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Synthesis, molecular and crystal structures, and characteristic features of electronic structures of salicylamide-based B,Si-containing chelates

A. A. Korlyukov,[a]★ ***K. A. Lyssenko,***[a] ***M. Yu. Antipin,***[a] ***A. G. Shipov,***[b] ***O. A. Zamyshlyaeva,***[b]
E. P. Kramarova,[b] ***Vad. V. Negrebetsky,***[b] ***S. A. Pogozhikh,***[c] ***Yu. E. Ovchinnikov,***[c] ***and Yu. I. Baukov***[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: alex@xrlab.ineos.ac.ru
[b]*Russian State Medical University*
1 ul. Ostrovityanova, 117997 Moscow, Russian Federation.
Fax: +7 (095) 434 0329. E-mail: baukov.rgmu@mtu-net.ru
[c]*Novosibirsk State Pedagogical University,*
28 ul. Vilyuiskaya, 630126, Novosibirsk, Russian Federation.
E-mail: ovchin@hotmail.ru

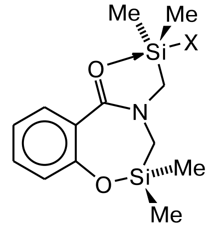
The reaction of 4-(2-hydroxybenzoyl)-2,2,6,6-tetramethyl-2,6-disilamorpholine with $BF_3 \cdot Et_2O$ afforded (O—B)-chelate 4-[2-(difluoroboroxy)benzoyl]-2,2,6,6-tetramethyl-2,6-disilamorpholine. Treatment of the latter with $BF_3 \cdot Et_2O$ or $SOCl_2$ gave rise to products of the disilamorpholine ring opening, *viz.*, (O—B)-chelate 2-(difluoroboroxy)-*N*,*N*-bis(dimethylfluorosilylmethyl)benzamide or 2-(difluoroboroxy)-*N*,*N*-bis(dimethylchlorosilylmethyl)benzamide, respectively. The structures of the compounds synthesized were confirmed by X-ray diffraction analysis and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. High-precision X-ray diffraction study and quantum-chemical calculations demonstrated that the coordination O→Si bond is absent in the two last-mentioned compounds.

Key words: 2,6-disilamorpholines, pentacoordinate silicon compounds, tetracoordinate boron compounds, X-ray diffraction study, electron density distribution, quantum-chemical calculations.

Earlier, a broad scope of the synthesis of silaoxaaza- and siladiazaheterocycles with the use of unsubstituted and functionally substituted carboxamides and chloro(chloromethyl)dimethylsilane as a cyclosilylating reagent has been exemplified by the preparation of six-membered 1-oxa-4-aza-2-silacyclanes,[1—3] 4-acyl-2,6-disilamorpholines,[1,4] and 4-acyl-2,6-disilapiperazines.[5] The formation of the target products was demonstrated[1—5] to proceed through intermediate pentacoordinate silicon compounds, which are more reactive in nucleophilic substitution reactions than the corresponding tetrahedral silicon derivatives[6] and can be synthesized also by the reactions of silacyclanes with electrophilic reagents.[7]

In the case of salicylamide and *N*-methylsalicylamide, analogous cyclosilylation reactions with the use of the hexamethyldisilazane—chloro(chloromethyl)dimethylsilane system afforded 1-oxa-4-aza-2-silabenzocycloheptan-5-one derivatives.[8,9] In particular, this method was used for the preparation of (O—B)-chelate 4-(chlorodimethylsilylmethyl)-2,2-dimethyl-1-oxa-4-aza-2-silabenzocycloheptan-5-one (**1**) from salicylamide. Compound **1** was used for the synthesis of the corresponding fluoride **2** and 4-(2-hydroxybenzoyl)-2,2,6,6-tetramethyl-2,6-disilamorpholine (**3**).

As part of our investigation, we synthesized B,Si-containing chelates starting from disilamorpholine **3** and established the molecular and crystal structures of these chelates by X-ray diffraction analysis.



1, **2**

X = Cl (**1**), F (**2**)

Under rather mild conditions, the reaction of disilamorpholine **3** with $BF_3 \cdot Et_2O$ afforded (O—B)-chelate, *viz.*, 4-[2-(difluoroboroxy)benzoyl]-2,2,6,6-tetramethyl-2,6-disilamorpholine (**4**). Its structure was established by elemental analysis, spectroscopy, and X-ray diffraction analysis.

It should be noted that the (2-hydroxybenzoyl)acetamide derivative, which bears an analogous boron-containing fragment with a chelate ring involving the OBF_2O group, has been used earlier[10] in the synthesis of 2-aminochromones.

