Synthesis and crystal and molecular structures of cation-anionic complexes of five-coordinate silicon-containing disiloxane dications with lactamomethyl and *N*-methylacetamidomethyl C,O-chelating ligands

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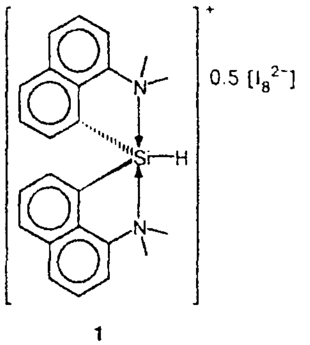
The reactions of bis(chloromethyl)dichlorosilane with *N*-trimethylsilyl lactams and *N*-trimethylsilyl-*N*-methylacetamide taken in a ratio of 1 : 2 followed either by treatment with $HgCl_2$ in the presence of atmospheric moisture or by hydrolysis under a wet atmosphere afforded cation-anionic complexes, which contain disiloxane dications of the general formula $[L_2SiOSiL_2]^{2+}$ (L is the lactamomethyl or *N*-methylacetamidomethyl bidentate ligand) and hexachlorodimercurate, tetrachloromercurate, and hydroxonium trichloride counter-ions, respectively. X-ray diffraction analysis demonstrated that the disiloxane dications in these complexes contain two five-coordinate Si atoms and occur as silicenium ions stabilized through two O→Si coordination bonds. In the case of lactamomethyl ligands, the disiloxane dications exist as diastereomers whose bischelate ligands adopt opposite configurations, whereas when *N*-methylacetamidomethyl ligands are present, the bischelate ligands adopt identical configurations. The first example of the presence of a hydroxonium trichloride ion as a counter-ion in the crystal has been found. It consists of the hydroxonium cation, which holds three Cl^- anions through strong hydrogen bonds.

Key words: silicenium ions, five-coordinate silicon; cation-anionic complexes, X-ray diffraction analysis; quantum-chemical calculations, MNDO/PM3 method.

The possibility of stabilization of silicenium cations through intramolecular coordination bonding represents a new line of investigations of hypervalent compounds of silicon (see, for example, the review 1, Ref. 2, and references cited therein). However, the available data concern mainly compounds with C,N-chelating ligands.[1,2] In particular, the structures of five-coordinate silyl cations **1** [3] and **2** [4] of the general formula $[R_2SiH]^+$, which are stabilized through two intraionic N→Si coordination bonds, were established by X-ray diffraction analysis.



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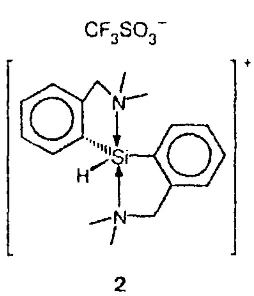

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Most known compounds in which the five-coordinate Si atom bears two O,O- or two C,O-chelating ligands exist as anions[5—10] containing O_4SiX or O_2C_2SiX coordination units (X = C or Hal). Some their germanium analogs occur also as anions.[11,12] Recently, we have studied for the first time[13] the disilicenium dication $[R_2SiOSiR_2]^{2+}$, which contains O_3SiC_2 fragments as central coordination units, using 1,1,3,3-tetrakis[(2-oxopyrrolidino)methyl]disiloxane ditriflate (**3**) as an example. Its structure in the solid state was established by X-ray diffraction analysis. Conductometric study in solution confirmed the structure of the cation.

In this work, we report the results of synthesis of new cation-anionic complexes that contain disiloxane dications of the general formula $[L_2SiOSiL_2]^{2+}$ (L is the

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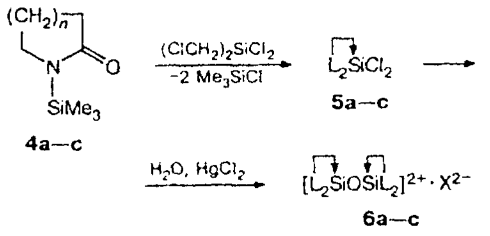
lactamomethyl or *N*-methylacetamidomethyl bidentate ligand). Three of them were studied by X-ray diffraction analysis.

Results and Discussion

Disiloxane ditriflate **3**, which has been described previously, was prepared by the reaction of 1-trimethylsilyl-2-pyrrolidone (**4a**) with bis(chloromethyl)dichlorosilane (the ratio of the reagents was 2 : 1) followed by treatment of the amorphous hygroscopic powder of dichloride **5a** that formed with trimethylsilyl triflate under conditions of concurrent hydrolysis under the action of atmospheric moisture.[13] Using the above-mentioned procedure for the synthesis, we studied the reactions of silyl lactams with bis(chloromethyl)dichlorosilane followed by addition of mercuric chloride with the aim of stabilizing disiloxane cation-anionic complexes by nonnucleophilic anions. As a result, new cation-anionic complexes **6a—c** with hexachlorodimercurate ($Hg_2Cl_6^{2-}$) and tetrachloromercurate ($HgCl_4^{2-}$) ions as anions were prepared (Scheme 1). The structures of complexes **6b,c** were confirmed by X-ray diffraction analysis.

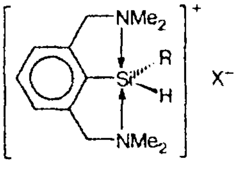
Scheme 1



$L = \overline{CH_2(CH_2)_nCH_2CON}CH_2$; *n* = 1 (**a**), 2 (**b**), 3 (**c**)

X = Hg_2Cl_6 (**6a,c**), $HgCl_4$ (**6b**)

It should be noted that the previously studied complexes **7**,[2] in which five-coordinate silyl cations $[R_2SiH]^+$ are stabilized by two intraionic N→Si coordination bonds, are powders, which are very unstable in air and sensitive to moisture. For most of these compounds, attempts to obtain reliable data of elemental analysis were unsuccessful. Their structures in solutions were established by NMR spectroscopy.



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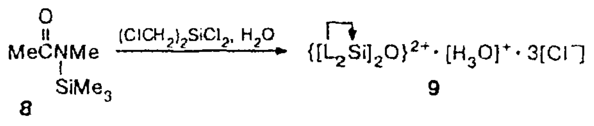
X = Cl, Br, I, BF_4, CF_3SO_3

Dichlorides **5a—c** are also very sensitive to atmospheric moisture. When performing the reaction of bis(chloromethyl)dichlorosilane with the derivative of acyclic amide, *N*-trimethylsilyl-*N*-methylacetamide (**8**), under conditions which did not exclude exposure to atmospheric moisture (Scheme 2), we obtained a product in a rather high yield (74%). According to X-ray diffraction data, this product is disiloxane cation-anionic complex **9** with a hydroxonium trichloride ion as the anion.

Scheme 2



L = MeC(O)N(Me)CH_2

As in the case of disiloxane ditriflate **3**,[13] the IR spectra of complexes **6a—c** and **9** have two absorption bands in the 1500—1700 cm^{-1} region, namely, at 1500—1510 (w) and 1580—1620 cm^{-1} (s), which belong to strongly bonded stretching vibrations ν(C=O) and ν(C=N) characterizing the N$\cdots$C$\cdots$O fragment of the chelating ligand.[13,14] These spectral data indicate that the Si atoms in complexes **6a—c** and **9** are five-coordinate. The absorption bands ν(C=O) of nonchelating lactamo- or amidomethyl ligands are absent, which indicates that both the lactamo- and amidomethyl ligands in the complexes are bidentate, and the O→Si coordination bond is rather strong.

The ^1H, ^{13}C, and ^{29}Si NMR spectra of complexes **6a—c** and **9** have two sets of signals with different integrated intensities (Tables 1 and 2). A superposition of the signals hinders the determination of their multiplicity.

In both cases, the data in Tables 1 and 2 are indicative of insignificant differences in the chemical shifts of the signals in the ^1H and ^{13}C NMR spectra. In the ^1H NMR spectra, only characteristic signals of anisochronous protons of the prochiral NCH_2Si group are well resolved. These signals are observed as a quartet of an AB system. In solutions of complexes **6a—c** in DMSO-d_6, these signals are observed as a superposition of two quartets. In a solution of complex **9** in CD_2Cl_2, the signals of the protons of the NCH_2Si group are also observed as two quartets of an AB system. In a solvent with stronger donor properties (DMSO-d_6), one quartet is transformed into a broadened singlet. The ratio of integrated intensities of two sets of signals depends both on the structure of the bidentate ligand and on the nature of the solvent (see Table 1). Thus, in the case of complex **9**, the ratio of two sets of signals changes from ~70 : 30 to ~60 : 40 in going from CD_2Cl_2 to DMSO-d_6.

