Synthesis and molecular and crystal structures of mono- and bis-chelate hypercoordinate silicon compounds containing the C,O-chelating 2,2-dimethyl-4-oxo-2,3-dihydro-1,3-oxazin-3-ylmethyl ligand

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New mono- and bis-chelate hypercoordinate silicon complexes containing the monoanionic C,O-chelating 2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl ($BonCH_2$) ligand were synthesized starting from 2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-4-one (**1**) through its TMS derivative **2**. The reactions of compound **2** with the chlorosilylmethylating agents $ClCH_2SiMe_2Cl$, $ClCH_2SiMeCl_2$, and $(ClCH_2)_2SiCl_2$ followed by the transformations of the initially formed chlorosilanes $BonCH_2SiMe_2Cl$ (**3**), $BonCH_2SiMeCl_2$ (**6**), and $[(BonCH_2)_2Si(Cl)]^+Cl^-$ (**8**), respectively, into the target products afforded neutral mono-chelates, *viz.*, monofluoride $BonCH_2SiMe_2F$ (**5**) and difluoride $BonCH_2SiMeF_2$ (**7**), and the bis-chelate disiloxane cation-anion complexes $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot Cl^- \cdot ClHCl^-$ (**9**) and $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot 2TfO^-$ (**10**). The reaction of ditriflate **10** with boron trifluoride etherate produced fluoride triflate $(BonCH_2)_2Si(F)OTf$ (**11**). The X-ray diffraction study of compounds **5**, **7**, **9**, **10**, and **11**, as well as of NH-heterocycle **1** and disiloxane $(BonCH_2SiMe_2)_2O$ (**4**) studied earlier, demonstrated that the Si atoms in complexes **5**, **7**, **9**, and **10** are pentacoordinate through the formation of an intramolecular O→Si bond. The coordination of silicon in fluoride triflate **11** can be described as 5+1. In disiloxane **4**, one of two Si atoms is pentacoordinate. Dinuclear cation-anion complexes **9** and **10** contain the diastereomeric bis-silylium ions $\{[(BonCH_2)_2Si]_2O\}^{2+}$, which differ in the configuration of the chiral bis-chelate fragments $(BonCH_2)_2Si$. In complex **9**, these fragments have opposite configurations (ΛΔ); in ditriflate **10**, the same configurations (ΛΛ).

Key words: hypervalence, pentacoordinate silicon compounds, silylium ions, synthesis, X-ray diffraction study.

Intramolecular complexes with monoanionic amidomethyl or related C,O-chelating ligands (LCH_2) belong to hypercoordinate silicon derivatives,[1] which have been studied in most detail in recent years.[1b,d] Methods for the synthesis have been extensively developed,[1b,d,2a—e,3a,b] the reactivity,[4a—d] structures,[1b,d,5a,b—f] and stereodynamic behavior have been studied,[6] and biological activities of compounds prepared with the use of these derivatives as the starting reagents or intermediate products have been investigated.[7] In addition, these derivatives are used as models for studying hypervalence[1b,5f] and simulating the nucleophilic substitution at the silicon atom.[1b,d,5b—e,8a—c]

The influence of different factors, in particular, the nature and number of electronegative monodentate ligands and the reaction conditions, on the structure of the central coordination unit and the degree of the intramolecular (intraionic) O→Si coordination interaction in such mono- and bis-C,O-chelate compounds has been studied in sufficient detail.[1b,d,2e,5f] The effect of the nature of the bidentate ligand on these characteristics is much less known. Nevertheless, stability of the intramolecular O→Si coordination bond in derivatives of six- and seven-membered lactams, their acyclic analogs,[4b] and 2-quinolinone[5d] was found to be higher than that of five-membered lactam derivatives. It was also found that the intramolecular O→Si coordination bond is dramatically weakened in a 4-oxazolidinone derivative, *i.e.*, upon the introduction of an acceptor ether oxygen atom into the five-membered lactam ring.[4b,5b]

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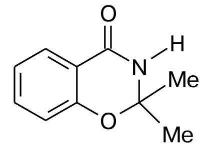
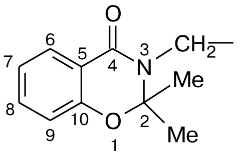
In the present study, we synthesized new mono- and bis-chelate hypercoordinate silicon complexes with the rather bulky C,O-chelating 2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl (BonCH_2) ligand starting from 2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-4-one (**1**) and established the structures of the new compounds by X-ray diffraction. Besides, taking into account the presence of the annelated benzene ring in this ligand, we expected that easily crystallizable and high-melting point derivatives would be prepared, which may be of considerable importance in the case of compounds with a weak intramolecular O→Si coordination bond.



BonH (**1**)



BonCH_2

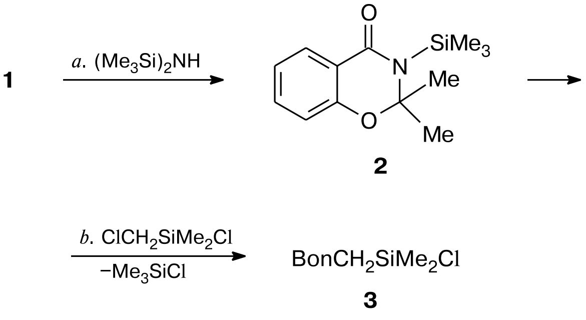
In addition, the structures of the previously characterized compounds, *viz.*, disiloxane containing BonCH_2 ligands at the Si atom[4b] and heterocyclic compound **1**,[9] which was used as the starting compound in the synthesis of new complexes with the BonCH_2 ligand, were determined by X-ray diffraction.

Results and Discussion

Synthesis and structures of mono- and bis-C,O-chelate silicon complexes

We used NH-heterocyclic compound **1** as the starting reagent. This compound can easily be prepared by condensation of salicylamide with acetone in the presence of trimethylchlorosilane.[9] Earlier,[4b] we have synthesized the first representative of neutral monochelate pentacoordinate silicon complexes with the BonCH_2 ligand, *viz.*, chloride BonCH_2SiMe_2Cl (**3**),[4b] starting from heterocyclic compound **1** through the formation of its TMS derivative **2** followed by the reaction of the latter with $ClCH_2SiMe_2Cl$ (Scheme 1, reactions *a* and *b*; the multistep scheme of these reactions was described in the literature[1b]). The pentacoordinate state of the Si atom has been established by X-ray diffraction.[4b,5b]

Scheme 1



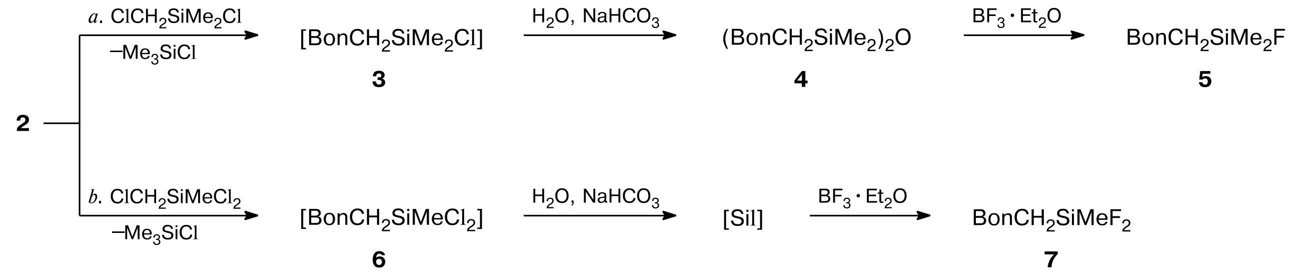
Disiloxane $(BonCH_2SiMe_2)_2O$ (**4**) was synthesized by hydrolysis of chloride **3** in the presence of a base ($NaHCO_3$); however, this compound was not characterized in detail.[4b]

Monochelate complexes. In the present study, we prepared fluoride $BonCH_2SiMe_2F$ (**5**) by the one-pot synthesis from TMS derivative **2** and dimethylchloromethylchlorosilane followed by hydrolysis of intermediate chloride **3** in the presence of $NaHCO_3$ giving rise to disiloxane **4** and the treatment of the latter with $BF_3 \cdot Et_2O$ (Scheme 2, path *a*). The yield of fluoride **5** was 65%.

Analogously, difuloride **7** was prepared in 35% yield by the one-pot synthesis with the use of methylchloromethyldichlorosilane as the dichlorosilylmethylating agent through intermediate dichloride **6** and a mixture of oligosiloxanes without their isolation (Scheme 2, path *b*).

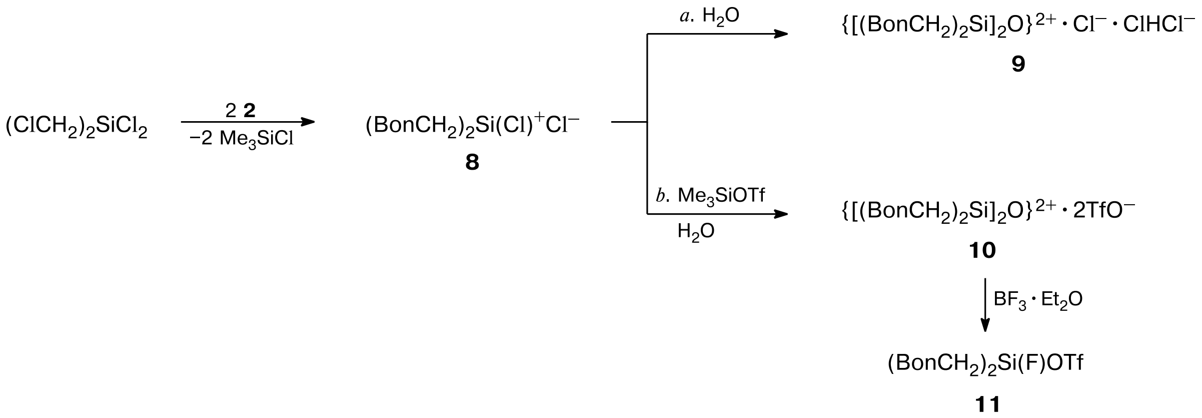
Bis-chelate complexes. We developed an approach to the synthesis of bis-chelate silicon complexes with the BonCH_2 ligand based on the reaction of bis(chloromethyl)dichlorosilane with TMS derivative **2** in a ratio of 1 : 2. Earlier,[3] the analogous reaction with *N*-TMS-lactams and *N*-TMS-*N*-methylacetamide under conditions, which do not prevent exposure to atmospheric moisture, has been demonstrated to give, through the

Scheme 2



Sil are oligosiloxanes.