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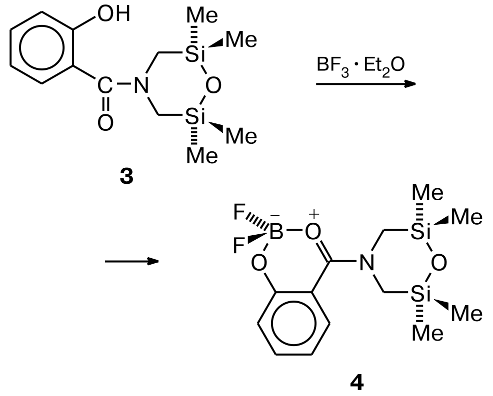
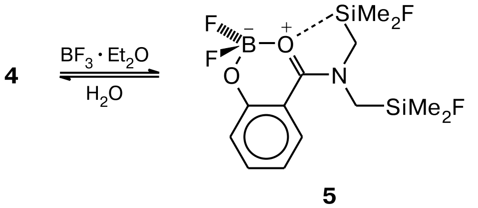


(1)

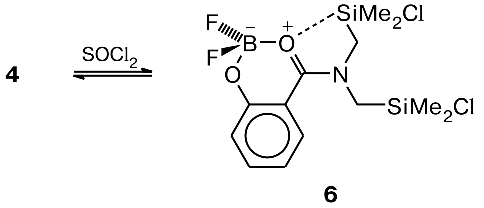
The reaction (1) was accompanied by the disilamorpholine ring opening to give 2-(difluoroboroxy)-*N*,*N*-bis(dimethylfluorosilylmethyl)benzamide (**5**) containing the (O—B)-chelate fragment as a by-product. An increase in the amount of $BF_3 \cdot Et_2O$ and more drastic reaction conditions facilitate the formation of tetrafluoride **5** as the major product. Apparently, this is attributable to two successive processes, *viz*., boronation at the hydroxy group to form (O—B)-chelate **4** (reaction (1)) followed by the disilamorpholine ring opening in chelate **4** giving rise to the final tetrafluoride **5** (reaction (2)). The latter reaction was carried out separately. However, the possibility of boronation, ring opening, and transboronation at the oxygen atom in the presence of $BF_3 \cdot Et_2O$ occurring as competitive reactions cannot be ruled out.



(2)

It should be noted that only the Si—F bonds in tetrafluoride **5** are subjected to hydrolysis under mild conditions to give the starting disilamorpholine, *viz*., difluoride **4**.

The direct reaction of disilamorpholine **3** with an excess of $BF_3 \cdot Et_2O$ also affords tetrafluoride **5**. The disilamorpholine ring opening in difluoride **4** with retention of the (O—B)-chelate fragment occurs also in the reaction with thionyl chloride to give a dichloro analog of tetrafluoride **5**, *viz*., (O—B)-chelate 2-(difluoroboroxy)-*N*,*N*-bis(chlorodimethylsilylmethyl)benzamide (**6**) (reaction (3)). The results of X-ray diffraction study of compounds **5** and **6** provide evidence for an interaction between one of the silicon atoms and the oxygen atom of the amide fragment, which is already involved in the donor-acceptor bond with the boron atom. The nature of this interaction is discussed below.



(3)

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **4**, **5**, and **6** are consistent with the proposed structures. These spectra show double sets of signals of the CH_2N and $SiMe_2$ groups. The low-field positions of the signals in the ^{29}Si NMR spectra of compounds **5** and **6** (δ_{Si} ~19—28, see the Experimental section) are indicative of the absence of the intramolecular O→Si interaction in the liquid phase. For example, the signals for the silicon atoms in (O—Si)-chelate *N*,*N*-bis(fluorodimethylsilylmethyl)acetamide $MeC(O)N(CH_2SiMe_2F)_2$ are observed at δ_{Si} −23.5 (Si^V) and 29.0 (Si^{IV}).[7] Hence, the spectral patterns of compounds **4**, **5**, and **6** may be associated with hindered amide rotation in the molecules of these compounds. Earlier, this effect has been observed for *N*-acylated 2,6-disilamorpholines[1] and -piperazines.[5]