In both cases, the ^{29}Si NMR spectra show signals at higher field (up to −70 ppm, see Table 2) compared to those of the model compound $(ClMe_2Si)_2O$ (δ ^{29}Si 9.8),[15] which is indicative of a hypervalent state of the Si atom. In a series of complexes **6a—c**, the largest upfield shift of the ^{29}Si signal is observed for compound **6b**, which may be a result of a higher degree of the intramolecular O→Si interaction in this complex. In the

Table 1. Chemical shifts and spin-spin coupling constants in the ^{1}H NMR spectra of compounds **6a—c**, **9** (in DMSO-d_6)

Compound	δ ($^2J_{HH}$/Hz)						Concentration of diastereomers (%)
	H(3)	H(4)	H(5) (m)	H(6) (m)	H(7) (m)	NCH$_2$	
6a	2.77 (m)	2.15 (m)	3.60			2.53 (m)	76
	2.76 (m)	1.89 (m)	3.29			2.54 (m)	24
6b	2.40 (m)	1.76 (m)	1.79	3.44		2.56, 2.64 (dd, J = 16)	80
	2.40 (m)	1.75 (m)	1.79	3.44		2.51, 2.61 (dd, J = 16)	20
6c	2.70 (m)	1.52 (m)	1.63	1.79	3.69	2.79, 2.85 (dd, J = 16)	78
	2.73 (m)	1.51 (m)	1.63	1.79	3.67	2.60, 2.79 (dd, J = 16)	22
9	2.22 (s)[a]	3.15 (s)[b]				2.62, 2.69 (dd, J = 16.3)	60
	2.25 (s)[a]	3.18 (s)[b]				2.62 (br.s)	40
9[c]	2.26 (s)[a]	3.24 (s)[b]				2.71, 2.90 (dd, J = 17.3)	70
	2.29 (s)[a]	3.21 (s)[b]				2.73, 2.97 (dd, J = 17)	30

[a] MeC(O). [b] NMe. [c] The spectrum was obtained in CD_2Cl_2.

Table 2. Chemical shifts in the ^{13}C and ^{29}Si NMR spectra of compounds **6a—c**, **9** (in DMSO-d_6)

Compound	δ ^{13}C							δ ^{29}Si
	C(3)	C(4)	C(5)	C(6)	C(7)	NCH$_2$	C=O	
6a	26.86	17.87	49.19			32.93	180.61	−41.5
	26.86	17.83	49.19			32.81	180.59	−46.6
6b	26.52	18.66	21.05	48.48		36.87	174.20	−64.6
	26.51	18.63	21.01	48.47		36.87	174.19	−67.6
6c	30.91	28.63	25.29	21.66	50.80	38.90	179.85	−62.2
	30.90	28.63	25.20	21.47	49.9	38.89	174.19	−66.7
9	16.52[a]	37.37[b]				38.29	175.16	−64.3
	16.58[a]	37.38[b]				37.96	175.16	−68.8
9[c]	17.55[a]	38.42[b]				39.16	175.83	−63.7
	17.54[a]	38.46[b]				39.17	175.83	−69.7

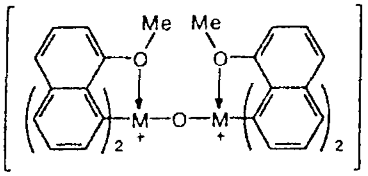
[a] MeC(O). [b] NMe. [c] The spectrum was obtained in CD_2Cl_2.

^{13}C NMR spectrum of complex **6b**, the signal of the C atom of the carbonyl group is observed at higher field compared to those of the other complexes under study because of an increase in the paramagnetic contribution to the shielding constant of ^{13}C(=O). Previously, we have observed the strengthening of the O→M interaction in derivatives of valerolactam in solution when studying hypervalent compounds of silicon, germanium, and tin, namely, derivatives of amides and lactams with C,O-chelating ligands.[16]

An increase in the temperature of solutions of complexes **6a—c** and **9** in DMSO-d_6 is accompanied by substantial changes in the ^{1}H NMR spectra. Thus, both quartets of the protons of an AB system of the NCH$_2$Si group undergo broadening followed by coalescence into singlets with an averaged chemical shift. The free energy of activation ($\Delta G^{\neq}$) of the polytopic rearrangement, which was determined at the temperature of coalescence, is 17.9±0.4, 18.5±0.3, and 16.4±0.6 kcal mol^{-1} for complexes **6b,c** and **9**, respectively. When CD_2Cl_2 (which exhibits low donor ability) was used as the solvent, only an insignificant broadening of the signals of the protons of the NCH$_2$Si group of complex **9** was observed up to 50 °C. The value of $\Delta G^{\neq}$, which was estimated based on the line-shape analysis, is >19 kcal mol^{-1}. Previously, an analogous increase in the barrier of polytopic rearrangements as the donor ability of the solvent decreases was observed in the case of halides of five-coordinate silicon.[16]

It should be mentioned that in the temperature range used, we did not detect exchange between protons, which are observed in the ^{1}H NMR spectra as independent quartets. This is indicative of the presence of two rather stable diastereomers in solutions of the complexes under study. The configurations of their chiral coordination polyhedra remain unchanged or change simultaneously in the course of the exchange observed.

Note that complexes **10** have been synthesized recently.[17] Their dications are disilicenium or digermacenium ions that contain 8-methoxynaphthyl C,O-chelating ligands, which are to a large extent analogous to those discussed in this work.



10

M = Si, Ge

The scheme of formation of cation-anionic complexes **3**, **6a—c**, and **9** can be understood taking into account the results obtained in the studies of the reactions of nucleophilic substitution of the halogen atom in six-coordinate (O—Ge)-bischelate bis(lactamomethyl)dichlorogermanes L_2GeCl_2 with trimethylsilyl triflate, trimethylsilyl halides (Me_3SiBr or Me_3SiI), or salts of lithium (LiBr, LiI, or $LiClO_4$) or silver (AgF or $AgBF_4$). The structures of the initial compounds and the final products of these reactions were established by X-ray structural analysis.[18] The directions of these reactions depend on the nature of monodentate ligands in the final product and are independent of the ratio of the reagents. In the case of readily leaving groups, products of replacement of one halogen atom by the nucleophile $L_2Ge(Cl)X$ ($X = OTf^-$, I^-, BF_4^-, or ClO_4^-) were formed. In these products, the C and O atoms and monodentate ligands are in *trans* positions with respect to each other. In other cases, both Cl atoms were substituted to form compounds L_2GeY_2 (Y = F or Br), whose coordination units have configurations identical to those observed in the initial dichlorides, *i.e.*, the C atoms are in *trans* positions and the halogen atoms and coordinated O atoms are in *cis* positions with respect to each other.

The formation of products of monosubstitution of the halogen atom in the *trans*-$L_2Ge(Cl)X$ compounds (solutions of these compounds exhibit a high conductivity), which are essentially analogs of the disiloxane cation-anionic complexes under study, can be explained as follows. When one Cl atom in dichloride L_2GeCl_2 is replaced by a nucleophile, which is a more readily leaving group compared to the chloride ion, monochloride $L_2Ge(Cl)X$ is formed whose hypervalent Cl—Ge—X fragment has the shortened Cl—Ge bond and the substantially elongated (close to ionic) Ge—X bond. This prevents the substitution of the second Cl atom in monochlorides $L_2Ge(Cl)X$ and faciltates reactions that proceed with substitution of readily leaving groups X.

Taking into account these data, it can be suggested that, apparently, in the reactions that afford complexes **3**, **6a—c**, and **9** (see Schemes 1 and 2), dichlorides L_2SiCl_2 initially undergo hydrolysis to form the disiloxane group after which the remaining Cl atom is replaced by the corresponding anion.

