and $C_5H_5N^+H$ type form hydrogen bonds with the oxygen atoms of the spirocyclic system and lead to coordination at the silicon atom closer to a square pyramid than in the analogous compounds with tetraalkylammonium cations $R^1{}_4N^+$.

A detailed analysis of the zwitterionic λ^5Si-organospirosilicates **51** confirms that the structure of this type of compound is determined by the presence of inter- and intramolecular hydrogen bonds. This becomes particularly clear during comparison of the pyrrolidinoethylbis(tetrabromo-1,2-phenylenediolato)-λ^5Si-silicate **51** [R, M^+ = $CH_2CH_2N^+H(CH_2)_4$, X = Br] and its monohydrate. In contrast to the little-distorted square-pyramidal geometry of the silicon for the two independent molecules of the hydrate, the coordination polyhedron of the anhydrous compound is a distorted bipyramid.

The effect of a more complex condensed system on the structure of the spirocyclic anionic silicates **52** was investigated. In the *tert*-butyl silicate **52** (R = *t*-Bu, M^+ = Et_4N) the change from the trigonal-bipyramidal coordination to square-pyramidal (80.3%) is less clearly defined than in the analogous *tert*-butylbis(1,2-phenylenediolato)-λ^5Si-silicate **51** (91.4%).

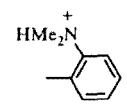
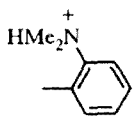
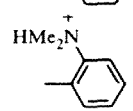
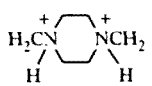
1,8-Dihydroxynaphthalene and 2-hydroxy-3-methylbenzoic acid form anionic spirosilicates **57** [215] and **58** [198] with six-membered heterocycles, in which the silicon atom has a trigonal-bipyramidal coordination distorted toward a square pyramid.

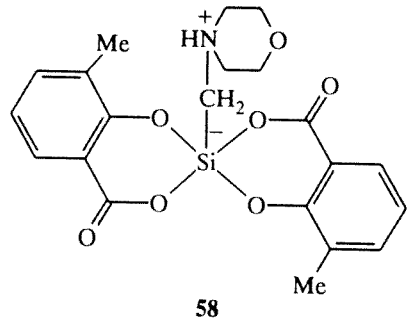


K^+(18-crown-6)

57

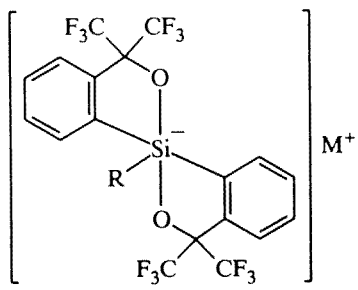
TABLE 10. Geometric Parameters of the Anions in the Silicates **50**

R^+	Solvate	X	r(Si-R) (Å)	r(Si-O) (Å)	$O_{(1)}$-Si-$O_{(3)}$; $O_{(2)}$SiO$_{(4)}$, (°)	$O_{(1)}$-Si-$O_{(4)}$; $O_{(2)}$-Si-$O_{(3)}$, (°)	$O_{(1)}$-Si-$O_{(2)}$; $O_{(3)}$-Si-$O_{(4)}$, (°)	Change from TBP to SP %	Ref.
		H	1,8741(14)	1,7365(12)	165,14(5) 137,77(5)	87,66(6) 84,27(6)	89,09(6) 88,36(6)	51,7	[193]
		Me	1,889(2)	1,7310(12)	168,95(5) 133,62(5)	88,70(5) 85,08(5)	89,29(5) 88,32(5)	38,4	[193]
		Ph	1,882(2)	1,7246(12)	173,28(5) 127,15(6)	89,17(6) 86,94(6)	88,98(6) 89,03(6)	20,6	[193]
$CH_2N^+Me_2H$	H_2O	CH_2COOH	1,888(4)	1,731(2)	175,07(11) 127,45(12)	89,58(10) 87,65(11)	89,12(10) 89,43(10)	18,7	[194]
$CH_2N^+MeH_2$		Me	1,889(2)	1,7342(14)	176,98(5)			5,4	[195]
$CH_2N^+Et_3$	MeCN	Ph	1,882(2)	1,7348(14)	172,40(7)			16.0	[195]
$OCH_2CH_2N^+Me_2H$	DMF	Ph	1,652(3)	1,741(3)	174,96(11) 124,52(11)	87,82(11) 89,19(11)	89,02(11) 89,32(11)	13,9	[196]
	$8H_2O$	Me	1,884(6)	1,725(4)	176,1(2) 124,3(2)	90,1(2) 87,9(2)	88,9(2) 90,0(2)	11,5	[197]
$CH_2N^+Me_2H$		X_2C=Ph(H)C	1,884(8)	1,725(5)	176,60(23) 124,37(0.27)	89,46(22) 88,56(25)	89,49(25) 89,34(22)		[198]