Scheme 3



formation of unstable and easily hydrolyzable dichlorosilanes $[(LCH_2)_2Si(Cl)]^+Cl^-$,[3c] the cation-anion dinuclear bis-chelate complexes $[(LCH_2)_2SiOSi(CH_2L)_2]^{2+} \cdot 2X^-$, where LCH_2 is a lactamomethyl *n*-membered (L^nCH_2, $n = 5$ (**a**), 6 (**b**), or 7 (**c**)) or the *N*-methylacetamidomethyl (**d**) bidentate monoanionic C,O-chelating ligand, and X^- is an anion of low nucleophilicity ($X^- = OTf^-$, $HgCl_3^-$, $0.5HgCl_4^{2-}$ (in the presence of Me_3SiOTf or $HgCl_2$), or $2X^- = (H_3O^+) \cdot 3Cl^-$ (in the absence of additives)).[3a,b] The X-ray diffraction study demonstrated that the disiloxane dications $[(LCH_2)_2SiOSi(CH_2L)_2]^{2+}$ involved in the complexes contain the pentacoordinate bis-C,O-chelate silylium ions stabilized by an intraionic O→Si coordination interaction.[3a,b]

Bis-chelate dichloride $[(BonCH_2)_2Si(Cl)]^+Cl^-$ (**8**) is also hydrolytically unstable (nevertheless, we obtained satisfactory elemental analysis data for this compound). A single crystal grown for the X-ray diffraction study was found to be a dinuclear disiloxane cation-anion complex, *viz.*, chloride hydrogen dichloride $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot Cl^- \cdot ClHCl^-$ (**9**) (Scheme 3, path *a*).

Another procedure for the synthesis of bis-chelate silicon complexes with the $BonCH_2$ ligand, which is based on the reaction of dichloride **8** with trimethylsilyl triflate followed by the addition of water to the reaction mixture, afforded the disiloxane cation-anion complex $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot 2TfO^-$ (**10**) (Scheme 3, path *b*). Earlier,[3a] we have applied this procedure only to 1-TMS-2-pyrrolidone; the resulting ditriflate $\{[(L^5CH_2)_2Si]_2O\}^{2+} \cdot 2TfO^-$ (**10a**) was the first representative of cation-anion complexes containing silylium ions stabilized by O→Si coordination, which was characterized by X-ray diffraction.

It appeared that the disiloxane group Si—O—Si in dicationic complex **10** is cleaved by boron trifluoride etherate to give fluoride triflate **11** in high yield (92%). The latter compound is the first representative of bis-C,O-chelate silicon complexes with different monodentate ligands, in which coordination of the Si atom can be described as 5+1.

The structures of mono- and bis-chelates **5** and **7**—**11** were determined by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction (except for dichloride **8**). Some compounds were characterized by conductivity measurements and cryoscopy.

The determination of the molecular weights of fluorides **5** and **7** by the cryoscopic method demonstrated that, under the above-mentioned conditions (benzene, 0.6—1.2 mmol L^{-1}, $T = 275$ K), these compounds are monomers (poorly associated). This is the difference between these compounds and dichloride $MeC(O)N(CH_2SiMe_2Cl)_2$, which exists as a monomer in dilute solution but is associated to a large degree at higher concentrations (0.1 mol L^{-1}).[5a]

The conductivity of monochelate chloride **3**, bis-chelate dinuclear ditriflate **10**, and mononuclear fluoride triflate **11** in CH_2Cl_2 was determined. A comparison of the molar conductivities of these compounds and a series of their Si- and Ge-containing analogs[3a,10a] (Table 1) shows that chlorides **3** and $L^5CH_2SiMe_2Cl$ (**3a**), like other mono-C,O-chelate chlorides and fluorides studied earlier,[2c,3a] are covalently bonded halides, whose conductivity is similar to that of tetracoordinate chloro- and fluorosilanes (and of the solvent). To the contrary, the substantially higher conductivity of bis-chelate complexes **10** and **11** comparable to that of ditriflate **10a**[3a] and the Ge analogs $[(L^6CH_2)_2Ge(Cl)]^+TfO^-$ (**12b**), $[(L^7CH_2)_2Ge(Cl)]^+TfO^-$ (**12c**), and $[(L^7CH_2)_2Ge(F)]^+BF_4^-$ (**13c**)[10a] is indicative of the formation of free ions (or ion pairs) in solution.

IR spectroscopy. The IR spectra of 2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-4-one derivatives contain not only NCO coupled stretching absorption bands but also additional absorption bands of the aromatic system conjugated with the amide fragment and the O atom of the heterocycle annelated to the benzene ring in the

Table 1. Molar conductivity of mono- and bis-C,O-chelate silicon and germanium complexes in CH_2Cl_2 at 25 °C

Compound	C /mmol L^{-1}	Λ /mS cm^2 mol^{-1}
3	65	6
3a	188	39
	18	166
	1.8	460
10	4.86	10910
	0.486	25700
	0.0486	72000
10a	9	4050
	0.9	10550
	0.15	21000
11	2.5	14600
	0.25	30000
12b	5.7	1554
12c	10	1592
13c	1.36	4040
	0.136	12500

1700—1400 cm^{-1} region. The spectrum of the staring NH-heterocycle **1** recorded in acetonitrile shows an intense absorption band of the carbonyl group at 1687 cm^{-1} along with two medium and weak absorption bands at 1620 and 1580 cm^{-1}, respectively, which were assigned to vibrations of the aromatic system with conjugated fragments.

The pentacoordinate state of the Si atoms in monochelates **5** and **7** and bis-chelate complexes **10** and **11** is evidenced by low-frequency shifts of the absorption bands of the carbonyl group in the above-mentioned region and the appearance of additional absorption bands of the amide fragment. In particular, two intense absorption bands at 1630 and 1620 cm^{-1} and medium bands at 1487 cm^{-1}, which were assigned to coupled stretching vibrations ν(C=O) and ν(C=N) characterizing the fragment of the chelate ligand, are observed in the 1700—1400 cm^{-1} region of the spectra of fluorides **5** and **7** in solutions. This is evidence of the presence of the intramolecular O→Si coordination bond in these compounds, like in other neutral C,O-chelate pentacoordinate fluoro- and chlorosilanes[**2b,c**] (*cf.*, for example, the positions of these absorption bands (1608 and 1520 cm^{-1}, CH_2Cl_2) in monofluoride $L^7CH_2SiMe_2F$ (**5c**)[**2c**]). The positions of the absorption bands of the NCO fragment in compounds **5** and **7** are different from that in compound **5c**. This is most likely associated with the fact that molecules **5** and **7** contain the aromatic moiety conjugated with the O atom and the NCO fragment, which causes low-frequency shifts of vibrations of the aromatic ring to 1580 and 1504 cm^{-1} (**5**) and 1580 and 1520 cm^{-1} (**7**).

The above-mentioned region of the IR spectra of cation-anion complexes **10** and **11** in solution, like those of disiloxane ditriflate **10a**[**3a**] and other disiloxane cation-anion complexes,[**3b**] also contain two absorption bands at 1630—1624 (s) and 1471—1478 (m) cm^{-1} belonging to the corresponding vibrations of the chelate ring. Strongly coupled vibrations of the aromatic fragments are observed at 1610 (s), 1565 (w), 1524 (m) cm^{-1} and 1610 (s), 1560 (m), 1520 (m) cm^{-1} for compounds **10** and **11**, respectively.

Such absorption bands belonging to strongly coupled vibrations of the chelate and aromatic rings are observed also in the spectrum of dichloride **8**. However, we do not discuss these bands in detail because of the possible partial transformation of the latter compound into dinuclear complex **9** under the conditions of the spectral measurement.

NMR spectroscopy. The ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of compounds **5** and **7—11** are consistent with the proposed structures. In the ^{19}F NMR spectra of monochelates **5** and **7**, the downfield shift of the signal (δ_F −120.7 and −123.7, respectively) relative to the signal of the tetrahedral fragment Me_3SiF (δ_F −158)[**11a**] and, correspondingly, the upfield shift of the signal in the ^{29}Si NMR spectra (δ_{Si} −12.9 and −51.3) compared to the signal of the tetrahedral fragment Me_3SiF (28.1)[**11b**] (see the Experimental section) are indicative of the presence of an intramolecular O→Si interaction in the liquid phase. In difluoride **7**, this interaction is, as expected, stronger. For comparison, the signals for the F atoms in the spectrum of (O→Si)-chelate *N*,*N*-bis(dimethylfluorosilylmethyl)acetamide $MeC(O)N(CH_2SiMe_2F)_2$ are observed at δ −116.7 (Si^V) and −159.8 (Si^{IV});[**11a**] the signals for silicon, at δ −23.5 (Si^V) and 29.0 (Si^{IV}).[**11c**]

At room temperature, the ^{19}F NMR spectrum of difluoride **7** shows only one signal for the F atoms (δ_F −123.7). This is an evidence of an exchange involving the axial and equatorial F atoms, which is rather fast on the NMR time scale.