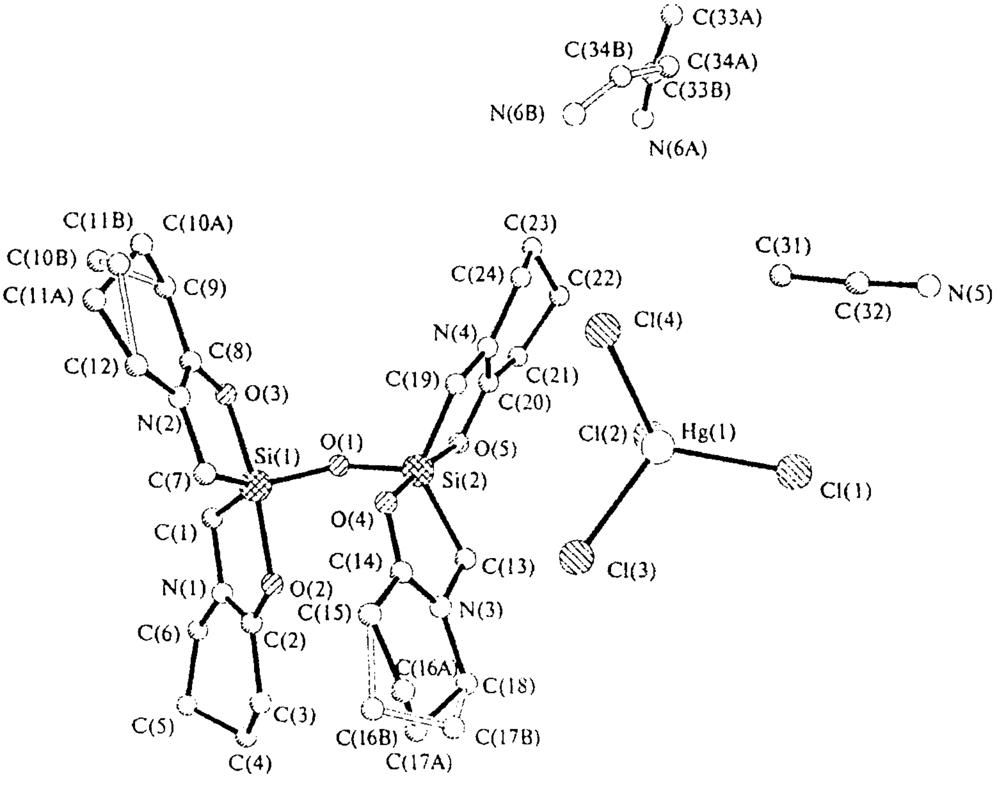


Fig. 1. Crystal structure of complex **6b** (H atoms are omitted; two acetonitrile molecules of solvation are shown).

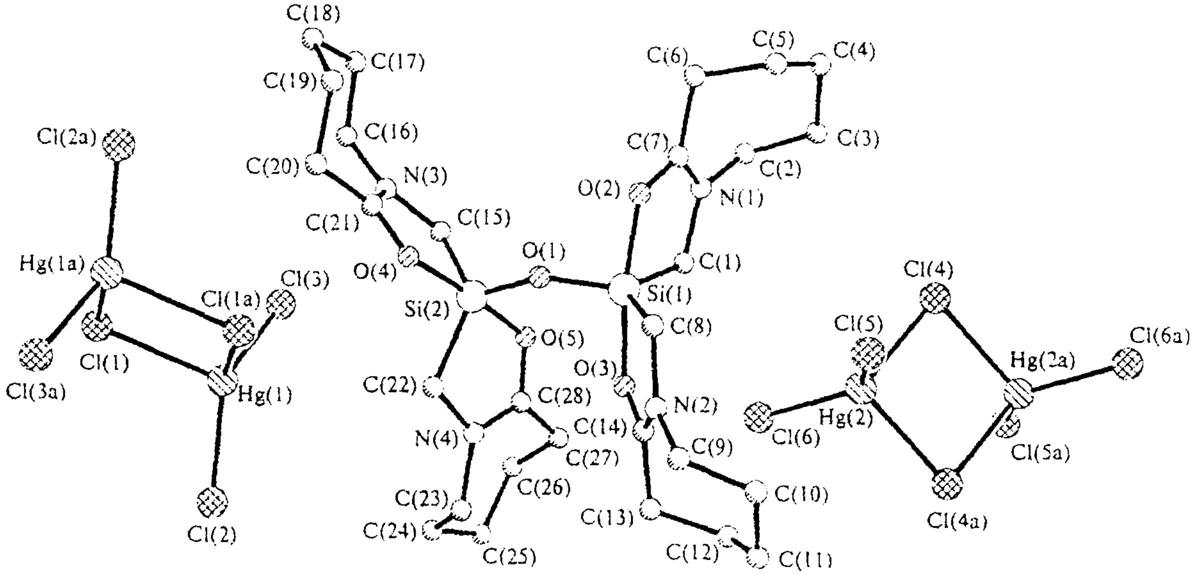


Fig. 2. Crystal structure of complex **6c** (H atoms are omitted; the atoms related to the initial atoms by an inversion center are marked with the letter "a").

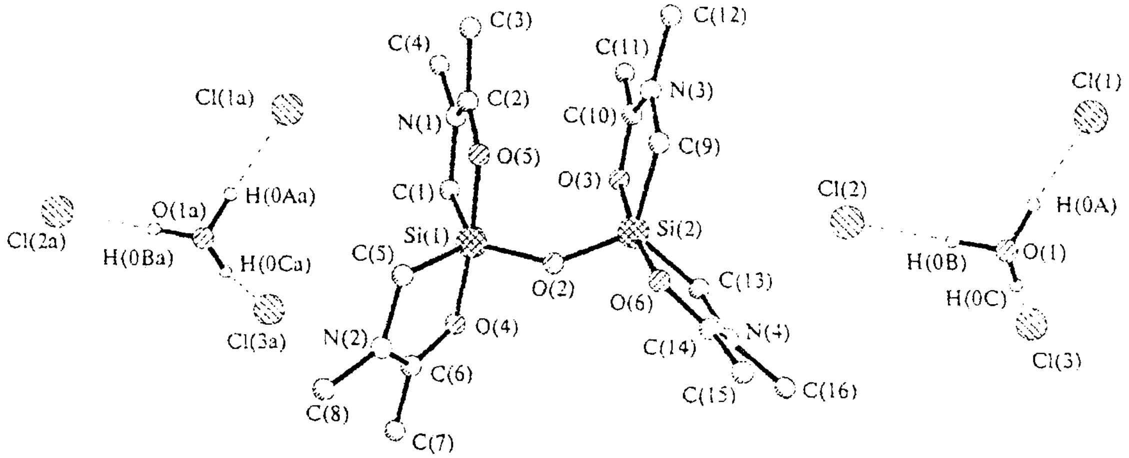


Fig. 3. Crystal structure of complex **9** (the H atoms of the hydroxonium ion and the H...Cl bonds are shown; the counter-ions, whose atoms are marked with the letter "a", are related to the initial counter-ions by the transformation 1 + *x*, 1 + *y*, *z*).

As in the case of disiloxane ditriflate **3** studied previously,[13] the coordination environment about the Si atoms in complexes **6b,c** and **9** (Figs. 1—3) is a nearly ideal trigonal bipyramid (the Si atoms deviate from the equatorial plane by 0—0.03 Å). The O→Si coordination bonds with the participation of the coordinating O atoms of the bidentate ligand are axial.

The spatial configurations of the disiloxane dications in complexes **6b,c** and **9** are different. The bischelate spiro system SiL$_2$ with the linear hypervalent O—Si—O bond does not have a symmetry plane or a symmetry center, *i.e.*, this system is chiral. Therefore, the L$_2$SiO fragments of the dioxolane dication [L$_2$SiOSiL$_2$]$^{2+}$ can adopt either identical or different configurations. It appeared that the disiloxane dications in complexes **6b,c** and **9** are diastereomers with different (below, they are denoted as (25)-Si(1),($\overline{25}$)-Si(2) diastereomers) and identical ((25)-Si(1),(25)-Si(2) diastereomer) configurations of the chiral L$_2$SiO fragments,* respectively.

The causes of the formation of different diastereomers of the dications in cation-anionic complexes **6b,c**

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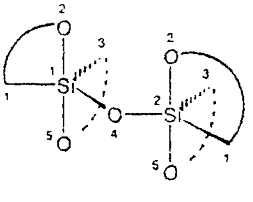
* We used the conventional notation of trigonal-bipyramidal stereoisomers (see, for example, Ref. 16) according to which substituents directly bonded to the central atom are arbitrarily denoted by numbers (from 1 to 5). The configuration of a particular chiral center is denoted by numbers, which correspond to the numbers of the axial ligands (for example, 25) if the ordinal numbers of the equatorial ligands increase in a clockwise direction. If the ordinal numbers of the equatorial ligands increase in a counterclockwise direction (as in the case of the enantiomeric configuration), the numbers denoting the axial ligands are marked with overscribed bars ($\overline{25}$).