58

In contrast to compounds **49-54**, in the silyl anions of compounds **59** (Table 13), **60** [219], and **61** [220], the heterocycle only contains one oxygen atom. The silicon in the derivatives **59** and **60** is trigonal-bipyramidal with axial oxygen atoms, while in the cyanosilicate **61** the corners of the trigonal bipyramid are occupied by an oxygen atom and the carbon of the cyano group. It should be noted that the average length of the Si—O bonds in the silyl anions **59** and **61** is greater than in compounds **49-54**.



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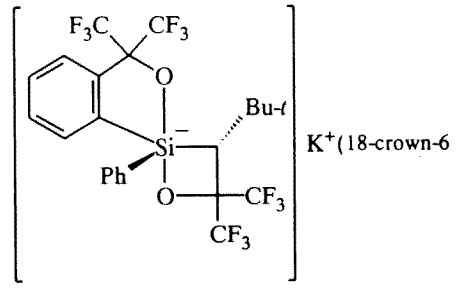

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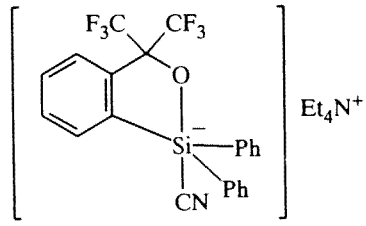
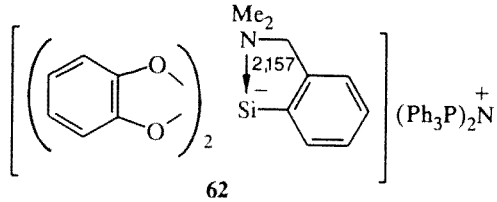


61

In addition to the derivatives of diols with a pentacoordinated silicon atom, the structure of the spirocyclic silicates **62-63**, in which the silicon is hexacoordinated, has also been studied.



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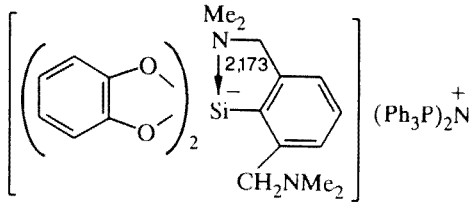

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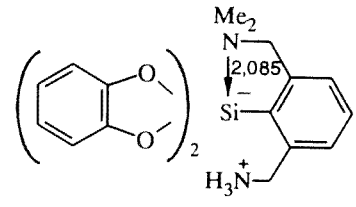
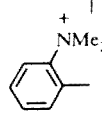
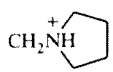
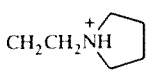
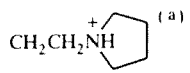