X-ray diffraction study of compounds 4, 5, and 6. Related compounds **4**, **5**, and **6** contain the following identical or analogous molecular fragments: the bicyclic fragment *A* and the $—CH_2SiMe_2X(1)$ groups (*B* and *C*, where X(1) = F(1) or Cl(1)). These fragments are linked by the planar-coordinated N(1) atom (Figs 1 and 2). Therefore, the overall conformations of the molecules can be described by several torsion angles listed in Table 1. Molecule **4** is more rigid than analogs **5** and **6**, because the groups *B* and *C* in **4** are involved in the six-membered oxaazadisilinane ring. In all three compounds, the bicyclic fragments *A* adopt virtually identical conformations, as evidenced by the corresponding torsion angles ψ_7 and ψ_8 (see Table 1). The six-membered boron-containing ring adopts a sofa conformation with the boron atom deviating from the C(7)C(8)C(9)O(2) plane (planar within 0.03 Å) by 0.80, 0.76, and 0.78 Å in molecules **4**, **5**, and **6**, respectively. In these molecules, the torsion angles ψ_1 and ψ_2, which determine the twist of the planes of the substituents at the N(1) atom with respect to the plane of the bicyclic fragment, have also nearly equal values, analogs **5** and **6** being characterized by the smallest differences in these angles. The groups *B* and *C* in molecules **5** and **6** are highly labile, due to which the three-dimensional structure of **5** differs from that of analog **6**. The orientations of the group *C* with respect to the plane of the substituents at the N(1) atom and the plane of the bicyclic fragment *A* in compound **5** are similar to those in **6** (difference in the angle ψ_4 in these molecules is 13°). The orientations of the $Me_2X(2)Si(2)$ fragment relative to the NCSi(2) plane (rotation about the C—Si bond) in **5** and **6** differ by 27° (angles ψ_6). Let us mention the factors, which could in-

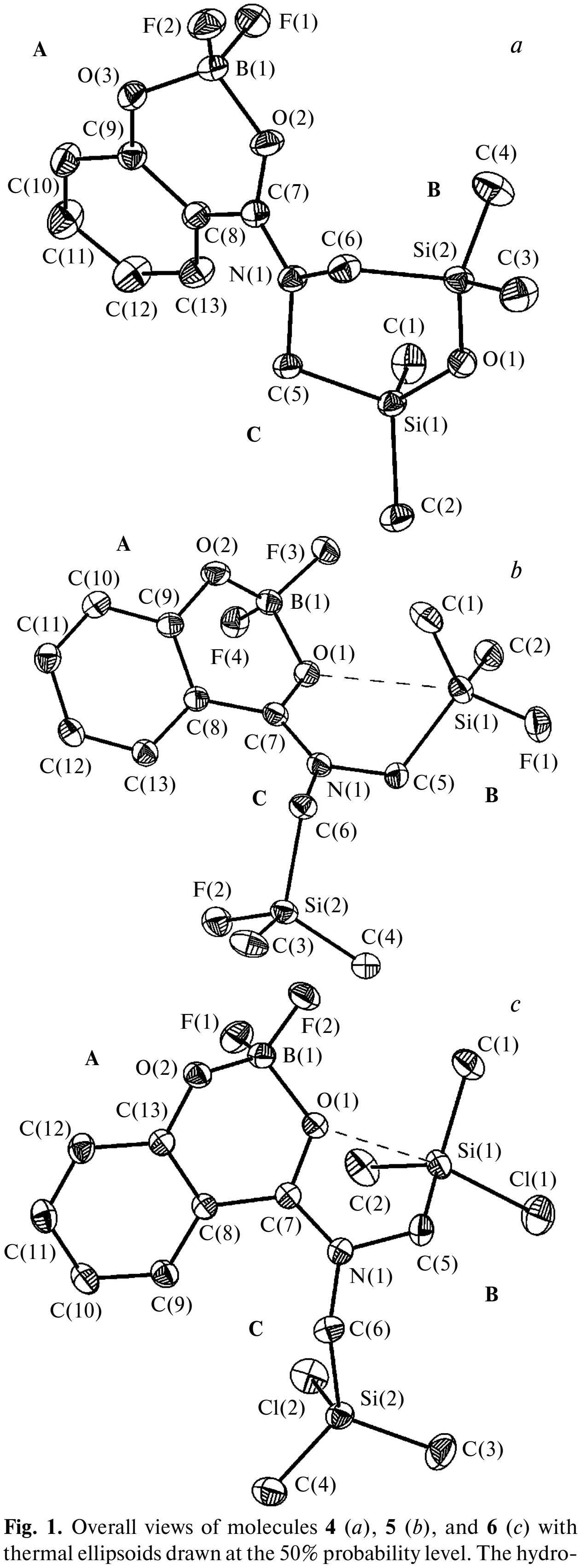


Fig. 1. Overall views of molecules **4** (*a*), **5** (*b*), and **6** (*c*) with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