The ^1H, ^{13}C, and ^{29}Si NMR spectra of bis-chelate mononuclear complexes **8** and **11** show one set of signals, whereas dinuclear complex **10** is characterized by two sets of signals. The signals for the Si atoms are observed at δ −(56.5—58.3) and −(64.5—65.0) for the mononuclear and dinuclear complexes, respectively, which is indicative of the pentacoordinate state of silicon in these compounds. Analogous upfield positions of the signals (δ_{Si} = −(41—70)) were observed[**3b**] in the spectra of the dinuclear bis-chelates $[(LCH_2)_2SiOSi(CH_2L)_2)]^{2+} \cdot 2X^-$, where LCH_2 is the lactamomethyl *n*-membered or *N*-methylacetamidomethyl C,O-chelating ligand, X^- = OTf^-, $HgCl_3^-$, or $0.5HgCl_4^{2-}$, and $2X^-$ = $H_3O^+ \cdot 3Cl^-$, described earlier.

The signal for the F atom at the Si atom in the spectrum of fluoride triflate **11** is observed at δ −78.3, which corresponds to the pentacoordinate state of silicon in this compound (see above).

The presence of two sets of signals of approximately equal intensities in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of ditriflate **10** (see the Experimental section) indicates that there are two diastereomeric disilylium dications $\{[(\mathrm{BonCH_2})_2\mathrm{Si}]_2\mathrm{O}\}^{2+}$, which differ in the configuration of the chiral bis-chelate fragments $(\mathrm{BonCH_2})_2\mathrm{Si}$ ($\Lambda\Delta$ and $\Lambda\Lambda$), in solution. Earlier,[3b] we have observed two sets of the corresponding signals for the diastereomeric dications $[(\mathrm{LCH_2})_2\mathrm{SiOSi}(\mathrm{CH_2L})_2)]^{2+}$.

X-ray diffraction study

In the structures of **4**, **5**, **7**, and **9—11**, the Si atoms are pentacoordinate (in molecule **4**, only one of two Si atoms). The benzoxazinone ligands ($\mathrm{BonCH_2}$) are bidentate and form C,O-chelate rings at the Si atoms. The six-membered oxazinone ring adopts a slightly distorted sofa conformation determined by the presence of four sp^2-hybridized atoms, due to which it is rather rigid and is observed in all the structures under consideration. In the pure form, the benzoxazinone bicyclic fragment is present in molecule **1** (Fig. 1).

The planarity of the O(1)C(4)C(9)C(10)N(1) fragment (within 0.08 Å) suggests a noticeable delocalization of π electrons (including the O(2) atom). Therefore, the influence of this fragment in chelates **4** and **5** on the parameters of the linear O(2)—Si—X hypervalent bond (X = O or F) would be expected to be substantially different from the influence of the acyclic amide group containing neutral substituents (for example, the saturated hydrocarbon fragments).

In the crystal structure, molecules **1** form centrosymmetric dimers (Fig. 2) linked by medium-strength hydrogen bonds (O(2)...H(1AA)—N(1A), 174°; O(2)...N(1A), 2.87 Å; the sum of the van der Waals radii of the O and N atoms is 3.07 Å).[12]

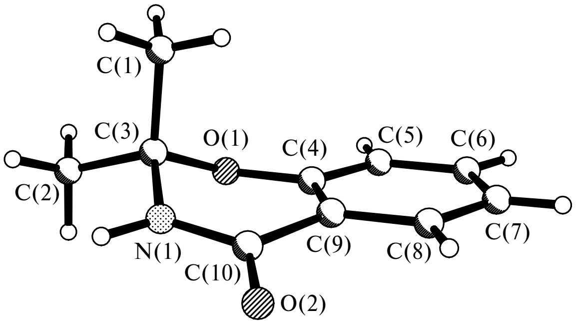


Fig. 1. Molecular structure of **1** in the crystal.

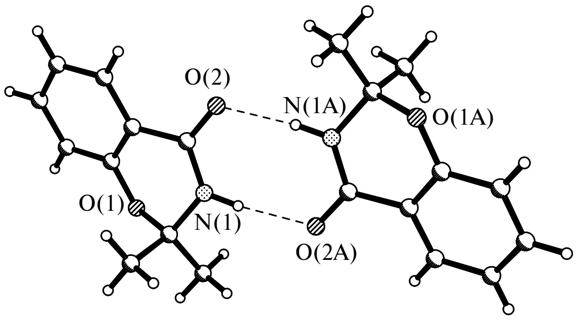


Fig. 2. Intermolecular hydrogen bonds in the crystal of **1**.

The main structural feature of **4**, **5**, **7**, and **9—11** is the presence of the O→Si(CYZ)—X hypervalent units (X = F or O; Y and Z = C, O, or F), in which the Si atom is pentacoordinate. The O→Si distance (O atom corresponds to the O(2) atom in molecule **1**), which determines the degree of an additional interaction of the Si atom, strongly depends on the nature of the second electronegative X atom in the linear O—Si—X fragment (Tables 2 and 3). In molecule **4** (Fig. 3), like in disiloxane $[\mathrm{MeC(O)N(CHMePh)CH_2SiMe_2}]_2\mathrm{O}$ (**4e**) studied earlier[4c] (Table 4), the donor-acceptor O→Si bond is very weak. The presence of intermolecular interactions is suf-

Table 2. Bond lengths in the structures of **1**, **4**, **5**, **7**, and **9—11**

Bond	*d*/Å
Compound **1**	
O(1)—C(4)	1.367(4)
O(1)—C(3)	1.446(3)
O(2)—C(10)	1.242(3)
N(1)—C(10)	1.330(4)
N(1)—C(3)	1.456(4)
C(4)—C(9)	1.386(4)
C(9)—C(10)	1.469(4)
Compound **4**	
Si(1)—O(1)	1.637(7)
Si(1)—C(1)	1.848(8)
Si(1)—C(2)	1.855(8)
Si(1)—C(3)	1.891(8)
Si(1)...O(2)	2.565(6)
Si(2)—O(1)	1.619(7)
Si(2)—C(14)	1.842(8)
Si(2)—C(15)	1.845(8)
Si(2)—C(16)	1.901(8)
Si(2)...O(4)	3.676(6)
Compound **5**	
Si(1)—F(1)	1.666(1)
Si(1)—C(2)	1.853(2)
Si(1)—C(3)	1.857(2)
Si(1)—C(1)	1.896(2)
Si(1)—O(1)	2.216(2)
Compound **7**	
Si(1)—F(2)	1.608(1)
Si(1)—F(1)	1.652(1)
Si(1)—C(2)	1.847(2)
Si(1)—C(1)	1.888(2)
Si(1)—O(1)	2.020(1)
Compound **9**	
Si(1)—O(1)	1.623(2)
Si(1)—O(2)	1.876(2)
Si(1)—O(4)	1.879(2)
Si(1)—C(1)	1.882(3)
Si(1)—C(12)	1.891(3)
Si(1)...Cl(1)	3.922(2)
Si(2)—O(1)	1.618(2)
Si(2)—O(8)	1.863(2)
Si(2)—O(6)	1.871(2)
Si(2)—C(23)	1.878(3)
Si(2)—C(34)	1.884(3)
Si(1)...Cl(1A)*	3.931(3)
Compound **10**	
Si(1)—O(1)	1.629(4)
Si(1)—O(11)	1.853(4)
Si(1)—C(112)	1.879(5)
Si(1)—C(101)	1.884(5)
Si(1)—O(13)	1.886(4)
Si(1)...O(42)	4.044(5)
Si(2)—O(1)	1.630(4)
Si(2)—O(21)	1.864(4)
Si(2)—O(23)	1.868(4)
Si(2)—C(212)	1.880(5)
Si(2)—C(201)	1.881(5)
Si(2)...O(31)	3.467(7)
Compound **11**	
Si(1)—F(1)	1.601(1)
Si(1)—O(1)	1.828(2)
Si(1)—O(3)	1.832(2)
Si(1)—C(1)	1.879(2)
Si(1)—C(12)	1.886(2)
Si(1)...O(5)	3.187(2)

* The atom is generated by the symmetry operation 1 + *x*, *y*, *z*.