64

TABLE 11. Geometric Parameters of the Anions in the Silicates **51**

R	M^+	Solvate	X	r(Si-R) (Å)	r(Si-O) (Å)	$O_{(1)}$-Si-$O_{(3)}$, $O_{(2)}$-Si-$O_{(4)}$, (°)	$O_{(1)}$-Si-$O_{(4)}$, $O_{(2)}$-Si-$O_{(3)}$, (°)	$O_{(1)}$Si$O_{(2)}$, $O_{(3)}$Si$O_{(4)}$, (°)	Change from TBP to SP, %	Ref.
1	2	3	4	5	6	7	8	9	10	11
Bu	Et_4N^+		H	2,01(3)	1,754(9)	159,4(8) 139,0(8)	84,7(5)	88,1(5)	63,8	[199]
t-Bu	Et_4N^+		H	1,888(6)	1,755(4)	151,0(2) 146,7(2)	83,3(2) 84,7(2)	87,8(2)	91,4	[199]
C_6H_{11} [a]	$Me_2N^+H_2$		H	1,861(7)	1,751(4)	153,1(2) 144,3(2)	84,6(2) 83,7(2)	87,6(2) 87,8(2)	90,1 76,7	[190]
Ph	Me_4N^+		H	1,888(1)	1,747(9)	167,7(4) 127,9(4)	87,1(4)	87,6(4)	29,5	[200]
Ph	Et_3N^+H		H	1,871(3)	1,745(2)	161,1(1) 138,6(1)	84,56(9) 85,7(1)	87,95(9) 89,5(1)	59,4	[201]
Ph	Et_4N^+		Cl	1,854(4)	1,754(4)	152,9(2) 147,3(2)	84,8(2) 84,6(2)	87,8(2) 87,6(2)	90	[187]
Ph	Et_3N^+H		2,4-*t*-Bu 3,5-H	1,868(8)	1,763(5)	167,9(2) 127,8(3)	86,9(2) 86,7(2)	88,9(2) 86,9(2)	29,0	[201]
o-ClC_6H_4 [b]	$C_5H_5N^+H$		H	1,888(8)	1,745(5)	168,4(3) 130,5(3)	84,5(2) 89,4(3)	87,5(2) 89,0(3)	33,2	[202]
-C_6H_4-	2[Et_3N^+H]		H		1,748	162,0				[203]
1-Np	$C_5H_5N^+H$		H	1,875(6)	1,755(4)	160,0(2) 137,8(2)	86,5(2) 83,3(2)	87,8(2) 88,4(2)	58,7	[202]
1-Np	Et_4N^+		H	1,909(10)	1,740(6)	168,3(3) 129,1(3)	85,6(3) 86,7(3)	88,9(3) 88,9(3)	30,8	[199]
F [a]	Et_4N^+		H	1,603(4)	1,721(5)	166,2(3) 143,1(3)	86,1(2) 89,3(2)	89,4(2) 89,3(2)	68,7 52,8	[204]

TABLE 11. (continued)

R	M^+	Solvate	X	r(Si-R) (Å)	r(Si-O) (Å)	$O_{(1)}$-Si-$O_{(3)}$; $O_{(2)}$-Si-$O_{(4)}$, (°)	$O_{(1)}$-Si-$O_{(4)}$; $O_{(2)}$-Si-$O_{(3)}$, (°)	$O_{(1)}SiO_{(2)}$; $O_{(3)}SiO_{(4)}$, (°)	Change from TBP to SP, %	Ref.
1	2	3	4	5	6	7	8	9	10	11
F	K^+18-crown-6		H	1,600(8)	1,730(9)	171,2(5) 133,1(5)			36,1	[205]
		0,5MeCN	H	1,878(2)	1,740(2)	160,65(8) 144,68(8)	86,76(8) 83,54(8)	89,04(8) 89,02(8)	69,1	[206]
$CH_2N^+Me_2H$ [a]			H	1,891(2)	1,742(2)	176,60(6) 119,09(7)	88,91(6) 89,41(6)	89,60(6) 89,48(6)		[207]
		MeCN	Br	1,888(6)	1,742(3)	176,0(2) 121,3(2)	88,8(2) 89,7(2)	88,7(1) 88,9(2)	7	[208]
			Br	1,880(9)	1,740(9)	171,4(5) 122,2(5)	85,0(5) 87,9(4)	88,8(4) 90,4(4)	34,9	[207, 209]
 [a]		H_2O	Br	1,87(3)	1,75(2)	154(1) 150(1)	84,9(9) 85,0(9)	88,0(9) 88,6(9)	96,3 86,2	[207, 209]

a) For two independent molecules.

b) Mixture with the *n*-derivative.