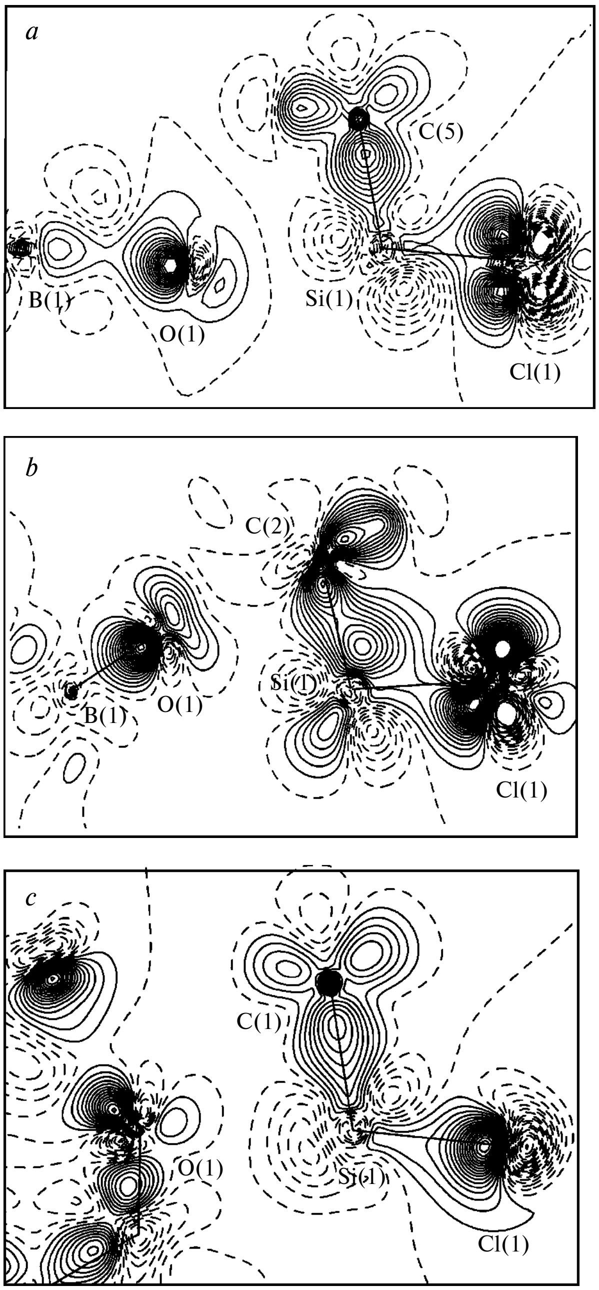


Fig. 2. Experimental deformation electron density (DED). Sections through the O(1)Si(1)C plane and the plane involving the C=C(5), C(2), and C(1) atoms. Positive contours (electron density accumulation) are solid, and negative contours (electron density depletion) are dashed. The maps are contoured at 0.05 e Å^{-3} intervals.

fluence the conformation of the fragment *C* in molecules **5** and **6**. In compound **5**, the observed conformation of the group *C* is, apparently, determined by the short F(2)...H(13)C(13) contact (2.25 Å). In molecule **6**, the corresponding Cl(2)...H(3)C(9) distance is 3.2 Å, *i.e.*, it is noticeably larger than the sum of the van der Waals radii of the H and Cl atoms (3.0 Å).[11] Therefore, the confor-

Table 1. Torsion angles (ψ) characterizing the conformations of molecules **4**, **5**, and **6**

Angle	ψ/deg		
	4	**5**	**6**
O(1)—C(7)—N(1)—C(5) (ψ_1)	—	−5.4	−6.4
O(2)—C(7)—N(1)—C(6) (ψ_1)	0.3	—	—
O(1)—C(7)—N(1)—C(6) (ψ_2)	—	166.8	157.0
O(2)—C(7)—N(1)—C(5) (ψ_2)	177.9	—	—
C(7)—N(1)—C(5)—Si(1) (ψ_3)	—	61.9	−48.6
C(7)—N(1)—C(6)—Si(2) (ψ_4)	—	111.8	122.7
N(1)—C(5)—Si(1)—F(1) (ψ_5)	—	130.8	—
N(1)—C(5)—Si(1)—Cl(1) (ψ_5)	—	—	−139.9
N(1)—C(6)—Si(2)—F(2) (ψ_6)	—	−54.3	—
N(1)—C(6)—Si(2)—Cl(2) (ψ_6)	—	—	−28.7
C(9)—C(8)—C(7)—O(1) (ψ_7)	−28.4	−25.3	—
C(13)—C(8)—C(7)—O(1) (ψ_7)	—	—	−22.4
C(8)—C(7)—O(1)—B(1) (ψ_8)	—	12.1	5.4
C(8)—C(7)—O(2)—B(1) (ψ_8)	9.6	—	—

mation of this moiety in the molecules depends substantially on intermolecular interactions.