Table 3. Bond lengths (*d*) in the structure of **6b**

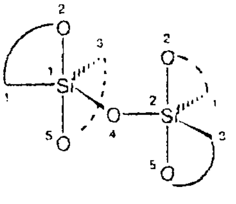
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Hg(1)—Cl(1)	2.453(3)	O(3)—C(8)	1.300(10)	C(2)—C(3)	1.493(13)	C(16A)—C(17A)	1.37(5)
Hg(1)—Cl(2)	2.489(3)	O(4)—C(14)	1.281(10)	C(3)—C(4)	1.505(14)	C(16B)—C(17B)	1.58(5)
Hg(1)—Cl(3)	2.497(3)	O(5)—C(20)	1.317(11)	C(4)—C(5)	1.50(2)	C(17A)—C(18)	1.63(4)
Hg(1)—Cl(4)	2.484(3)	N(1)—C(1)	1.467(11)	C(5)—C(6)	1.496(14)	C(17B)—C(18)	1.40(7)
Si(1)—O(1)	1.625(6)	N(1)—C(2)	1.301(11)	C(8)—C(9)	1.477(13)	C(20)—C(21)	1.507(13)
Si(1)—O(2)	1.885(6)	N(1)—C(6)	1.482(11)	C(9)—C(10A)	1.56(3)	C(21)—C(22)	1.49(2)
Si(1)—O(3)	1.849(6)	N(2)—C(7)	1.449(12)	C(9)—C(10B)	1.49(5)	C(22)—C(23)	1.41(2)
Si(1)—C(1)	1.865(8)	N(2)—C(8)	1.307(12)	C(10A)—C(11A)	1.56(4)	C(23)—C(24)	1.55(2)
Si(1)—C(7)	1.887(9)	N(2)—C(12)	1.489(12)	C(10B)—C(11B)	1.40(7)	N(5)—C(32)	1.27(3)
Si(2)—O(1)	1.628(6)	N(3)—C(13)	1.470(11)	C(11A)—C(12)	1.40(2)	N(6A)—C(34A)	1.05(3)
Si(2)—O(4)	1.870(6)	N(3)—C(14)	1.319(11)	C(11B)—C(12)	1.84(5)	N(6B)—C(34B)	1.39(12)
Si(2)—O(5)	1.842(6)	N(3)—C(18)	1.452(11)	C(14)—C(15)	1.498(12)	C(31)—C(32)	1.41(3)
Si(2)—C(13)	1.878(9)	N(4)—C(19)	1.457(11)	C(15)—C(16A)	1.42(2)	C(33A)—C(34A)	1.48(4)
Si(2)—C(19)	1.879(9)	N(4)—C(20)	1.288(12)	C(15)—C(16B)	1.63(4)	C(33B)—C(34B)	1.5(2)
O(2)—C(2)	1.286(10)	N(4)—C(24)	1.461(13)				



(2S)-Si(1),($\overline{2S}$)-Si(2)-**3**,

(2S)-Si(1),($\overline{2S}$)-Si(2)-**6b**,

(2S)-Si(1),($\overline{2S}$)-Si(2)-**6c**



(2S)-Si(1),(2S)-Si(2)-**9**

and **9** remain unclear and call for further investigation.* Note that the L_2SiO fragments of the dication in disiloxane ditriflate **3** have different configurations,[13] *i.e.*, this dication is similar to those in complexes **6b,c**. Their conformations in the crystals are similar. The maximum difference in the corresponding pseudotorsion C—Si...Si—C and O—Si...Si—O angles is 13°.

The corresponding bond lengths and bond angles in the dications of **6b,c** and **9** have similar values (Tables 3—8) and are virtually identical to the corresponding values in the structure of **3**. A comparison of the Si—O distances in the linear hypervalent fragments of these cations and of the anions with analogous valence environments about the silicon atoms[6—9] ($O—SiC_2X—O$, X = C or F) demonstrated that the distances in the cations are slightly larger (by ~0.05 Å) due, apparently, to the lower electron density in the hypervalent fragment.

The values of the Si—O—Si angle are approximately equal in all the dications (144—147°) and are close to the equilibrium value in siloxane unstrained structures.[19] When the Si atoms bear bulky substituents, the Si—O—Si bridges in the crystals are often linear.[20,21] However, in the structures of **3**, **6b,c**, and **9**, the intramolecular interaction between the bidentate ligands at different Si atoms is not so substantial, as evidenced by the ligand—ligand interatomic distances, which are close to the corresponding sums of the van der Waals radii of the atoms, as well as (indirectly) by the presence of a contact of only one pair of the ligands in each dication.

The geometric parameters of the counter-ions in the structures of **6b,c** have standard values. According to the Cambridge Structural Database,[22] the Hg—Cl bond lengths in the hexachlorodimercurate ion $Hg_2Cl_6^{2-}$ vary in the ranges of 2.30—2.43 Å (*exo*) and 2.47—3.12 Å (*endo*), which are close to the corresponding bond lengths for this ion in complex **6c** (2.37—2.39 and 2.61—2.64 Å, respectively). The Hg—Cl bond lengths in the tetrachloromercurate ion $HgCl_4^{2-}$ in the structure of **6b** (2.46—2.50 Å) also agree with the known values (2.40—2.56 Å).[22]

The hydroxonium trichloride ion, which was first found as a counter-ion in the structure of **9**, has a complex structure. The $O^+—H...Cl^-$ hydrogen bonds, which hold the Cl^- anions at the hydroxonium cation, are characterized by the following parameters (in the course of refinement of the structure, the O—H distances were fixed (0.96 Å)): O...Cl, 2.833—2.887(5) Å; O—H, 0.96 Å; H...Cl, 1.81—1.91 Å; and the O—H...Cl angle is 175—180°. The H...Cl distances are larger than the bond length in the HCl molecule by only 0.5—0.6 Å, *i.e.*, these hydrogen bonds are strong. The C—O—H...Cl^- hydrogen bond with the close parameters was found in the structure of disiloxane with the four-coordinate Si atom.[23]

Quantum-chemical calculations of the dications in compounds **3**, **6c**, and **9** and in their diastereomers (performed by the semiempirical PM3 method with the use of the known parameter set[24]) demonstrated that the structure of the coordination unit in the gaseous phase is close to that determined by X-ray diffraction study.

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* Among the known compounds with the $[L_2SiX]^-$ anions that contain the hypervalent $O—SiC_2X—O$ unit, the structure of $[(C_6H_4(CF_3)_2CO)_2SiC_6H_{11}]^-Et_4N^+$ was reported,[4] which belongs to the space group $P2_1$. However, the authors of Ref. 4 did not discuss the reasons for the existence of only one enantiomer of the anion in the crystals obtained (the absolute configuration was not determined).