TABLE 12. Geometric Parameters of the Anions in the Silicates **52**

R	M^+	Solvate	r(Si-R) (Å)	r(Si-O) (Å)	$\frac{O(1)\text{-}Si\text{-}Q(3)}{O(2)\text{-}Si\text{-}Q(4)}$ (°)	$\frac{O(1)\text{-}Si\text{-}Q(4)}{O(2)\text{-}Si\text{-}Q(3)}$ (°)	$\frac{O(1)\text{-}Si\text{-}Q(2)}{O(3)\text{-}Si\text{-}Q(4)}$ (°)	Change from TBP to SP, %	Ref.
t-Bu	Et_4N^+		1,871(7)	1,755(5)	153,3(2) 143,0(3)	84,3(2) 83,8(2)	87,2(2) 87,3(2)	80,3	[201]
Ph	$C_5H_5N^+H$		1,871(3)	1,744(2)	152,1(1) 150,9(1)	83,9(1) 85,5(1)	88,2(1) 88,5(1)	97,6	[202]
		MeCN	1,906(5)	1,739(3)	172,8(2) 128,4(2)	86,9(1) 88,5(2)	88,6(2) 89,8(2)	20,5	[210]
		MeCN	1,879(3)	1,745(2)	153,6(1) 150,1(1)	85,9(1) 84,0(1)	88,6(1) 88,1(1)	89,6	[211, 212]
		Me_2CO	1,888(4)	1,739(3)	176,9(1) 119,2(1)	88,7(1) 89,3(1)	90,1(1) 89,0(1)		[213]
		$MeNO_2$	1,875(8)		173,2(3) 129,6(3)	87,6(3) 87,8(3)	90,2(3) 89,2(3)	25,3	[213]

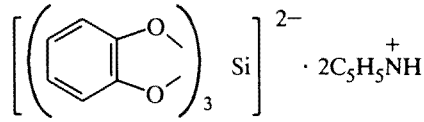
TABLE 13. Geometric Parameters of the Anions in the Silicates **59**

R	M^+	r(Si-R) (Å)	r(Si-O) (Å)	O-Si-O(°)	Ref.
Ph[a]	Me_4N^+	1,944(9)	1,819(9) 1,810(9)	171.1(4)	[216]
C_6H_{11}	Et_4N^+	1,889(6)	1,855(4) 1,823(4)	170,5(2)	[190]
Ph_3Si	Et_4N^+	2,403(3)	1,831(5) 1,838(5)	171,8(2)	[217]
F[a]	$(Me_2N)_3S^+$	1,631(3)	1,789(4) 1,784(4)	176,4(2)	[218]

a) The average values for two independent molecules.

It was shown by x-ray crystallographic analysis that the anions in compounds **62** [221], **63** [222], and **64** [223, 224] are octahedral. The N→Si donor bonds in the derivatives **62** (2.157 Å) and **63** (2.173 Å) differ little, and in addition it was found that only one dimethylaminomethyl group in the silicate **63** is coordinated with the silicon atom, whereas the other does not enter into intramolecular interaction. The N→Si bond in the zwitterionic silicate **64** is shorter (2.085 Å), while the hydrogen atom of the ammonium group forms a strong hydrogen bond with the oxygen atom of the spirosilicate fragment [r(NH···O) = 1.62 Å].

Each of the three cyclic ligands at the silicon in compound **65** is nonplanar, and the largest deviation from the plane amounts to 0.037 Å. The geometry of the anion is almost octahedral. The departures from the ideal D_3 symmetry are due to the strong electronic effects in the crystal lattice, and all the O—Si—O angles therefore differ from the ideal angles of 90 and 180° in the octahedron. The strains in the rings affect the values of the OCC angles (113°), which are significantly smaller than 120° [225, 226]. In compound **65** the Si—O bonds are nonequivalent (1.765-1.813 Å), and they differ little from the values characteristic of the anionic derivatives of pentacoordinated silicon.