The arrangement of the groups *B* in molecules **5** and **6** differs from that of the groups *C*. In molecules **5** and **6**, the Si(1) atoms deviate in opposite directions from the O(1)C(7)N(1)C(5) plane (torsion angles ψ_3, see Table 1), the overall configuration of the fragment being similar in both molecules (deviations of the Si(1) atom are 1.44 and −1.36 Å, respectively). In both molecules, the Si(1)...O(1) distance is smaller than the sum of the van der Waals radii of these atoms (3.5 Å)[11] by more than 0.5 Å. The average value of the C—Si—C bond angles is 113.9° (in the groups *C*, the corresponding average angle is 111.3°). The F(1) and Cl(1) atoms are in the vicinity of the Si(1)...O(1) line; the O...Si—X angles are larger than 160° (Tables 2 and 3). In addition, the Si—X bonds in the groups *B* are elongated, although insignificantly, compared to the analogous bonds in the groups *C*. The above-mentioned characteristic features are indicative of the occurrence of a weak O...Si interaction in molecules **5** and **6**.

The geometric parameters of the slightly distorted trigonal-bipyramidal environment about the Si(1) atoms in the structures of **5** and **6**, *viz.*, the Si(1)...O(1) distances and the deviations $\Delta\Omega$ of the solid angle formed by the equatorial Si—C bonds of the Si(1) atoms from 2π (latter value corresponds to the symmetrical hypervalent O—Si—Hal bond), agree well with the empirical relationship between these parameters revealed for pentacoordinate silicon compounds.[12]

This type of interactions for two-coordinate O atoms was observed for the first time. However, it is known that these atoms can be additionally coordinated by various

Table 2. Selected bond lengths and bond angles in molecules **4**, **5** (X = F), and **6** (X = Cl)

Parameter	Crystal			Isolated molecule (MPW1PW91/6-311G(d) calculations)	
	4	**5**	**6**	**5**	**6**
Bond		*d*/Å			
Si(1)...O(1)	—	2.918(2)	2.831(1)	2.990	2.816
Si(1)—X(1)	—	1.620(1)	2.084(1)	1.642	2.117
Si(1)—X(2)	—	1.608(1)	2.0629(9)	1.634	2.083
B(1)—O(1)	—	1.523(2)	1.521(2)	1.553	1.553
B(1)—O(2)	1.518(2)	—	—	—	—
B(1)—O(2)	—	1.448(2)	1.447(2)	1.461	1.457
B(1)—O(3)	1.442(2)	—	—	—	—
Si—C$_{\text{mean}}$	1.866	1.864(2)	1.864(2)	1.875	1.881
O(1)—C(7)	1.302(2)	1.305(2)	1.301(1)	1.282	1.282
C(13)—O(2)	1.346(2)	1.345(2)	1.347(1)	1.282	1.282
B—F$_{\text{mean}}$	1.381	1.380(2)	1.386(2)	1.368	1.369
N(1)—C(7)	1.318(2)	1.312(2)	1.315(1)	1.333	1.333
Si(1)—O(1)	1.6397(9)	—	—	—	—
Si(2)—O(1)	1.641(1)	—	—	—	—
Angle	ω/deg				
O(1)—Si(1)—X(1)	—	162.7(2)	162.8(1)	158.7	162.3
O(1)—B(1)—O(2)	—	109.8(1)	109.32(9)	106.7	106.4
O(1)—B(1)—O(3)	109.2(1)	—	—	—	—
C—Si(1)—X(1)	—	104.73(7)	108.89(7)	105.5	104.26
X(2)—Si(2)—C	—	107.37(7)	107.77(6)	107.00	108.07
C—Si(1)—C	110.68(7)	113.74(8)	113.95(7)	113.10	113.87
C—Si(2)—C	110.76(8)	111.46(8)	111.08(7)	111.80	110.80
Si(1)—O(1)—Si(2)	130.79(6)	—	—	—	—

Table 3. Topological parameters of molecules **5** and **6** in the crystals and in the isolated state