Table 3. Bond angles in the structures of **1**, **4**, **5**, **7**, and **9—11**

Angle	ω/deg
Compound **1**	
C(4)—O(1)—C(3)	115.5(2)
C(10)—N(1)—C(3)	123.5(3)
O(1)—C(3)—N(1)	109.0(2)
O(1)—C(4)—C(9)	121.0(3)
C(4)—C(9)—C(10)	118.8(3)
O(2)—C(10)—N(1)	122.8(3)
N(1)—C(10)—C(9)	115.0(3)
Compound **4**	
C(1)—Si(1)—C(2)	115.7(4)
C(1)—Si(1)—C(3)	116.9(4)
C(2)—Si(1)—C(3)	114.9(4)
O(2)...Si(1)—O(1)	169.6(3)
C(14)—Si(2)—C(15)	109.8(4)
C(14)—Si(2)—C(16)	112.5(4)
C(15)—Si(2)—C(16)	109.4(4)
Si(2)—O(1)—Si(1)	165.1(5)
Compound **5**	
C(2)—Si(1)—C(3)	118.2(1)
C(2)—Si(1)—C(1)	115.5(1)
Compound **5**	
C(3)—Si(1)—C(1)	121.5(1)
F(1)—Si(1)—O(1)	172.5(1)
Compound **7**	
F(2)—Si(1)—C(2)	116.0(1)
F(2)—Si(1)—C(1)	117.0(1)
C(2)—Si(1)—C(1)	124.7(1)
F(1)—Si(1)—O(1)	173.8(1)
Compound **9**	
O(2)—Si(1)—O(4)	172.2(1)
O(1)—Si(1)—C(1)	119.3(1)
O(1)—Si(1)—C(12)	117.9(1)
C(1)—Si(1)—C(12)	122.8(2)
O(1)—Si(1)...Cl(1)	179.7(1)
O(8)—Si(2)—O(6)	170.6(1)
O(1)—Si(2)—C(23)	115.2(1)
O(1)—Si(2)—C(34)	111.4(1)
C(23)—Si(2)—C(34)	133.3(2)
Si(2)—O(1)—Si(1)	165.0(2)
O(1)—Si(1)...Cl(1)*	172.0(1)
Compound **10**	
Si(1)—O(1)—Si(2)	144.8(2)
O(1)—Si(1)—C(101)	116.2(2)
O(1)—Si(1)—C(112)	120.7(2)
C(112)—Si(1)—C(101)	123.1(2)
O(11)—Si(1)—O(13)	171.9(2)
O(1)—Si(1)...O(42)	161.1(2)
O(21)—Si(2)—O(23)	169.7(2)
O(1)—Si(2)—C(212)	115.6(2)
O(1)—Si(2)—C(201)	111.7(2)
C(212)—Si(2)—C(201)	132.7(3)
O(1)—Si(2)...O(31)	165.2(2)
Compound **11**	
O(1)—Si(1)—O(3)	170.4(1)
F(1)—Si(1)—C(1)	109.5(1)
F(1)—Si(1)—C(12)	108.3(1)
C(1)—Si(1)—C(12)	142.2(1)
F(1)—Si(1)...O(5)	167.6(1)

* The atom is generated by the symmetry operation 1 + *x*, *y*, *z*.

ficient for complete cleavage of this bond in one of the chemically equivalent halves of the molecule, whereas the O(2)→Si distance in another half of the molecule (2.57 Å) is ~1 Å shorter than the sum of the van der Waals radii of the atoms, which is indicative of a rather strong interaction.

It cannot be ruled out that violation of the symmetry of the three-dimensional structure of molecule **4** in the crystal is determined not only by the favorable crystal packing. Thus, the arrangement of the O(4) atom of the adjacent molecule at a distance of 4.17 Å from the Si(2) atom on the O(1)—Si(2) line may be indicative of the presence of a weak, for example, electrostatic coordination. In the crystal structure of disiloxane with acyclic amide ligands **4e**, the intramolecular O→Si interactions are symmetric, and the corresponding distances are 2.82 Å, *i.e.*, they are slightly longer than those in the structure of **4**. In the completely symmetric structure, the O atom of disiloxane is involved simultaneously in two hypervalent bonds (O→Si—O—Si←O fragment), resulting in a weakening of the O→Si components. Therefore, the donor properties of the amide group in the benzoxazinone ligand are apparently slightly weakened.

This conclusion is confirmed by a comparison of the structures of mono- and difluorides **5** and **7** (Figs 4 and 5) with the analogs $MeC(O)N(CHMePh)CH_2SiMe_2F$ **(5e)**[13a] and $MeC(O)N(Me)CH_2SiMeF_2$ **(7d)**[13b] (see Table 4), which, like molecule **4e**, contain the acyclic amide group. Although the O→Si bond in the hypervalent O—Si—F fragment is stronger than that in the O—Si—O

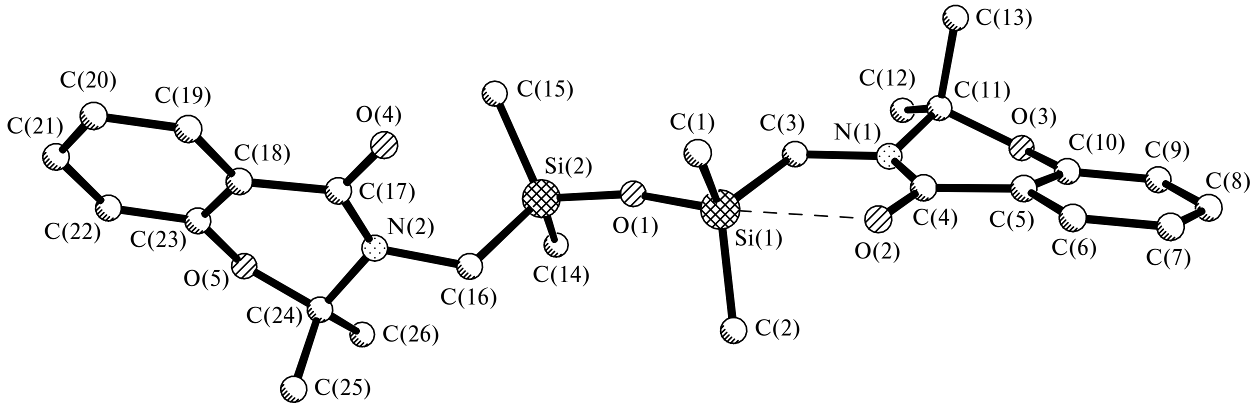


Fig. 3. Molecular structure of $(BonCH_2SiMe_2)_2O$ (**4**) in the crystal. The H atoms are omitted.

Table 4. Selected geometric parameters and the degree of approximation of the configuration of the central coordination unit (η_{eq}, η_{ax}, and η_Ω) to the ideal TBP in pentacoordinate monochelates **3—7** and related compounds

Compound	d/Å		O—Si—X angle /deg	$\Delta\Omega^a$	$\eta_{eq}{}^b$	$\eta_{ax}{}^b$	$\eta_\Omega{}^b$
	O—Si	Si—X			%		
3	1.987	2.313	172.1	0.42	99	90	13
3c	1.950	2.315	171.7	0.26	99	91	8
3e	1.975	2.306	170.8	0.17	99	92	6
4	2.565	1.637	169.9	2.08	60	38	66
4e	2.821	1.631	167.4	2.67	21	18	85
5	2.216	1.666	172.5	1.29	87	63	41
5e	2.149	1.668	172.7	1.08	90	69	34
6c^c	1.907	2.256	173.3	0.42	98	88	13
7	2.019	1.649	173.8	0.91	93	74	29
7d	1.985	1.651	172.6	0.87	94	76	28
14	2.217	1.621	171.0	1.43	82	62	46

[a] Ω is the solid angle formed by three equatorial bonds of the central Si atom; $\Delta\Omega = 2\pi - \Omega$ (0 for a symmetrical TBP and π for a tetrahedron).

[b] The degree of pentacoordination of the Si atom: $\eta_{ax} = \{[109.5 - (1/3)\Sigma_{n=1}^{3}\theta_n]/(109.5 - 90)\}\cdot 100\%$ and $\eta_{eq} = 100\% - \{[120 - (1/3)\Sigma_{n=1}^{3}\varphi_n]/(120 - 109.5)\}$, where φ_n are the angles between the equatorial bonds of the Si atom and θ_n are the angles between the axial and equatorial bonds;[14a] the parameter $\eta_\Omega = (\Delta\Omega/\pi)\cdot 100\%$ characterizes the deviation of the configuration from a symmetrical TBP.[14b]

[c] The structure is disordered; the data for the configuration with an occupancy of 0.75 are given.

fragment in disiloxanes **4** and **4e** and, consequently, it is less sensitive to changes in the electronic structure of the bidentate ligand, the O→Si distances in the structures of **5** and **7** are 0.04—0.05 Å longer than those in the above-mentioned analogs. In the molecules of the corresponding chlorides **3** (see Ref 4b) and $MeC(O)N(CHMePh)CH_2SiMe_2Cl$ (**3e**),[13a] in which the O→Si interaction is even stronger, the replacement of the acyclic amide group by the benzoxazinone bicyclic fragment leads to an increase in the length of this component of the hypervalent bond by less than 0.02 Å.

The effect of replacement of the Me group in the equatorial environment of the Si atom by the F atom on this bond was estimated by comparing the parameters of the hypervalent bonds in molecules **5** and **7**. Both components of the hypervalent bond are shortened but the shortening is strongly asymmetrical (Si—F is shortened by only 0.014 Å, whereas O→Si, by 0.2 Å). It should be noted that the replacement of the Me group by the Cl atom in chloride analogs with O→Si bonds having similar lengths, for example, in going from monochloride $L^7CH_2SiMe_2Cl$ (**3c**) to dichloride $L^7CH_2SiMeCl_2$ (**6c**), leads to an approximately equal shortening (by 0.04—0.06 Å) of both components.[5b,13c] This fact suggests that the electronic structure of the O→Si—F hypervalent bond is strongly asymmetrical, *e.g.*, the Si—F component is much more rigid.

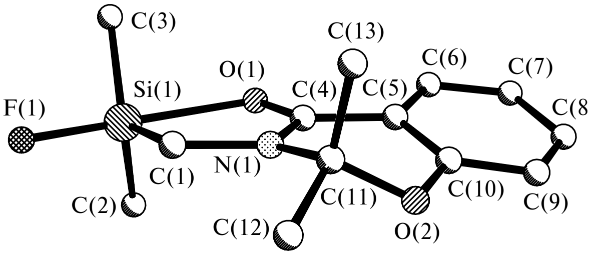


Fig. 4. Molecular structure of fluoride $BonCH_2SiMe_2F$ (**5**) in the crystal. The H atoms are omitted.