Table 4. Bond angles (ω) in the structure of **6b**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Cl(1)—Hg(1)—Cl(2)	109.16(11)	C(14)—O(4)—Si(2)	113.0(5)	C(12)—C(11A)—C(10A)	113(2)
Cl(1)—Hg(1)—Cl(3)	109.50(10)	C(20)—O(5)—Si(2)	112.7(6)	C(11B)—C(10B)—C(9)	104(5)
Cl(1)—Hg(1)—Cl(4)	112.78(10)	C(2)—N(1)—C(1)	114.4(7)	C(10B)—C(11B)—C(12)	110(3)
Cl(2)—Hg(1)—Cl(3)	108.90(10)	C(2)—N(1)—C(6)	124.7(7)	C(11A)—C(12)—N(2)	112.5(14)
Cl(4)—Hg(1)—Cl(2)	111.18(10)	C(1)—N(1)—C(6)	120.7(7)	N(2)—C(12)—C(11B)	106(2)
Cl(4)—Hg(1)—Cl(3)	105.20(10)	C(8)—N(2)—C(7)	115.7(7)	N(3)—C(13)—Si(2)	106.9(6)
O(1)—Si(1)—O(3)	93.2(3)	C(8)—N(2)—C(12)	124.3(8)	O(4)—C(14)—N(3)	118.4(8)
O(1)—Si(1)—C(1)	115.6(4)	C(7)—N(2)—C(12)	119.8(8)	O(4)—C(14)—C(15)	119.6(8)
O(3)—Si(1)—C(1)	90.8(3)	C(14)—N(3)—C(18)	124.7(8)	N(3)—C(14)—C(15)	121.9(8)
O(1)—Si(1)—O(2)	94.6(3)	C(14)—N(3)—C(13)	114.5(7)	C(16A)—C(15)—C(14)	114.3(13)
O(3)—Si(1)—O(2)	172.2(3)	C(18)—N(3)—C(13)	120.2(7)	C(14)—C(15)—C(16B)	110(2)
C(1)—Si(1)—O(2)	85.5(3)	C(20)—N(4)—C(19)	115.3(8)	C(17A)—C(16A)—C(15)	116(3)
O(1)—Si(1)—C(7)	120.2(4)	C(20)—N(4)—C(24)	123.4(9)	C(16A)—C(17A)—C(18)	114(3)
O(3)—Si(1)—C(7)	85.9(4)	C(19)—N(4)—C(24)	121.1(8)	C(17B)—C(16B)—C(15)	108(3)
C(1)—Si(1)—C(7)	124.2(4)	N(1)—C(1)—Si(1)	108.1(5)	C(18)—C(17B)—C(16B)	112(5)
O(2)—Si(1)—C(7)	90.6(3)	O(2)—C(2)—N(1)	119.2(8)	C(17B)—C(18)—N(3)	118(3)
O(1)—Si(2)—O(5)	93.6(3)	O(2)—C(2)—C(3)	119.0(8)	N(3)—C(18)—C(17A)	108(2)
O(1)—Si(2)—O(4)	94.1(3)	N(1)—C(2)—C(3)	121.7(8)	N(4)—C(19)—Si(2)	107.3(6)
O(5)—Si(2)—O(4)	172.3(3)	C(2)—C(3)—C(4)	113.9(8)	N(4)—C(20)—O(5)	118.3(8)
O(1)—Si(2)—C(19)	116.2(4)	C(5)—C(4)—C(3)	112.7(9)	N(4)—C(20)—C(21)	123.9(9)
O(5)—Si(2)—C(19)	86.1(3)	C(6)—C(5)—C(4)	111.6(9)	O(5)—C(20)—C(21)	117.8(9)
O(4)—Si(2)—C(19)	91.2(3)	N(1)—C(6)—C(5)	112.4(8)	C(22)—C(21)—C(20)	112.4(9)
O(1)—Si(2)—C(13)	118.0(4)	N(2)—C(7)—Si(1)	107.0(6)	C(23)—C(22)—C(21)	112.0(10)
O(5)—Si(2)—C(13)	90.0(3)	O(3)—C(8)—N(2)	117.7(8)	C(22)—C(23)—C(24)	113.9(11)
O(4)—Si(2)—C(13)	85.7(3)	O(3)—C(8)—C(9)	118.7(8)	N(4)—C(24)—C(23)	109.8(10)
C(19)—Si(2)—C(13)	125.8(4)	N(2)—C(8)—C(9)	123.6(9)	N(5)—C(32)—C(31)	176(3)
Si(1)—O(1)—Si(2)	144.8(4)	C(8)—C(9)—C(10B)	116(2)	N(6A)—C(34A)—C(33A)	171(5)
C(2)—O(2)—Si(1)	112.3(5)	C(8)—C(9)—C(10A)	110.7(13)	N(6B)—C(34B)—C(33B)	159(10)
C(8)—O(3)—Si(1)	113.3(6)	C(11A)—C(10A)—C(9)	109(2)		

Table 5. Bond lengths (*d*) in the structure of **6c**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Hg(1)—Cl(1)	2.612(5)	Si(2)—O(4)	1.83(1)	N(3)—C(15)	1.48(2)	C(11)—C(12)	1.52(2)
Hg(1)—Cl(2)	2.392(4)	Si(2)—O(5)	1.86(1)	N(3)—C(16)	1.48(2)	C(12)—C(13)	1.53(2)
Hg(1)—Cl(3)	2.393(5)	Si(2)—C(15)	1.86(1)	N(3)—C(21)	1.31(2)	C(13)—C(14)	1.48(2)
Hg(1)—Cl(1a)	2.632(4)	Si(2)—C(22)	1.87(2)	N(4)—C(22)	1.45(2)	C(16)—C(17)	1.48(2)
Hg(2)—Cl(4)	2.608(6)	O(2)—C(7)	1.28(2)	N(4)—C(23)	1.48(2)	C(17)—C(18)	1.51(3)
Hg(2)—Cl(5)	2.370(9)	O(3)—C(14)	1.28(2)	N(4)—C(28)	1.32(2)	C(18)—C(19)	1.55(2)
Hg(2)—Cl(6)	2.376(5)	O(4)—C(21)	1.29(2)	C(2)—C(3)	1.52(3)	C(19)—C(20)	1.51(2)
Hg(2)—Cl(4a)	2.644(7)	O(5)—C(28)	1.28(2)	C(3)—C(4)	1.54(3)	C(20)—C(21)	1.47(2)
Si(1)—O(1)	1.63(1)	N(1)—C(1)	1.45(2)	C(4)—C(5)	1.53(3)	C(23)—C(24)	1.50(2)
Si(1)—O(2)	1.35(1)	N(1)—C(2)	1.51(2)	C(5)—C(6)	1.55(3)	C(24)—C(25)	1.52(2)
Si(1)—O(3)	1.86(1)	N(1)—C(7)	1.29(2)	C(6)—C(7)	1.51(2)	C(25)—C(26)	1.53(2)
Si(1)—C(1)	1.87(2)	N(2)—C(8)	1.46(2)	C(9)—C(10)	1.49(3)	C(26)—C(27)	1.58(2)
Si(1)—C(8)	1.90(1)	N(2)—C(9)	1.47(2)	C(10)—C(11)	1.56(3)	C(27)—C(28)	1.45(2)
Si(2)—O(1)	1.62(1)	N(2)—C(14)	1.29(2)				

Thus, full optimization (with the use of all independent parameters) of the real geometry of the dications in the crystals of compounds **3**, **6c**, and **9** resulted in a slight decrease in the axial bond lengths in the hypervalent fragments (from 1.863—1.924 to 1.812—1.815 Å for **3**, from 1.863—1.849 to 1.799—1.800 Å for **6c**, and from 1.882—1.832 to 1.804—1.797 Å for **9**), in a virtual retention of the siloxane bond length (from 1.604—1.640 to 1.638 Å, from 1.617—1.627 to 1.636 Å, and from 1.633 to 1.639—1.641 Å, respectively), and in a substantial increase in the Si—O—Si bond angle (from 145°, 147°, and 144° to 167°, 179°, and 163°, respectively) and in the O—Si—O bond angle in the hypervalent fragment (to 179°) as well as in a change in the orientation of the bonded bidentate ligands of two five-coordinate fragments with respect to each other to form a conformation, which resembles a four-blade propeller in the eclipsed projection along the two Si atoms (Fig. 4).

The cleavage of one O→Si coordination bond in the dications of compounds **3**, **6c**, and **9** causes an increase in