Bond	Crystal **6**	MPW1PW91/6-311G(d)	
		5	**6**
		$\rho(r)$/e • Å^{-3}	
Si(1)—X(1)	0.72	0.78	0.59
Si(2)—X(2)	0.78	0.81	0.63
Si—C	0.98	0.83	0.77
B(1)—O(2)	0.95	0.81	0.82
B(1)—O(1)	1.04	1.07	1.16
		$\nabla^2\rho(r)$/e • Å^{-5}	
Si(1)—Cl(1)	−1.39	20.97	3.95
Si(2)—Cl(2)	−1.80	21.77	4.60
Si—C	−5.80	5.12	4.61
B(1)—O(2)	10.38	10.85	10.82
B(1)—O(1)	16.84	13.98	22.14
		$E^e(r)$/H • Å^{-3}	
Si(1)—Cl(1)	−0.50	−0.13	−0.32
Si(2)—Cl(2)	−0.60	−0.13	−0.34
Si—C	−0.91	−0.50	−0.48
B(1)—O(1)	−0.50	−0.51	−0.53
B(1)—O(2)	−0.47	−0.79	−0.73

cations in directions corresponding to the O...Si bonding vector in compounds **5** and **6**, although these directions are not favorable.[13] They could become more favorable due, apparently, to asymmetry of the O(1)—B(1) and O(1)—C(7) bonds. The former bond is substantially elongated (~1.52 Å) compared to the standard value (1.47 Å) for the tetracoordinate B atom, whereas the latter bond length (see Table 2) is typical[14,15] of compounds bearing a boron-containing ring of this type. One cannot make an unambiguous conclusion about the presence of an interaction between the Si(1) and O(1) atoms based only on the structural data. Hence, we carried out quantum-chemical calculations of isolated molecules **5** and **6** using the density functional theory (MPW1PW91/6-311G(d)) and performed high-precision X-ray diffraction study of the crystal of compound **6**.

Electronic structures of compounds 5 and 6. Quantum-chemical calculations demonstrated that the structures of isolated molecules **5** and **6** are similar to those in the crystals (see Table 2). The calculated geometry of the coordination unit of the Si(1) atom agrees, on the whole, well with the experimental data. The Si(1)...O(1) interatomic distance in dichloride **6** is even somewhat shorter than the experimental value. This fact is unexpected because the Si...O(N) interatomic distances in isolated molecules of five- and six-membered monochelates and silatranes are substantially longer than the corresponding distances in their crystals.[16—18]

The results of study of the electronic structures of compounds **5** and **6** are of most interest. We used the topological theory known as "Atoms in Molecules" (AIM), which was developed by Bader,[19] as the main theoretical approach. This method is based on the topological analysis of the calculated or experimental electron density distribution $\rho(r)$ and allows one not only to demonstrate the presence of interaction between atoms but also to reveal its nature and estimate its strength.[20—24] The experimental electron density function was reproduced from the results of high-precision X-ray diffraction study of the crystal of **6**. The functions $\rho(r)$ of isolated molecules **5** and **6** were calculated by the quantum-chemical MPW1PW91/6-311G(d) method.

Qualitative analysis of the character of chemical bonds in the crystal of **6** using sections of the experimental deformation electron density (DED, see Fig. 2) showed that its accumulation on the Si(1)...O(1) line is at most 0.1 e Å^{-3}. This is indicative of the fact that none of the electron pairs of the O(1) atom is localized on the Si(1)...O(1) line. The DED maxima corresponding to the lone pairs of the O(1) atom are located at an angle of approximately 35° with respect to the Si(1)...O(1) line. Therefore, these lone pairs together with the B(1)—O(1) and C(7)—O(1) bonds form an imaginary tetrahedron.

Topological analysis of the functions $\rho(r)$ (see Table 3) in the crystal of **6** and isolated molecules **5** and **6** revealed the presence of the critical points (CP) (3, −1) in the regions of all the expected bonds. The critical points CP (3, −1) for the C—C, N—C, and O—C bonds are characterized by negative values of the Laplacian of the electron density $\nabla^2\rho(r)$ and the local electron energy density $E^e(r)$, which corresponds to shared (covalent) interactions in terms of the AIM theory. The Si—F and B—O bonds correspond to interactions of an intermediate type ($\nabla^2\rho(r) > 0$, $E^e(r) < 0$ at CP (3, −1)), which is consistent with the calculated data for organometallic compounds containing such bonds.[19,20]

The electron densities $\rho(r)$ and $E^e(r)$ at the CPs (3, −1) for the Si(1)—X(1) bonds in molecules **5** and **6**, which serve (according to the AIM theory) as criteria of the strength of interatomic interactions, are substantially lower that those at the CPs (3, −1) for the Si(2)—X(2) bonds. Therefore, the analysis of the topological characteristics of the Si(1)—X(1) and Si(2)—X(2) bonds confirms the assumption (which was based on the analysis of these bond lengths) that the Si(1)—X(1) bond is weaker compared to the Si(2)—X(2) bond. Presumably, this weakening is associated with the presence of the intramolecular O(1)→Si(1) coordination bond in compounds **5** and **6**.