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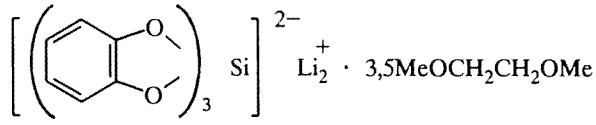


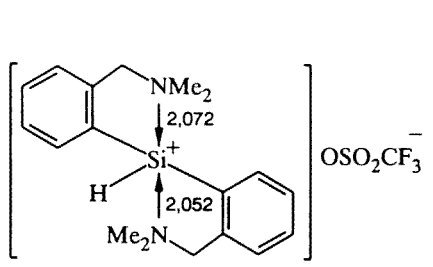
66

The silicon atom in the 1,2-dimethoxyethane solvate **66** [178] is surrounded by the six oxygen atoms of three pyrocatechol groups and has an octahedral coordination. Each of the lithium cations is also at the center of an octahedron formed by three oxygen atoms of the SiO_6 octahedra and three oxygen atoms of the dimethoxyethane. The Si—O distances (1.7723-1.7930 Å) lie in the region characteristic of the silicate **65**.

The ionic structure of these compounds is confirmed unambiguously by the x-ray crystallographic analysis of bis[2-(dimethylaminomethyl)phenyl]silyl triflate **67** [118] and the complex of bis[8-(dimethylamino)naphthyl]silane with iodine **68** [227]. Unlike the previously examined [2-(dimethylaminomethyl)phenyl]phenylsilyl triflate **15** [SiX_3 = Si(H)Ph(OSO_2CF_3)] [118] with an Si—O bond of 1.951 Å, interaction between the oxygen and silicon atoms is absent in compound **67**, and the shortest Si—O distance amounts to 4.165 Å, which is greater than the sum of the van der Waals radii. The coordination at the silicon atom is a trigonal bipyramid with the nitrogen atoms of the two dimethylaminomethyl groups at the corners and with N→Si distances of 2.052 and 2.072 Å. These bonds are shorter than in the neutral derivatives of pentacoordinated silicon, containing 2-(dimethylaminomethyl)phenyl substituents.

In compound **68**, the shortest Si—I distance (5.036 Å) is significantly greater than the sum of the van der Waals radii. In addition, the ions form alternating layers in the crystal. This indicates the absence of covalent interactions between the silicon

and the iodine. The silicon is trigonal-bipyramidal. The three σ-bonded atoms lie in the equatorial plane, and the two nitrogen atoms are in the axial positions. The N→Si distances (2.08 and 2.06 Å) are very close in value to the distances in compound **67**.



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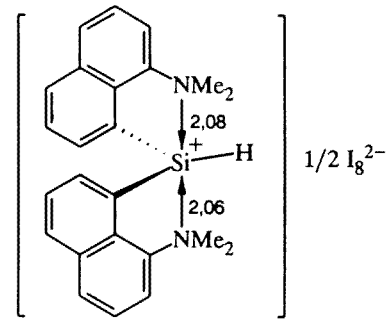
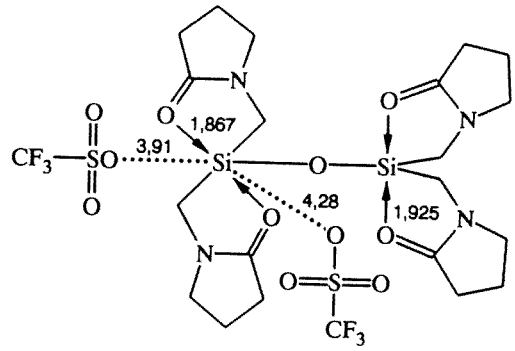


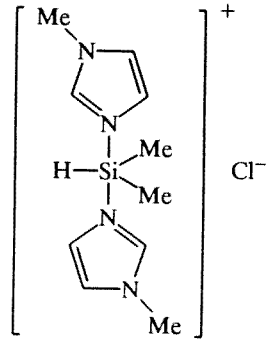
68

In the bistriflate of 1,1,3,3-tetrakis[1-(2-oxopyrrolidinyl)methyl]disiloxane **69** [228], the shortest interionic Si—O_{Tf} contacts (3.91 and 4.28 Å) were only found for one silicon atom of the siloxane fragment, for which they exceed 4.5 Å. The disiloxane fragment is nonlinear (Si—O—Si angle 145.3°), and the silicon atoms have a trigonal-bipyramidal configuration with the oxygen atoms of the carbonyl groups at the corners of the pyramid.