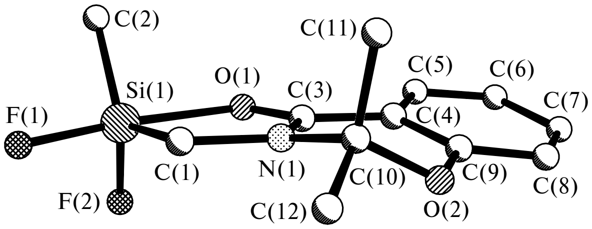


Fig. 5. Molecular structure of difluoride $BonCH_2SiMeF_2$ (**7**) in the crystal. The H atoms are omitted.

An estimation of the degree of distortion of the trigonal-bipyramidal (TBP) configuration of the central coordination unit in monochelates **3—7** and related compounds based on the parameters η_{eq} and η_{ax} (the degree of pentacoordination)[4a] and the more integrated parameter η_Ω proposed in our study[14b] (see Table 4; see notes to this table for the determination of these parameters) confirms the conclusions, which have been made based on a comparison of the lengths of the corresponding bonds. This is most clearly demonstrated by the parameter η_Ω characterizing the deviation of the configuration from the symmetrical TBP (planar equatorial environment of the Si atom). An increase in this parameter in analogous molecules is associated with a weakening of the donor properties of the C=O group. Actually, the deviations toward the tetrahedral configuration in disiloxanes **4** and **4e** are 66 and 85%, respectively; in monofluorides **5** and **5e**, 41 and 34%; in monochlorides **3** and **3c,e**, 6—13%. For silicon halides with the $BonCH_2$ ligand, the degree of approach to the symmetrical TBP is somewhat smaller.

By contrast, the replacement of the N atom in the $C(O)NCH_2$ fragment by the O atom (*i.e.*, in compounds containing the $C(O)OCH_2$ fragment, in which O→Si coordination is also present) has a more substantial effect on the parameters of the hypervalent bond. For example, η_Ω for difluoride $PhCOOCH_2SiMeF_2$ (**14**)[13d] is larger than that for **7** and **7d** by 17 and 18%, respectively. The length of the component of the O→Si hypervalent bond increases by ~0.2—0.3 Å (see Table 4).

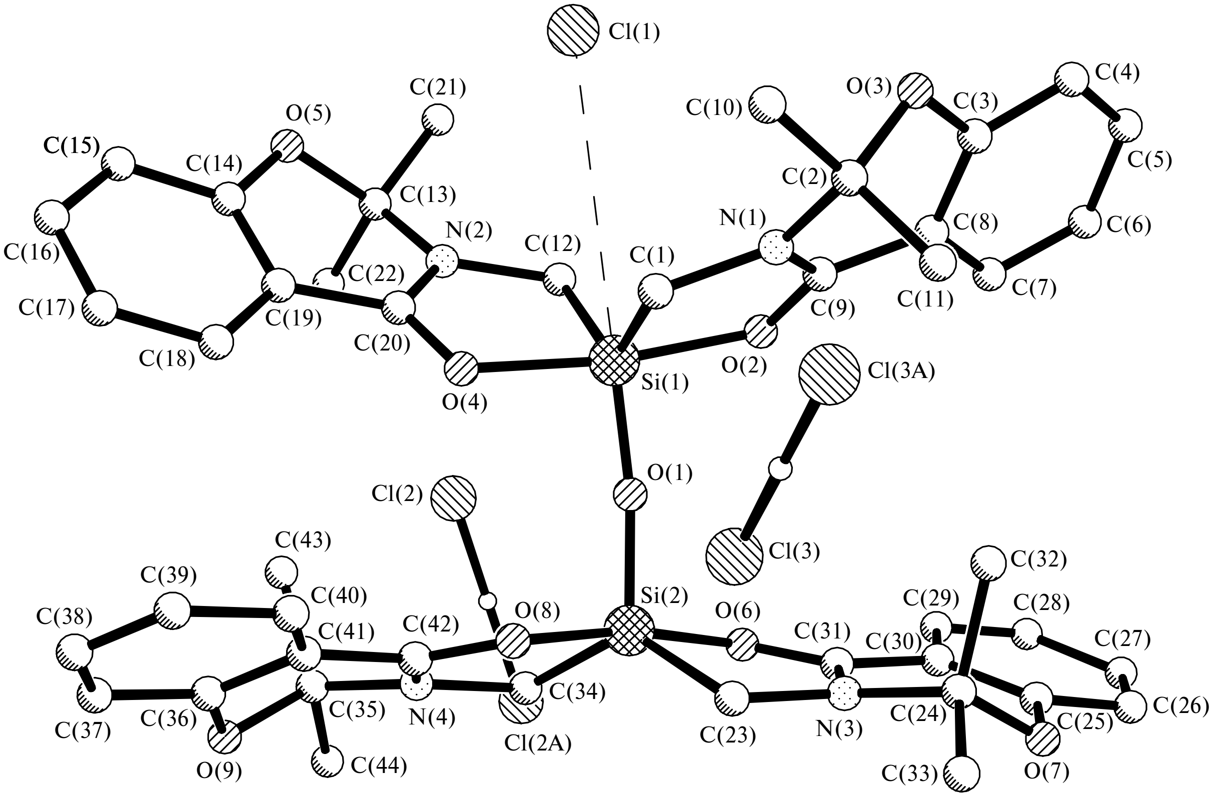


Fig. 6. Structure of the dinuclear cation-anion complex $\{[(\text{BonCH}_2)_2\text{Si}]_2\text{O}\}^{2+} \cdot \text{Cl}^- \cdot \text{ClHCl}^-$ (**9**) in the crystal. Two ClHCl^- anions are crystallographically independent (occupy the inversion centers 0.5, 0.5, 0 and 0, 1, 0.5) and belong simultaneously to two different complexes. The positions of the H atoms are shown only for the anions.

The dications in dinuclear cation-anion complexes **9** (Figs 6 and 7) and **10** (Fig. 8) consist of two bis-chelate fragments linked by a siloxane bridge. The fragments are chiral. Hence, regardless of the chirality of the space group of the crystal, the dications can contain fragments adopting either the same (ΛΛ) or different (ΛΔ) configurations.[15] Earlier, we have studied the crystal structures containing similar dications having both configurations.[3b] In the crystal of **9**, the dications adopt a ΛΔ configuration; in the crystal of **10**, ΛΛ. Therefore, the $\{[(\text{BonCH}_2)_2\text{Si}]_2\text{O}\}^{2+}$ dications in the structures of **9** and **10** are diastereomers having different configurations.

The shortest interatomic cation—anion distances in dinuclear complexes **9** and **10** are somewhat larger than the sums of the van der Walls radii[12] of the corresponding atoms: the Si...Cl⁻ distances in **9** (3.92 and 3.93 Å; see Fig. 7) are larger than this sum by ~0.2 Å.

In dinuclear complex **10** (see Fig. 8), one of the Si...OTf⁻ distances (3.47 Å) is virtually equal to the sum of the van der Walls radii of the Si and O atoms, whereas another distance (4.04 Å) is larger than this sum by 0.6 Å. At the same time, this more distant anion is disordered over two positions, whereas the coordination TBP polyhedron of the Si(2) atom is substantially opened toward the anion (C—Si(2)—C bond angle is 10°

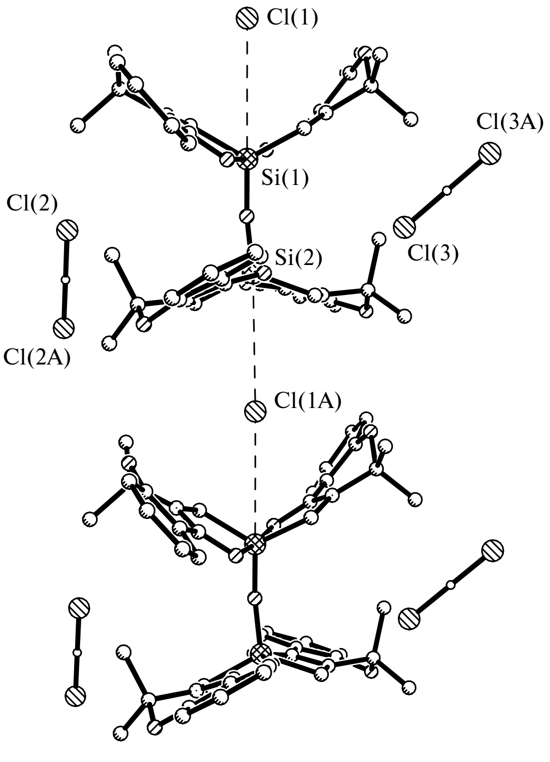


Fig. 7. Fragment of the crystal structure of complex **9**.