An interesting characteristic feature of the Si—C and Si—Cl bonds in dichloride **6** is that their CPs (3, −1) are located in the vicinity of the interface between the regions of electron density depletion and accumulation. In the crystals, the CPs (3, −1) for the Si—C and Si—Cl bonds fall in the region of accumulation of $\rho(r)$ ($\nabla^2\rho(r) < 0$), whereas these critical points in the isolated molecules are in the region of electron density depletion ($\nabla^2\rho(r) > 0$). In all cases, the sign of the local energy density is negative. Therefore, in the crystal the bonds under consideration correspond to shared interactions, whereas the calculated values correspond to interactions of an intermediate type. Analysis of the Si—C and Si—Cl bond lengths demonstrated that the calculated values are slightly larger than those determined from the experiment. Apparently, elongation of the calculated Si—C and Si—Cl bonds in molecule **6** leads to a shift of the corresponding CPs (3, −1) toward the region of electron density depletion and a change in the type of interactions.

The topological analysis revealed no CP (3, −1) on the Si(1)...O(1) line, which is indicative of the absence of the O(1)→Si(1) coordination bond in molecules **5** and **6**.

The latter fact does not contradict an elongation of the Si(1)—X(1) bond compared to the Si(2)—X(2) bond observed in molecules **5** and **6**. In dichloride **6**, the calculated dipole moment is very high (8.63 D), which is evidence that the positive and negative charges in this compound are localized on opposite sides of the molecule. An analogous charge distribution is observed in tetrafluoride **5**, in spite of the fact that its dipole moment is substantially smaller (3.6 D), which is attributable to the fact that the Si—F bond has a lower ability to be polarized compared to the Si—Cl bond. The Mulliken population analysis of the charge distribution (we did not use the more advanced NBO scheme because of restrictions imposed by the available software) demonstrated that the negative charge is accumulated in the region of the OBF_2O fragment (the charges for the O(1), O(2), and F atoms are, on average, −0.37, −0.32, and −0.26 e, respectively), whereas the silicon atoms bear the highest positive charges (aver., 1.15 e).

The short distance between the Si(1) atom and the OBF_2O fragment indicates that the intramolecular Coulomb interaction between these atoms is responsible for a substantial elongation of the Si(1)—X(1) bond compared to the Si(2)—X(2) bond.

To summarize, analysis of the electronic structures of molecules **5** and **6** and NMR spectroscopic study of these molecules showed that the intramolecular O(1)→Si(1) coordination interaction, which could be assumed based on the structure of the coordination unit of the silicon atom, is absent in these compounds.

Experimental

The IR spectra of solutions were recorded in KBr cells on a two-beam Specord IR-75 spectrometer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of solutions in $CDCl_3$ were measured on a Varian XL-400 spectrometer operating at 400.0, 100.6, and 79.5 MHz, respectively, with Me_4Si as the internal standard.

The synthesis of the starting 4-(2-hydroxybenzoyl)-2,2,6,6-tetramethyl-2,6-disilamorpholine (**3**) has been described earlier.[9]

(O—B)-Chelate 4-[2-(difluoroboroxy)benzoyl]-2,2,6,6-dimethyl-2,6-disilamorpholine (4). Boron trifluoride etherate (1.3 g, 9 mmol) was added dropwise to disilamorpholine **3** (4.0 g, 13.5 mmol), which was placed in a flask equipped with a dephlegmator, a thermometer, and a condenser. The reaction mixture was heated until elimination of the ether ceased and then cooled. Crystals were prepared by the addition of diethyl ether (10 mL). The yield of compound **4** was 2.1 g (45%), m.p. 167—170 °C (toluene). Found (%): C, 45.58; H, 5.83, N, 4.14. $C_{13}H_{20}BF_2NO_3Si_2$. Calculated (%): C, 45.48; H, 5.87; N, 4.08. IR ($CHCl_3$), ν/cm^{-1}: 1620 (NCO), 1600 (Ar). ^{1}H NMR ($CDCl_3$), δ: 0.17 and 0.26 (both s, 2 $SiMe_2$); 3.35 and 3.50 (both s, 2 CH_2); 6.85 (t), 7.09 (d), 7.52 (t), 7.55 (d) (4 H, H arom., $^3J_{H,H}$ = 8.3 Hz). ^{29}Si NMR ($CDCl_3$), δ: 8.8 and 11.7 (both s). Crystals of difluoride **4** suitable for X-ray diffraction study were grown by recrystallization from toluene.