Table 6. Bond angles (ω) in the structure of **6c**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Cl(1)—Hg(1)—Cl(2)	102.3(2)	O(5)—Si(2)—C(15)	90.2(6)	O(2)—C(7)—C(6)	119(2)
Cl(1)—Hg(1)—Cl(3)	116.9(2)	O(1)—Si(2)—C(22)	116.7(6)	N(1)—C(7)—C(6)	123(1)
Cl(2)—Hg(1)—Cl(3)	125.3(2)	O(4)—Si(2)—C(22)	92.2(6)	Si(1)—C(8)—N(2)	107(1)
Cl(1)—Hg(1)—Cl(1a)	88.1(1)	O(5)—Si(2)—C(22)	85.1(6)	N(2)—C(9)—C(10)	115(1)
Cl(2)—Hg(1)—Cl(1a)	112.3(1)	C(15)—Si(2)—C(22)	122.4(7)	C(9)—C(10)—C(11)	113(1)
Cl(3)—Hg(1)—Cl(1a)	105.8(1)	Si(1)—O(1)—Si(2)	147.1(7)	C(10)—C(11)—C(12)	116(1)
Cl(4)—Hg(2)—Cl(5)	105.7(3)	Si(1)—O(2)—C(7)	114(1)	C(11)—C(12)—C(13)	115(1)
Cl(4)—Hg(2)—Cl(6)	109.5(2)	Si(1)—O(3)—C(14)	113(1)	C(12)—C(13)—C(14)	113(1)
Cl(5)—Hg(2)—Cl(6)	133.6(3)	Si(2)—O(4)—C(21)	114(1)	O(3)—C(14)—N(2)	119(1)
Cl(4)—Hg(2)—Cl(4a)	90.6(2)	Si(2)—O(5)—C(28)	114(1)	O(3)—C(14)—C(13)	112(1)
Cl(5)—Hg(2)—Cl(4a)	98.9(3)	C(1)—N(1)—C(2)	120(1)	N(2)—C(14)—C(13)	121(1)
Cl(6)—Hg(2)—Cl(4a)	109.8(2)	C(1)—N(1)—C(7)	115(1)	Si(2)—C(15)—N(3)	108(1)
Hg(1)—Cl(1)—Hg(1a)	91.9(1)	C(2)—N(1)—C(7)	125(1)	N(3)—C(16)—C(17)	114(1)
Hg(2)—Cl(4)—Hg(2a)	89.4(2)	C(8)—N(2)—C(9)	121(1)	C(16)—C(17)—C(18)	115(1)
O(1)—Si(1)—O(2)	93.5(5)	C(8)—N(2)—C(14)	115(1)	C(17)—C(18)—C(19)	113(1)
O(1)—Si(1)—O(3)	95.8(5)	C(9)—N(2)—C(14)	124(1)	C(18)—C(19)—C(20)	114(1)
O(2)—Si(1)—O(3)	170.4(5)	C(15)—N(3)—C(16)	123(1)	C(19)—C(20)—C(21)	114(1)
O(1)—Si(1)—C(1)	117.6(6)	C(15)—N(3)—C(21)	114(1)	O(4)—C(21)—N(3)	118(1)
O(2)—Si(1)—C(1)	85.2(6)	C(16)—N(3)—C(21)	124(1)	O(4)—C(21)—C(20)	120(1)
O(3)—Si(1)—C(1)	92.7(6)	C(22)—N(4)—C(23)	122(1)	N(3)—C(21)—C(20)	122(1)
O(1)—Si(1)—C(8)	116.2(6)	C(22)—N(4)—C(28)	116(1)	Si(2)—C(22)—N(4)	108(1)
O(2)—Si(1)—C(8)	88.5(6)	C(23)—N(4)—C(28)	122(1)	N(4)—C(23)—C(24)	112(1)
O(3)—Si(1)—C(8)	85.2(6)	Si(1)—C(1)—N(1)	108(1)	C(23)—C(24)—C(25)	115(1)
C(1)—Si(1)—C(8)	126.1(7)	N(1)—C(2)—C(3)	112(1)	C(24)—C(25)—C(26)	112(1)
O(1)—Si(2)—O(4)	92.2(5)	C(2)—C(3)—C(4)	115(2)	C(25)—C(26)—C(27)	112(1)
O(1)—Si(2)—O(5)	94.8(5)	C(3)—C(4)—C(5)	117(2)	C(26)—C(27)—C(28)	112(1)
O(4)—Si(2)—O(5)	173.0(5)	C(4)—C(5)—C(6)	114(2)	O(5)—C(28)—N(4)	116(1)
O(1)—Si(2)—C(15)	120.9(6)	C(5)—C(6)—C(7)	111(2)	O(5)—C(28)—C(27)	121(1)
O(4)—Si(2)—C(15)	85.8(6)	O(2)—C(7)—N(1)	119(1)	N(4)—C(28)—C(27)	123(1)

Table 7. Bond lengths (*d*) in the structure of **9**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Si(1)—O(2)	1.634(5)	Si(2)—C(13)	1.883(6)	N(1)—C(1)	1.478(9)	N(4)—C(13)	1.462(8)
Si(1)—O(4)	1.850(5)	Si(2)—C(9)	1.895(7)	N(2)—C(6)	1.314(9)	N(4)—C(16)	1.469(8)
Si(1)—O(3)	1.864(5)	O(3)—C(2)	1.301(8)	N(2)—C(8)	1.456(9)	C(2)—C(3)	1.47(1)
Si(1)—C(5)	1.870(7)	O(4)—C(6)	1.290(8)	N(2)—C(5)	1.469(8)	C(6)—C(7)	1.480(9)
Si(1)—C(1)	1.873(7)	O(5)—C(10)	1.296(9)	N(3)—C(10)	1.313(9)	C(10)—C(11)	1.48(1)
Si(2)—O(2)	1.634(5)	O(6)—C(14)	1.296(8)	N(3)—C(9)	1.460(8)	C(14)—C(15)	1.480(9)
Si(2)—O(6)	1.832(4)	N(1)—C(2)	1.310(9)	N(3)—C(12)	1.472(9)		
Si(2)—O(5)	1.883(5)	N(1)—C(4)	1.467(8)	N(4)—C(14)	1.304(9)		

Table 8. Bond angles (ω) in the structure of **9**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(2)—Si(1)—O(4)	92.6(2)	O(6)—Si(2)—C(13)	86.2(2)	C(6)—N(2)—C(8)	124.5(6)	O(4)—C(6)—N(2)	117.2(6)
O(2)—Si(1)—O(3)	93.2(2)	O(5)—Si(2)—C(13)	92.2(2)	C(6)—N(2)—C(5)	115.0(5)	O(4)—C(6)—C(7)	118.5(6)
O(4)—Si(1)—O(3)	174.1(2)	O(2)—Si(2)—C(9)	122.6(3)	C(8)—N(2)—C(5)	120.2(5)	N(2)—C(6)—C(7)	124.3(6)
O(2)—Si(1)—C(5)	117.8(3)	O(6)—Si(2)—C(9)	90.1(3)	C(10)—N(3)—C(9)	116.0(6)	N(3)—C(9)—Si(2)	108.0(4)
O(4)—Si(1)—C(5)	85.7(2)	O(5)—Si(2)—C(9)	84.6(3)	C(10)—N(3)—C(12)	125.3(6)	O(5)—C(10)—N(3)	116.9(6)
O(3)—Si(1)—C(5)	90.9(2)	C(13)—Si(2)—C(9)	121.4(3)	C(9)—N(3)—C(12)	118.6(6)	O(5)—C(10)—C(11)	119.0(7)
O(2)—Si(1)—C(1)	119.4(3)	Si(1)—O(2)—Si(2)	144.4(3)	C(14)—N(4)—C(13)	114.9(5)	N(3)—C(10)—C(11)	124.2(7)
O(4)—Si(1)—C(1)	91.8(3)	C(2)—O(3)—Si(1)	113.6(4)	C(14)—N(4)—C(16)	123.4(6)	N(4)—C(13)—Si(2)	106.7(4)
O(3)—Si(1)—C(1)	86.0(3)	C(6)—O(4)—Si(1)	114.4(4)	C(13)—N(4)—C(16)	120.2(5)	O(6)—C(14)—N(4)	117.7(6)
C(5)—Si(1)—C(1)	122.7(3)	C(10)—O(5)—Si(2)	114.5(4)	N(1)—C(1)—Si(1)	107.5(4)	O(6)—C(14)—C(15)	118.6(6)
O(2)—Si(2)—O(6)	93.1(2)	C(14)—O(6)—Si(2)	113.7(4)	O(3)—C(2)—N(1)	117.8(6)	N(4)—C(14)—C(15)	123.7(6)
O(2)—Si(2)—O(5)	94.1(2)	C(2)—N(1)—C(4)	122.8(6)	O(3)—C(2)—C(3)	118.7(6)		
O(6)—Si(2)—O(5)	172.6(2)	C(2)—N(1)—C(1)	114.9(5)	N(1)—C(2)—C(3)	123.5(6)		
O(2)—Si(2)—C(13)	116.0(3)	C(4)—N(1)—C(1)	121.5(6)	N(2)—C(5)—Si(1)	107.5(4)		

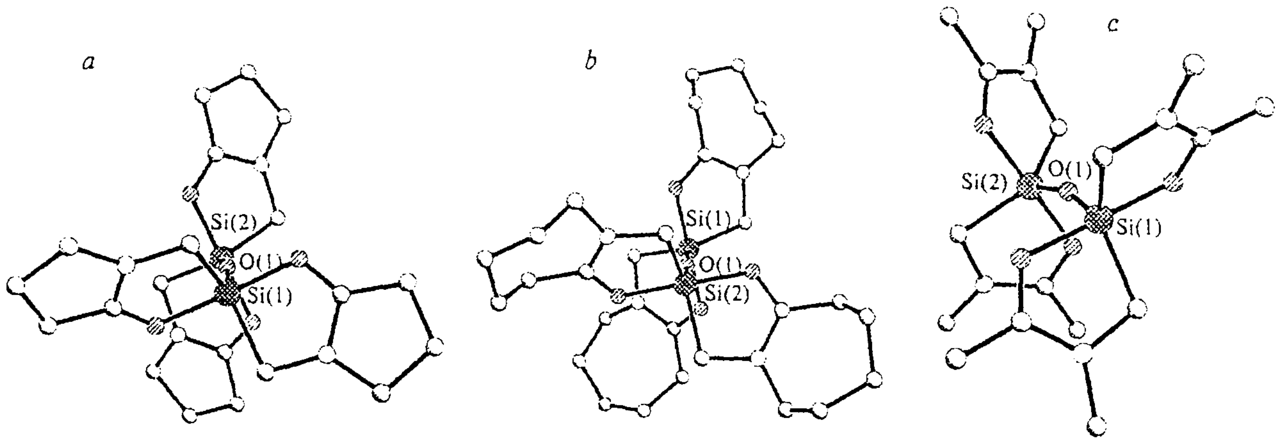

Fig. 4. Conformations of dications of complexes **3** (*a*), **6c** (*b*), and **9** (*c*) calculated by the PM3 method.

their energy by 11.6, 16.9, and 12.7 kcal mol^{-1}, respectively, which confirms the stabilizing role of the coordination bond in the formation of silicenium cations. The real barrier of transition between two optimized structures of the dications with four and three coordination bonds was not calculated. Note that in the optimized structures of the ions with three coordination bonds, the shortest distance between the noncoordinated O atom of the lactam fragment and the Si atom is ~3.5 Å.