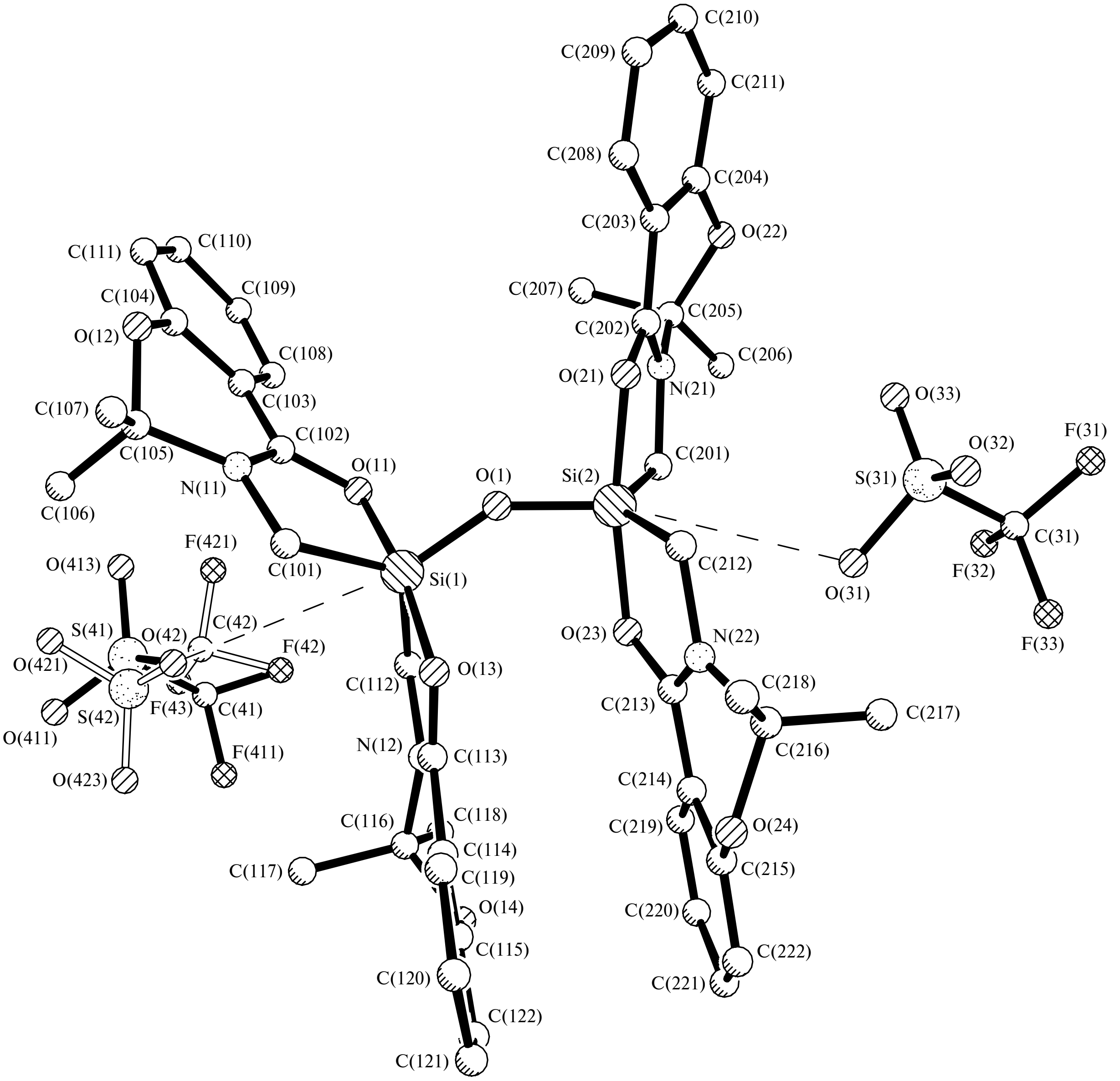


Fig. 8. Structure of the dinuclear cation-anion complex $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot 2TfO^-$ (**10**) in the crystal. The H atoms are omitted.

larger than the corresponding angle at the Si(1) atom, see Table 3).

Earlier,[3a] we have observed a similar asymmetry of interactions between the OTf^- anions and the dication in the structure of complex **10a**, which is analogous to **10** and in which the dication contains the five-membered lactamomethyl bidentate ligands. The shortest Si...OTf^- distance (3.91 Å) in this structure corresponds to an increase in the C—Si—C angle by 5°. The correlation between the above-mentioned parameters and its disappearance at Si...O distances, which are 0.5 Å larger than the sum of the van der Waals radii of the atoms, allow a consideration of the coordination of the corresponding Si atoms as 5+1. The linear O—Si...O fragment can be considered as the second hypervalent bond of this atom, which is obviously much weaker than the bond in the symmetrical O—Si—O fragment. For analogous hexacoordinate germanium analogs, the corresponding structural correlations were observed for a substantially larger number of compounds.[10a,b]

It should be noted that each Cl^- anion in the structure of **9** is coordinated by two Si atoms. Hence, it is not surprising that an additional (sixth) coordination of the Si atoms in this compound is weaker than that of the Si(2) atom in the structure of **10** (estimated based on the ratio of the interatomic distances to the sums of the van der Waals radii of the corresponding atoms). The monocoordinated chloride ion is known[16] to be a much poorer leaving group than the triflate ion. The $ClHCl^-$ anions in the structure of **9** are outside the coordination sphere of the Si atoms. The Cl...Si interactions for these anions should be considered as purely ionic.

The $ClHCl^-$ anions in the crystal structure of **9** have a symmetric structure (H atoms occupy the crystallographic inversion centers); the H—Cl distances are 1.55 and 1.56 Å. Five structures with analogous symmetric anions are stored in the Cambridge Structural Database.**[17]** In these compounds, the distances under consideration vary from 1.55 to 1.57 Å, *i.e.*, are virtually equal to those observed in complex **9**.

In the crystal structure, the molecular structure of complex **11** (Fig. 9) is to a certain degree analogous to the structure of one half of complex **10**, in which the siloxane O atom is replaced by the F atom. Hence, the coordination component of the weak (Tf)O→Si—F hypervalent bond is substantially stronger than that in the structure of **10**. The O→Si distance (3.187(2) Å) is 0.3 Å smaller than the sum of the van der Waals radii of these atoms. This feature of fluoride triflate **11** is similar to that of the germanium complexes $(LCH_2)_2Ge(X)Y$ (X = F or Cl; Y = OTf or I) studied earlier, in which the central atom also has coordination 5+1.**[10a,b]**

In the bis-chelate cations of complexes **9**—**11**, there are not only very weak hypervalent bonds involving the anions but also the strong symmetrical O→Si←O hypervalent bonds, in which the Si—O distances are only 0.2 Å longer than the usual valence bond with the tetrahedral Si atom. In the dinuclear dications of complexes **9** and **10**, these distances are 0.03—0.05 Å longer than those in the mononuclear cation of complex **11** (see Table 2). Apparently, this is due to the replacement of the siloxane O atom in complexes **9** and **10** by the more electron-withdrawing F atom in complex **11**, resulting in an increase in the effective positive charge on the silicon atom and, correspondingly, in a decrease in the Si—O distances in the O→Si←O fragment.

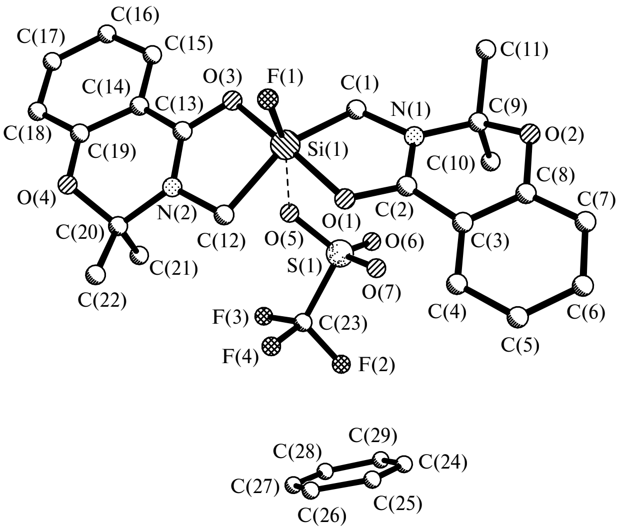


Fig. 9. Structure of the $[(BonCH_2)_2Si(F)]^+ \cdot OTf^- \cdot C_6H_6$ ($\mathbf{11} \cdot C_6H_6$) complex in the crystal. The H atoms are omitted.

This is a common feature, in particular, for mononuclear bis-C,O-chelate cation-anion silicon complexes. The replacement of the Cl atom in the cation of the $\{[MeC(O)N(Me)CH_2]_2Si(Cl)\}^+HCl_2^-$ complex (**8d**)**[3c]** by the F atom in the $\{[MeC(O)N(Me)CH_2]_2Si(F)\}BF_4$ complex (complete data on its structure will be published elsewhere) leads to a decrease in the average O—Si distance from 1.847 to 1.823 Å, *i.e.*, by 0.024 Å.

To summarize, the use of the C,O-chelating $BonCH_2$ ligand allowed the synthesis of new mono- and bis-chelate hypercoordinate silicon complexes, including compounds with unique structures, which have been previously inaccessible with the use of other amidomethyl and related C,O-chelating ligands.

Experimental

The IR spectra of ~5% solutions of the compounds were recorded on a Specord IR-75 instrument in KBr or CaF_2 cells. The ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of solutions of the compounds in CCl_4 or $CDCl_3$ were measured on a Varian XL-400 spectrometer (400.1, 100.6, 396, and 79.5 MHz, respectively). The ^1H, ^{13}C, and ^{29}Si chemical shifts were measured relative to Me_4Si as the internal standard; the ^{19}F shifts, relative to boron trifluoride etherate as the external standard.

The conductivity of solutions of the resulting compounds in CH_2Cl_2 (concentrations were 10^{-1}—10^{-5} mol L^{-1}) was measured on a Radelkis OK-102/1 conductometer (Hungary) equipped with OK-9023 electrodes with three platinum rings at ~25 °C and at an alternating current frequency of 80—3000 Hz. The relative error of measurements of the specific conductivity was ±1%.

2,2-Dimethylbenzo[2*H*]-1,3-oxazin-4-one (**1**),**[18a]** 2,2-dimethyl-3-trimethylsilylbenzo[2*H*]-1,3-oxazin-4-one (**2**),**[4b]** (O→Si)-chelate 1,1,3,3-tetramethyl-1,3-bis(2,2-dimethyl-4-oxo-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl)-1,3-disiloxane (**4**),**[4b]** and bis(chloromethyl)dichlorosilane**[18b]** were synthesized according to procedures described earlier.