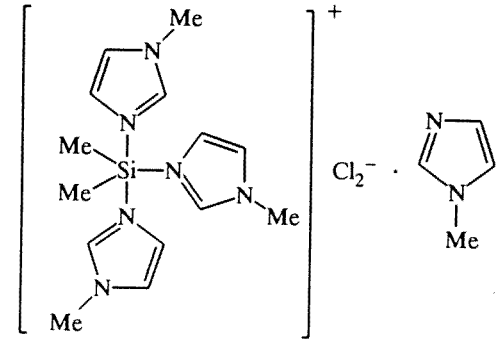


69

In reaction with N-methylimidazole, dimethylchloro- and dimethyldichlorosilane form the ionic compounds **70** and **71** [229] with pentacoordinated silicon. The distances from the silicon to the nitrogen atoms in the axial positions in the cation **70** are equal (2.034 and 2.005 Å), while in the cation **71** the equatorial Si—N bond (1.817 Å) is shorter than the axial bonds (1.983 and 2.023 Å).



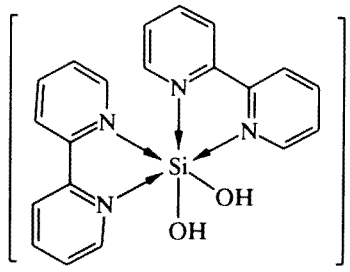
70



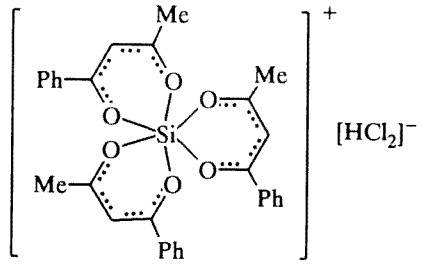
71

The structure of compounds **72** [230], **73** [231], and the complex of tetraiodosilane with dimethylformamide $[(Me_2NCHO)_6Si]I_4$ [232] with hexacoordinated octahedral silicon was studied by x-ray crystallographic analysis. In the cation **72**, the N→Si bonds in the *trans* position to the OH ligands (2.005 Å) are longer than the *cis* bonds (1.953 Å). The O—Si—O angle approximates to tetrahedral, and the N—Si—N angles of the two 2,2′-bipyridine ligands are small (80.4°) on account of the steric characteristics.

The length of the Si—O bonds in the cation with the dimethylformamide ligands (1.754-1.772 Å) and in the chelate complex **73** (1.752-1.779 Å) is identical.



72



73

* * *

After analysis of the results of structural investigations of the compounds of hypervalent silicon it should be noted that additional coordination with nitrogen, oxygen, and sulfur atoms as a rule leads to derivatives with five-membered heterocycles (silatranes, 2-dimethylaminomethylphenylsilanes, 8-dimethylamino-1-naphthylsilanes, aroyloxymethyltrifluorosilanes, N-silylmethyllactams, N-silylmethylacetamides, and spirocyclic 1,2-ethylenediolato-, 1,2-phenylenediolato-, and 3,4-naphthalenediolatosilicates). The formation of four- and six-membered heterocycles is observed much less often.

The data on the molecular structure of the compounds of silicon with increased coordination are extremely useful during the study of the reactivity (the structure of the intermediate complexes, reaction mechanisms). They are also essential for the analysis of the results of NMR-spectroscopic investigations and for the production of correlations between the geometric characteristics of molecules in the crystalline state and the NMR spectral parameters. The structural characteristics of organosilicon compounds may provide valuable information during the investigation of their biological activity.

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