For the cations that contain the L_2SiO fragments with different configurations, the calculated heats of formation of the two diastereomeric forms of the dications of compounds **3**, **6c**, and **9** are −52.9, −105.2, and −74.6 kcal mol^{-1}, respectively. For the cations that contain the L_2SiO fragments with identical configurations, the corresponding values are −52.2, −104.2, and −71.2 kcal mol^{-1}, respectively. In our opinion, the close values of the calculated heats of formation does not allow one to consider the diastereomer with identical configurations of the L_2SiO fragments as more favorable. The above-discussed data of NMR spectroscopy indicate that both diastereomers were formed as the final products of the reactions shown in Schemes 1 and 2. Apparently, the diastereomers were separated in the course of crystallization of samples prepared for X-ray diffraction analysis.

Experimental

The IR spectra of ~5% solutions of the compounds were recorded on a Specord IR-75 instrument in KBr cells. The ^1H, ^{13}C, and ^{29}Si spectra were obtained on a Varian XL-400 spectrometer (400.1, 100.6, and 79.5 MHz, respectively) with Me_4Si as the internal standard. The experiments with the use of ^2H NMR spectroscopy were carried out using the standard program packages available for the software of the Varian XL-400 spectrometer.

The initial *N*-trimethylsilyl lactams and *N*-trimethylsilyl-*N*-methylacetamide were synthesized according to procedures reported previously.[25]

Reaction of 1-trimethylsilyl-2-pyrrolidone (4a) with bis(chloromethyl)dichlorosilane and mercuric chloride. Bis(chloromethyl)dichlorosilane (0.96 g, 5 mmol) was added to compound **4a** (1.57 g, 10 mmol), and the reaction mixture was heated until Me_3SiCl (~1 mL) was removed. A mixture of MeCN (10 mL) and $HgCl_2$ (0.677 g, 2.5 mmol) was added to the residue, and the reaction mixture was refluxed for 0.5 h. The solvent (~1/2 of the volume) was removed. Heptane (30 mL) was added to the residue. The oil that formed was separated and crystallized by triturating with ether (5 mL). Rose crystals (1.92 g) were separated, dissolved in MeCN (15 mL) upon refluxing, and reprecipitated with ether. Recrystallization from DMF gave (O—Si)-tetrakischelate 1,1,3,3-tetrakis[(2-oxopyrrolidino)methyl]disiloxane hexachlorodimercurate (**6a**) in a yield of 0.73 g (54%); m.p. 250—253 °C. IR (MeCN), v/cm^{-1}: 1630 s, 1526 w. Found (%): C, 22.71; H, 3.64; N, 5.27. $C_{20}H_{32}Cl_6Hg_2N_4O_5Si_2$. Calculated (%): C, 22.27; H, 2.99; N, 5.19.

Reaction of 1-trimethylsilyl-2-piperidone (4b) with bis(chloromethyl)dichlorosilane and mercuric chloride. Bis(chloromethyl)dichlorosilane (0.96 g, 5 mmol) was added to silylamide **4b** (1.71 g, 10 mmol). After completion of the vigorous reaction and removal of Me_3SiCl, a mixture of MeCN (10 mL) and $HgCl_2$ (0.677 g, 2.5 mmol) was added to the residue, and the reaction mixture was heated to the boiling point. The crystalline precipitate that formed (1.7 g) was separated. Recrystallization from DMF gave (O—Si)-tetrakischelate 1,1,3,3-tetrakis[(2-oxopiperidino)methyl]disiloxane tetrachloromercurate (**6b**) in a yield of 1 g (71%); m.p. 301—303 °C. IR (MeCN), v/cm^{-1}: 1624 s, 1507 w. Found (%): C, 35.15; H, 4.90. $C_{24}H_{40}Cl_4HgN_4O_5Si_2 \cdot 2CH_3CN$. Calculated (%): C, 35.57; H, 4.80.

Reaction of 1-trimethylsilylperhydro-2-azepinone (4c) with bis(chloromethyl)dichlorosilane and mercuric chloride. Bis(chloromethyl)dichlorosilane (0.96 g, 5 mmol) was added to silylamide **4c** (1.85 g, 10 mmol). The reaction mixture was heated until Me_3SiCl (~1 mL) was removed, and MeCN (10 mL) and $HgCl_2$ (0.677 g, 2.5 mmol) were added to the residue. The reaction mixture was refluxed for 0.5 h. The solvent (~1/2 of the volume) was evaporated. Ether (30 mL) was added to the residue. The crystals that precipitated (2.5 g) were separated. Recrystallization from DMF gave (O—Si)-tetrakischelate 1,1,3,3-tetrakis[(2-oxohexahydroazepino)methyl]disiloxane hexachlorodimercurate (**6c**) in a yield of 0.8 g (54%); m.p. 256—258 °C. IR (MeCN), v/cm^{-1}: 1604 s, 1510 w.

Table 9. Atomic coordinates (×10^4) in the structure of **6b**

Atom	*x*	*y*	*z*
Hg(1)	24127(1)	22443(1)	1156(1)
Cl(1)	23455(3)	23581(2)	463(2)
Cl(2)	22883(3)	21300(2)	834(2)
Cl(3)	26137(2)	22129(2)	892(2)
Cl(4)	24208(2)	22692(2)	2437(1)
Si(1)	27360(2)	18627(1)	2558(1)
Si(2)	25661(2)	19821(1)	1844(1)
O(1)	26195(5)	19038(3)	2224(3)
O(2)	28207(5)	18830(3)	1774(3)
O(3)	26702(5)	18358(4)	3377(3)
O(4)	26987(5)	20416(3)	2033(3)
O(5)	24280(5)	19349(4)	1589(3)
N(1)	28099(6)	17530(4)	1673(4)
N(2)	28047(7)	19165(4)	3842(4)
N(3)	27063(6)	20325(4)	873(4)
N(4)	23640(6)	20207(5)	2354(4)
C(1)	27541(8)	17574(5)	2336(5)
C(2)	28433(7)	18202(5)	1440(4)
C(3)	29113(9)	18260(6)	809(5)
C(4)	29164(11)	17511(6)	400(6)
C(5)	29268(11)	16803(7)	860(6)
C(6)	28321(10)	16764(6)	1346(5)
C(7)	28418(8)	19210(5)	3136(5)
C(8)	27184(8)	18698(5)	3929(5)
C(9)	26731(10)	18537(7)	4617(5)
C(10A)	27175(23)	19160(18)	5169(14)
C(11A)	28473(24)	19307(16)	5082(12)
C(10B)	27562(43)	18640(27)	5237(20)
C(11B)	27898(56)	19425(36)	5206(25)
C(12)	28690(9)	19597(6)	4419(5)
C(13)	25915(7)	19980(5)	896(4)
C(14)	27530(8)	20551(5)	1487(5)
C(15)	28681(8)	20939(6)	1560(6)
C(16A)	29095(19)	21195(13)	918(13)
C(17A)	28885(30)	20703(29)	360(22)
C(16B)	29371(33)	20795(25)	860(21)
C(17B)	28516(46)	20953(50)	199(29)
C(18)	27535(9)	20484(6)	205(5)
C(19)	24821(7)	20484(5)	2403(5)
C(20)	23423(8)	19648(6)	1915(5)
C(21)	22253(8)	19292(6)	1769(5)
C(22)	21332(10)	19768(7)	2060(8)
C(23)	21673(10)	20076(9)	2728(8)
C(24)	22762(9)	20595(8)	2738(6)
N(5)	20582(20)	24496(15)	1114(12)
C(31)	21126(15)	23098(14)	1675(9)
C(32)	20872(19)	23833(22)	1365(13)
N(6A)	19981(35)	21535(24)	3299(22)
C(33A)	19869(30)	22658(12)	4154(10)
C(34A)	19909(30)	21966(21)	3688(16)
N(6B)	22556(60)	22631(30)	4078(27)
C(33B)	20195(109)	22454(71)	3749(79)
C(34B)	21369(101)	22608(34)	4037(39)