(O→Si)-Chelate 2,2-dimethyl-3-(dimethylfluorosilylmethyl)-2,3-dihydrobenzo-1,3-oxazin-4-one (5). A mixture of compound **2** (5 g, 0.02 mol) and $ClCH_2SiMe_2Cl$ (2.86 g, 0.02 mol) was heated in a distillation flask until elimination of Me_3SiCl ceased. The residue was dissolved in $CHCl_3$ (50 mL) and triturated with a sodium hydrocarbonate solution (2 g of $NaHCO_3$ in 20 mL of water). After 1 day, the layers were separated, and the organic layer was dried over $CaCl_2$. Then chloroform was evaporated, and $BF_3 \cdot Et_2O$ (0.99 g, 0.007 mol) was added to the residue. The reaction mixture was heated for 30 min until Et_2O was completely removed. The residue was refluxed in benzene (50 mL), the insoluble residue was filtered off, and the benzene solution was concentrated on an evaporator. The oil was crystallized with hexane. Compound **5** was obtained in a yield of 3.5 g (65%), m.p. 85—86 °C (hexane). The molar weight (cryoscopy, benzene): $M^{exp}{}_1 = 278$ (c = 0.6 mmol L^{-1}); $M^{exp}{}_2 = 263$ (c = 1.2 mmol L^{-1}). $M^{calc} = 267.37$. Found (%): C, 58.39; H, 6.93; N, 5.14. $C_{13}H_{18}FNO_2Si$. Calculated (%): C, 58.40; H, 6.78;

N, 5.24. IR ($CHCl_3$), ν/cm^{-1}: 1630 (s), 1580 (w), 1504 (m), 1487 (m). ^{1}H NMR ($CDCl_3$), δ: 0.33 (d, 6 H, $SiMe_2$, $^3J_{H,F}$ = 7.4 Hz); 1.64 (s, 6 H, CMe_2); 2.46 (s, 2 H, NCH_2); 6.91 (d, 1 H, H(9), $^3J_{H,H}$ = 7.9 Hz); 7.06 (t, 1 H, H(7), $^3J_{H,H}$ = 7.9 Hz); 7.47 (t, 1 H, H(8), $^3J_{H,H}$ = 7.9 Hz); 7.81 (d, 1 H, H(6), $^3J_{H,H}$ = 7.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 1.66 (d, $SiMe_2$, $^2J_{C,F}$ = 32 Hz); 23.20 (Me_2); 32.01 (d, NCH_2, $^2J_{C,F}$ = 40.4 Hz); 91.62, 114.62, 117.12, 122.25, 128.08, 135.27, 154.88 (C(2), C(5), C(7), C(6), C(9), C(8), C(10)); 162.56 (C=O). ^{19}F NMR ($CDCl_3$), δ: −120.7. ^{29}Si NMR ($CDCl_3$), δ: −12.9 (d, $^1J_{Si,F}$ = 258 Hz).

(O→Si)-Chelate 3-(difluoromethylsilylmethyl)-2,2-dimethyl-2,3-dihydrobenzo-1,3-oxazin-4-one (7). A mixture of compound **2** (5 g, 0.02 mol) and $ClCH_2SiMeCl_2$ (3.26 g, 0.02 mol) was heated in a distillation flask until elimination of Me_3SiCl ceased. The residue was dissolved in chloroform (50 mL) and triturated with a sodium hydrocarbonate solution (4 g of $NaHCO_3$ in 40 mL of water). After 1 day, the organic layers were separated and dried over $CaCl_2$. Then chloroform was evaporated, and $BF_3 \cdot Et_2O$ (1.85 g, 0.013 mol) was added to the residue. The reaction mixture was heated for 30 min until Et_2O was completely removed. The residue was refluxed in hexane (3×30 mL). The crystals that precipitated upon cooling were filtered off. Compound **7** was obtained in a yield of 1.9 g (35%), m.p. 107—109 °C (hexane). The molar weight (cryoscopy, benzene): $M^{exp}{}_1$ = 282 (*c* = 0.6 mmol L^{-1}); $M^{exp}{}_2$ = 273 (*c* = 1.2 mmol L^{-1}). M^{calc} = 271.34. Found (%): C, 53.11; H, 5.51; N, 5.14. $C_{12}H_{15}F_2NO_2Si$. Calculated (%): C, 53.12; H, 5.57; N, 5.16. IR ($CHCl_3$), ν/cm^{-1}: 1620 (s), 1580 (w), 1520 (m), 1487 (m). ^{1}H NMR ($CDCl_3$), δ: 0.42 (t, 3 H, SiMe, $^3J_{H,F}$ = 5.3 Hz); 1.66 (s, 6 H, CMe_2); 2.53 (t, 2 H, NCH_2, $^3J_{H,F}$ = 2.5 Hz); 6.95 (d, 1 H, H(9), $^3J_{H,H}$ = 8.3 Hz); 7.11 (t, 1 H, H(7), $^3J_{H,H}$ = 8.3 Hz); 7.53 (d, 1 H, H(6), $^3J_{H,H}$ = 8.3 Hz); 7.87 (t, 1 H, H(8), $^3J_{H,H}$ = 8.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.64 (t, SiMe, $^2J_{C,F}$ = 22.1 Hz); 24.79 (Me_2); 29.97 (t, NCH_2, $^2J_{C,F}$ = 30.1 Hz); 91.35, 112.68, 117.40, 122.66, 128.40, 136.40, 155.08 (C(2), C(5), C(7), C(6), C(9), C(8), C(10)); 163.75 (C=O). ^{19}F NMR ($CDCl_3$), δ: −123.7. ^{29}Si NMR ($CDCl_3$), δ: −51.3 (t, $^1J_{Si,F}$ = 249 Hz).

Reaction of 2,2-dimethyl-3-trimethyl-2,3-dihydrosilylbenzo-1,3-oxazin-4-one (2) with bis(chloromethyl)dichlorosilane. A mixture of compound **2** (2.49 g, 0.01 mol), $(ClCH_2)_2SiCl_2$ (0.98 g, 0.005 mol), and heptane (15 mL) was refluxed for 2 h. The precipitate that formed was filtered off. Bis(O→Si)-chelate bis(2,2-dimethyl-4-oxo-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl)dichlorosilane (**8**) was obtained in a yield of 2.3 g (97%), m.p. 182—184 °C (*o*-xylene—acetonitrile, 1 : 1). Found (%): C, 54.88; H, 5.07; N, 5.65; Si, 5.82. $C_{22}H_{24}Cl_2N_2O_4Si$. Calculated (%): C, 55.11; H, 5.04; N, 5.84; Si, 5.86. (Calculated (%) for compound **9**, $C_{44}H_{49}Cl_3N_4O_8Si_2$: C, 56.20; H, 5.25; N, 5.96; Si 5.97.) IR (MeCN), ν/cm^{-1}: 1610 (s), 1600 (w), 1550 (m), 1515 (m). ^{1}H NMR (CD_3CN), δ: 1.71 (s, 12 H, CMe_2); 2.99 (s, 4 H, NCH_2); 6.85 (d, 2 H, H(9), $^3J_{H,H}$ = 8.0 Hz); 7.05 (t, 2 H, H(7), $^3J_{H,H}$ = 8.0 Hz); 7.61 (t, 2 H, H(8), $^3J_{H,H}$ = 8.0 Hz); 7.82 (d, 2 H, H(6), $^3J_{H,H}$ = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 7.11 (SiMe); 25.56 (Me_2); 34.99 (NCH_2); 92.23, 111.47, 113.98, 119.10, 124.92, 139.13, 151.75 (C(2), C(5), C(7), C(6), C(9), C(8), C(10)); 159.51 (C=O). ^{29}Si NMR (CD_3CN), δ: −58.3.

In attempting to grow single crystals of dichloride **8** from a 1 : 1 *o*-xylene—acetonitrile mixture, we obtained crystals with m.p. 238—241 °C. The X-ray diffraction study demonstrated that these crystals are tetrakis(O→Si)-chelate 1,1,3,3-tetrakis(2,2-dimethyl-4-oxo-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl)disiloxane chloride hydrogen dichloride $\{[(BonCH_2)_2Si]_2O\}^{2+} \cdot Cl^- \cdot ClHCl^-$ (**9**).

Tetrakis(O→Si)-chelate 1,1,3,3-tetrakis(2,2-dimethyl-4-oxo-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl)disiloxane ditriflate (10). A mixture of dichloride **8** (2 g, 0.004 mol), trimethylsilyl triflate (1.8 g, 0.008 mol), and MeCN (15 mL) was refluxed for 2 h, and then several drops of H_2O were added. After 1 day, MeCN was evaporated, and Et_2O was added to the residue. The resulting amorphous substance was recrystallized upon the addition of water. Compound **10** was obtained in a yield of 2.3 g (97%), m.p. 279—281 °C (EtOH). Found (%): C, 48.70; H, 4.39; N, 5.01. $C_{46}H_{48}F_6N_4O_{15}S_2Si_2$. Calculated (%): C, 48.84; H, 4.27; N, 4.95. IR (CH_2Cl_2), ν/cm^{-1}: 1624 (s), 1610 (s), 1565 (w), 1524 (m), 1471 (m). ^{1}H NMR ($CDCl_3$), δ, First diastereomer: 1.58 and 1.65 (both s, 12 H each, CMe_2); 2.82 and 3.98 (both d, 8 H, NCH_2, $^2J_{H,H}$ = 12.1 Hz); 6.82 (d, 4 H, H(9), $^3J_{H,H}$ = 8.0 Hz); 7.09 (t, 4 H, H(7), $^3J_{H,H}$ = 8.0 Hz); 7.63 (t, 4 H, H(8), $^3J_{H,H}$ = 8.0 Hz); 7.72 (d, 2 H, H(6), $^3J_{H,H}$ = 8.0 Hz); Second diastereomer: 1.67 and 1.69 (both s, 12 H each, CMe_2); 2.54 and 4.02 (both d, 8 H, NCH_2, $^2J_{H,H}$ = 12.1 Hz); 6.99 (d, 4 H, H(9), $^3J_{H,H}$ = 8.0 Hz); 7.10 (t, 4 H, H(7), $^3J_{H,H}$ = 8.0 Hz); 7.66 (t, 4 H, H(8), $^3J_{H,H}$ = 8.0 Hz); 7.79 (d, 4 H, H(6), $^3J_{H,H}$ = 8.0 Hz). The ratio of diastereomers was 54 : 46. ^{13}C NMR ($CDCl_3$), δ, First diastereomer: 23.20, 25.49 (Me_2); 31.45 (NCH_2); 92.85, 110.80, 106.99, 112.08 (C(2), C(5), C(7), C(6)); 117.95 (CF_3, $^1J_{C,F}$ = 314.7 Hz); 128.07, 138.11, 155.54 (C(9), C(8), C(10)); 165.42 (C=O); Second diastereomer: 23.10, 25.27 (Me_2); 31.45 (NCH_2); 92.70, 110.72, 106.99, 112.09 (C(2), C(5), C(7), C(6)); 117.95 (CF_3, $^1J_{C,F}$ = 314.7 Hz); 128.00, 137.89, 155.49 (C(9), C(8), C(10)); 165.34 (C=O). ^{19}F NMR ($CDCl_3$), δ: −78.3. ^{29}Si NMR ($CDCl_3$), δ: −64.5, −65.0.