Table 10. Atomic coordinates (×10^4) in the structure of **6c**

Atom	*x*	*y*	*z*
Hg(1)	9670(1)	9551(1)	1051(1)
Hg(2)	5329(1)	4631(1)	3943(1)
Cl(1)	10759(2)	9241(3)	217(3)
Cl(2)	8937(2)	8297(3)	702(3)
Cl(3)	9970(3)	10247(3)	2570(3)
Cl(4)	5788(3)	5760(3)	5270(5)
Cl(5)	4677(6)	5402(7)	2604(6)
Cl(6)	6177(3)	3484(3)	4128(3)
Si(1)	7960(2)	8972(2)	3487(3)
Si(2)	6771(2)	7598(3)	3553(3)
O(1)	7300(5)	8421(6)	3772(7)
O(2)	7590(5)	9995(6)	3805(7)
O(3)	8477(5)	8041(6)	3169(7)
O(4)	6461(5)	7721(6)	4674(6)
O(5)	7005(5)	7362(6)	2381(6)
N(1)	7438(7)	10231(7)	2260(10)
N(2)	9327(6)	8478(7)	4413(8)
N(3)	5353(6)	7812(8)	3698(8)
N(4)	7551(7)	6258(7)	3178(8)
C(1)	7798(8)	9414(11)	2251(11)
C(2)	7223(10)	10734(14)	1348(15)
C(3)	7691(11)	11529(12)	1377(14)
C(4)	7504(12)	12255(11)	2000(18)
C(5)	7569(12)	12068(11)	3066(16)
C(6)	7061(11)	11342(11)	3262(16)
C(7)	7378(8	10487(9)	3093(13)
C(8)	8806(8)	9157(10)	4477(11)
C(9)	10048(9)	8435(11)	5074(13)
C(10)	10684(9)	8677(11)	4652(14)
C(11)	10908(9)	7968(10)	4008(13)
C(12)	10301(9)	646(10)	3198(12)
C(13)	9622(8)	7293(10)	3506(12)
C(14)	9123(8)	7967(9)	3704(11)
C(15)	5782(7)	7705(11)	2953(11)
C(16)	4536(8)	7861(10)	3476(11)
C(17)	4245(10)	8682(11)	3730(13)
C(18)	4257(9)	8799(11)	4779(12)
C(19)	5043(10)	8780(12)	5417(12)
C(20)	5432(9)	7937(10)	5404(10)
C(21)	5757(8)	7808(9)	4569(10)
C(22)	7204(8)	6549(9)	3929(11)
C(23)	8015(9)	5482(9)	3286(12)
C(24)	7657(9)	4773(10)	2652(11)
C(25)	7716(8)	4835(10)	1614(11)
C(26)	7315(9)	5609(10)	1112(11)
C(27)	7674(8)	6468(9)	541(10)
C(28)	7424(7)	6719(9)	2387(10)

Reaction of *N*-methyl-*N*-trimethylsilylacetamide (8) with bis(chloromethyl)dichlorosilane. Silylamide 8 (3.64 g, 25 mmol) was placed in a 50-mL flask, and bis(chloromethyl)dichlorosilane (2.45 g, 12.5 mmol) was added dropwise. After completion of the vigorous reaction, toluene (15 mL) was added, and the mixture was brought to boiling during 20 min. The oil that formed was recrystallized from a 1 : 1 toluene—acetonitrile mixture. (O—Si)-Tetrakischelate 1,1,3,3-tetrakis[(*N*-

Table 11. Atomic coordinates (×10^4) in the structure of **9**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cl(1)	−4299(2)	−6017(2)	6564(1)	C(1)	2353(6)	3881(7)	6900(3)
Cl(2)	−2457(2)	−2148(2)	5950(1)	C(2)	3384(6)	1881(7)	6816(3)
Cl(3)	−6597(2)	−2472(2)	6207(1)	C(3)	4269(7)	805(8)	6975(3)
O(1)	−4612(5)	−3829(5)	5804(2)	C(4)	3878(8)	2962(9)	7727(3)
Si(1)	1735(2)	3358(2)	6164(1)	C(5)	2518(6)	3802(6)	5543(3)
Si(2)	−249(2)	1193(2)	6261(1)	C(6)	1101(6)	5529(7)	5586(3)
O(2)	461(4)	2476(5)	6052(2)	C(7)	452(7)	6784(7)	5441(3)
O(3)	2770(4)	1903(5)	6309(2)	C(8)	2362(8)	5610(8)	4813(3)
O(4)	856(4)	4904(5)	6025(2)	C(9)	593(7)	−406(7)	6451(3)
O(5)	175(4)	1584(5)	7032(2)	C(10)	785(6)	667(8)	7326(3)
O(6)	−719(4)	603(5)	5541(2)	C(11)	1125(8)	854(9)	7939(3)
N(1)	3180(5)	2828(6)	7159(2)	C(12)	1708(8)	−1544(8)	7311(3)
N(2)	1930(5)	5008(5)	5301(2)	C(13)	−1974(6)	1384(7)	6296(3)
N(3)	1062(5)	−380(6)	7052(2)	C(14)	−1922(6)	568(7)	5391(3)
N(3)	1062(5)	−380(6)	7052(2)	C(15)	−2417(7)	17(7)	4833(3)
N(4)	−2628(5)	1059(6)	5737(2)	C(16)	−4004(6)	1023(9)	5635(4)

methylacetamido)methyl]disiloxane hydroxonium trichloride (**9**) was obtained in a yield of 2.5 g (74%), m.p. 170—171 °C (toluene). IR ($CHCl_3$), ν/cm^{-1}: 1590 s, 1510 w. Found (%): C, 34.97; H, 6.12; Si, 10.71. $C_{16}H_{35}Cl_3N_4O_6Si_2$. Calculated (%): C, 35.46; H, 6.51; Si, 10.36.

The sample of compound **9** suitable for X-ray diffraction study was prepared by threefold recrystallization from a 5 : 1 toluene—acetonitrile mixture followed by slow cooling of the solution.

X-ray diffraction analysis of compounds 6b,c and 9. Crystals of **6b** ($C_{24}H_{40}N_4O_5Si_2 \cdot HgCl_4 \cdot 2CH_3CN$) are monoclinic, a = 11.697(6) Å, b = 17.093(8) Å, c = 19.136(6) Å, β = 93.84(3)°, V = 3818(3) Å^3, d_{calc} = 1.645 g cm^{-3}, Z = 4, space group $P2_1/n$. There are two acetonitrile molecules of solvation per asymmetric unit. One of these molecules is disordered over two sites.

Crystals of **6c** ($C_{28}H_{48}N_4O_5Si_2 \cdot Hg_2Cl_6$) are monoclinic, a = 18.598(2) Å, b = 15.759(3) Å, c = 14.338(4) Å, β = 102.61(2)°, V = 4101(3) Å^3, d_{calc} = 1.929 g cm^{-3}, Z = 4, space group $P2_1/c$, $Hg_2Cl_6^{2-}$ counter-ions occupy two different inversion centers, and the dication is located in a general position.

Crystals of **9** ($C_{16}H_{32}N_4O_5Si_2 \cdot OH_3 \cdot Cl_3$) are monoclinic, a = 10.779(5) Å, b = 10.234(3) Å, c = 23.982(5) Å, β = 98.14(3)°, V = 2619(2) Å^3, d_{calc} = 1.375 g cm^{-3}, Z = 4, space group $P2_1/c$.

X-ray diffraction data sets were collected on Sintex P3/PC (**6b**) and Siemens P3/PC (**6c** and **9**) diffractometers (Mo-Kα radiation; graphite monochromator; θ/2θ scanning technique; $2\theta_{max}$ = 46° (**6b**), 48° (**6c**), and 50° (**9**); 5295 (**6b**), 5876 (**6c**), and 4910 (**9**) measured reflections). The structures were solved by direct methods and were refined based on F_i (**6c**) and F_i^2 (**6b**, **9**) by the least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The H atoms were placed in calculated positions and refined using the riding model with fixed C—H and O—H distances and thermal parameters half as large as the corresponding isotropic parameters of the C and O atoms to which the H atoms are bonded. The final values of the R factors were as follows: for **6b**, R_1 = 0.052, wR_2 = 0.121 using 3772 with $I > 3\sigma(I)$; for **6c**, R_1 = 0.049, R_w = 0.051 using 2876 reflections with $I > 3\sigma(I)$; for **9**, R_1 = 0.090, wR_2 = 0.264 using 3591 reflections with $I > 2\sigma(I)$.

All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package.[26] The atomic coordinates of compounds **6b,c** and **9** are given in Tables 9—11, respectively.

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