Bis(O→Si)-chelate bis(2,2-dimethyl-4-oxo-2,3-dihydrobenzo-1,3-oxazin-3-ylmethyl)fluorosilylium trifluoromethanesulfonate (11). A mixture of ditriflate **10** (1.1 g, 0.001 mol), $BF_3 \cdot Et_2O$ (0.14 g, 0.001 mol), and $CHCl_3$ (3 mL) was refluxed for 1 h. Then heptane (5 mL) was added. The resulting crystals were filtered off. Fluoride triflate **11** was obtained in a yield of 1.1 g (92%). After recrystallization, the solvate **11**$\cdot 0.5C_6H_6$ was isolated, m.p. 204—206 °C (benzene). Found (%): C, 50.66; H, 4.54; N, 4.22. $C_{26}H_{27}F_4N_2O_7SSi$. Calculated (%): C, 50.72; H, 4.41; N, 4.55. (Calculated (%) for compound **11**, $C_{23}H_{24}F_4N_2O_7SSi$: C, 47.91; H, 4.20; N, 4.86. Calculated (%) for compound **11**$\cdot C_6H_6$, $C_{29}H_{30}F_4N_2O_7SSi$: C, 53.20; H, 4.62; N, 4.28.) IR (CH_2Cl_2), ν/cm^{-1}: 1630 (s), 1610 (s), 1560 (m), 1520 (m), 1478 (m). ^{1}H NMR ($CDCl_3$), δ: 1.81 (s, 12 H, CMe_2); 2.95, 3.61 (dt, 4 H, NCH_2, $^1J_{H,H}$ = 16.8 Hz, $^1J_{H,H}$ = 15.1 Hz); 7.02 (d, 2 H, H(9), $^3J_{H,H}$ = 8.4 Hz); 7.17 (t, 2 H, H(7), $^3J_{H,H}$ = 8.4 Hz); 7.63 (t, 2 H, H(8), $^3J_{H,H}$ = 8.4 Hz); 7.80 (d, 2 H, H(6), $^3J_{H,H}$ = 8.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 23.57, 25.53 (Me_2); 31.19 (NCH_2); 92.85, 110.61, 123.14, 128.46 (C(2), C(5), C(7), C(6)); 117.87 (CF_3, $^1J_{C,F}$ = 318.7 Hz); 128.46, 138.18, 155.65 (C(9), C(8), C(10)); 165.77 (C=O). ^{19}F NMR ($CDCl_3$), δ: −78.3 (CF_3); −120.4 (SiF). ^{29}Si NMR ($CDCl_3$), δ: −56.5 (d, $^1J_{Si,F}$ = 251 Hz).

X-ray diffraction study of compounds 1, 4, 5, 7, 9, 10, and 11. Single crystals suitable for X-ray diffraction study were grown by recrystallization (**1** from acetone, disiloxane **4** from heptane, fluoride **5** from hexane, difluoride **7** from hexane, hydrochloride **9** from a 1 : 1 *o*-xylene—acetonitrile mixture, ditriflate **10** from ethanol, and fluoride triflate **11**$\cdot C_6H_6$ from benzene).

The crystallographic parameters and principal characteristics of X-ray diffraction study of compounds **1**, **4**, **5**, **7**, **9**, **10**, and **11** are given in Tables 5 and 6. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms. In the structures of **1**, **4**, and **10**, the

Table 5. Principal X-ray data collection and refinement statistics and crystallographic characteristics for compounds **1**, **4**, **5**, and **7**

Parameter	**1**	**4**	**5**	**7**
Molecular formula	$C_{10}H_{11}NO_2$	$C_{26}H_{60}N_2O_5Si_2$	$C_{13}H_{18}FNO_2Si$	$C_{12}H_{15}F_2NO_2Si$
Molecular weight	117.2	512.75	267.37	271.34
Diffractometer	«Siemens P3»	«Syntex P2$_1$»	«SMART CCD»	«SMART CCD»
T/K	293(2)	190(2)	120	120
a/Å	11.016(6)	11.985(5)	11.237(1)	8.241(2)
b/Å	6.068(3)	6.437(2)	16.646(1)	12.995(2)
c/Å	14.170(8)	35.05.(1)	9.440(1)	24.107(5)
α/deg	90	90	90	90
β/deg	106.29(4)	90	94.278(2)	90
γ/deg	90	90	90	90
V/Å^3	909.2(8)	2704(2)	1337.6(3)	2581.9(8)
d_{calc}/g cm^{-3}	1.295	1.259	1.328	1.396
Space group	$P2_1/n$	$Pca2_1$	$P2_1/c$	$Pbca$
Z	4	4	4	8
F(000)	376	1096	568	1136
Scanning mode	$\theta/2\theta$	$\Omega/2\theta$	$\Omega/2\theta$	$\Omega/2\theta$
$2\theta_{max}$/deg	50	56	60	60
Number of measured reflections	1704	3130	10901	19137
Number of independent reflections (R_{int})	1614 (0.022)	3130 (0.0)	3858 (0.030)	3720 (0.039)
Number of observed reflections with $I > 2\sigma(I)$	825	1468	2551	2776
Number of parameters in refinement	122	316	235	223
Absorption coefficient/cm^{-1}	0.91	1.69	1.81	2.00
R_1 ($I > 2\sigma(I)$)	0.075	0.072	0.062	0.061
wR_2 (based on all reflections)	0.1672	0.152	0.162	0.153

Table 6. Principal X-ray data collection and refinement statistics and crystallographic characteristics for compounds **9—11**

Parameter	**9**	**10**	**11**
Molecular formula	$C_{44}H_{49}Cl_3N_4O_9Si_2$	$C_{46}H_{48}N_4O_{15}S_2Si_2$	$C_{23}H_{24}F_4N_2O_7SSi \cdot C_6H_6$
Molecular weight	940.4	1131.18	654.7
Diffractometer	«Syntex P2$_1$»	«Siemens P3»	«Syntex P2$_1$»
T/K	133(2)	190(2)	153(2)
a/Å	11.045(5)	19.371(6)	12.235(5)
b/Å	13.229(7)	15.889(6)	14.250(5)
c/Å	16.898(7)	16.989(6)	17.929(5)
α/deg	79.67(4)	90	90
β/deg	84.09(4)	94.00(3)	108.97(3)
γ/deg	71.08(4)	90	90
V/Å^3	2295(2)	5216(3)	2956(2)
d_{calc}/g cm^{-3}	1.361	1.440	1.471
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Z	2	4	4
F(000)	984	2344	1360
Scanning mode	$\theta/2\theta$	$\omega/2\theta$	$\theta/2\theta$
$2\theta_{max}$/deg	50	48	52
Number of measured reflections	8283	8464	6119
Number of independent reflections (R_{int})	7828 (0.185)	8148 (0.096)	5838 (0.051)
Number of observed reflections with $I > 2\sigma(I)$	6238	5526	4359
Number of parameters in refinement	753	721	517
Absorption coefficient/cm^{-1}	3.10	2.39	2.26
R_1 ($I > 2\sigma(I)$)	0.064	0.081	0.043
wR_2 (based on all reflections)	0.272	0.218	0.111

H atoms are placed in calculated positions and refined using a riding model with fixed C—H distances and thermal parameters equal to $1.5U_C$ for the H atoms of the Me groups and $1.2U_C$ for the other H atoms (U_C are the equivalent thermal parameters of the corresponding C atoms). The H atom at the N(1) atom in the structure of **1** was refined isotropically. In the other structures, the H atoms were located in difference Fourier syntheses and refined isotropically.

All calculations were carried out with the use of the SHELXTL PLUS 5.0 program package.[19] For the X-ray diffraction data sets collected from crystals of **1** and **11**, the peak shapes were corrected using the PROFIT program.[20] For compound **4**, the absolute structure was determined based on the Flack parameter[21] of 0.083(0.277). In the crystal structure of **9**, the H(02) and H(03) atoms of the anions occupy special positions with occupancies of 0.5. In the structure of **10**, one of the anions is disordered over two positions with occupancies of 0.5. The solvent benzene molecule was found in the crystal structure of **11**. Selected bond lengths and bond angles are given in Tables 2 and 3. The complete data on the structures were deposited with the Cambridge Structural Database.[17] The X-ray diffraction study was carried out at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences).

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