(O—B)-Chelate 2-(difluoroboroxy)-*N*,*N*-bis(fluorodimethylsilylmethyl)benzamide (5). ***A.*** Boron trifluoride etherate (0.96 g, 6.8 mmol) was added dropwise to disilamorpholine **3** (2.0 g, 6.8 mmol), which was placed in a flask equipped with a dephlegmator, a thermometer, and a condenser. The reaction mixture was heated until elimination of the ether ceased and then cooled, after which benzene (5 mL) was added and compound **4** was obtained in a yield of 1.2 g (3.5 mmol), m.p. 168—171 °C (benzene). IR ($CHCl_3$), ν/cm^{-1}: 1620 (NCO), 1600 (Ar). The solvent was removed and the residue was crystallized by the addition of diethyl ether. Compound **5** was obtained in a yield of 0.5 g (1.4 mmol), m.p. 69—72 °C (diethyl ether). IR ($CHCl_3$), ν/cm^{-1}: 1620, 1585 (NCO), 1600 (Ar). ^{1}H NMR ($CDCl_3$), δ: 0.46 and 0.51 (both d, 2 $SiMe_2$, $^3J_{H,F}$ = 8.4 Hz); 3.34, 3.63 (both d, 2 CH_2, $^3J_{H,F}$ = 6.0 Hz); 6.97 (t), 7.18 (d), 7.54 (t), 7.55 (d) (4 H, H arom., $^3J_{H,H}$ = 8.3 Hz). ^{13}C NMR ($CDCl_3$), δ: −1.54 and –2.07 (both d, 2 $SiMe_2$, $^2J_{C,F}$ = 21.3 Hz); 45.89 and 46.54 (both d, 2 CH_2, $^2J_{C,F}$ = 29.1 Hz); 110.52, 119.35, 121.64, 127.68, 136.81, 161.58 (C arom.); 166.21 (C=O). ^{29}Si NMR ($CDCl_3$), δ: 26.8 (d, $^1J_{Si,F}$ = 287.1 Hz); 27.6 (d, $^1J_{Si,F}$ = 283.4 Hz). Found (%): C, 43.11; H, 5.45; N, 3.82. $C_{13}H_{20}BF_4NO_2Si_2$. Calculated (%): C, 42.74; H, 5.52; N, 3.83. Crystals of compound **5** suitable for X-ray diffraction analysis were grown from diethyl ether.

B. Boron trifluoride etherate (1.21 g, 8.5 mmol) was added dropwise to disilamorpholine **3** (1.5 g, 5.1 mmol). The reaction mixture was gradually heated to 165 °C and then cooled, after which benzene (5 mL) was added and the reaction mixture was brought to reflux. The benzene was removed from the filtrate and the residue was crystallized by adding diethyl ether. Compound **5** was obtained in a yield of 0.9 g (49%), m.p. 69—72 °C (diethyl ether). IR ($CHCl_3$), ν/cm^{-1}: 1620, 1585 (NCO), 1600 (Ar).

C. Boron trifluoride etherate (0.16 g, 1.16 mmol) was added dropwise to difluoride **4** (0.6 g, 1.75 mmol). The reaction mixture was slowly heated to 155 °C and then cooled, after which benzene (5 mL) was added and the reaction mixture was brought to reflux and filtered. The solvent was removed from the filtrate and the residue was crystallized by adding diethyl ether (2 mL). Tetrafluoride **5** was obtained in a yield of 0.4 g (63%), m.p. 69—72 °C (diethyl ether).

(O—B)-Chelate *N*,*N*-bis(chlorodimethylsilylmethyl)-2-(difluoroboroxy)benzamide (6). Freshly distilled thionyl chloride (0.25 g, 2.07 mmol) was added dropwise with stirring to a mixture of disilamorpholine **3** (0.6 g, 1.75 mmol) and anhydrous benzene (7 mL), the starting compound being dissolved. After one day, the crystals that precipitated were filtered off and compound **6** was obtained in a yield of 0.5 g (72%), m.p. 84—88 °C (benzene). ^{1}H NMR (CDCl$_3$), δ: 0.38 and 0.46 (both s, 2 SiMe$_2$); 3.38 and 3.59 (both s, 2 CH$_2$); 6.98 (t), 7.18 and 7.53 (both d), 7.57 (t) (4 H, H arom., $^3J_{\mathrm{H,H}}$ = 8.1 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.25 and 0.57 (both s, 2 SiMe$_2$); 47.67 and 49.98 (both s, 2 CH$_2$); 112.25, 118.99, 119.36, 128.01, 137.00, 162.87 (C arom.); 167.99 (C=O). ^{29}Si NMR (CDCl$_3$), δ: 19.1 and 24.6 (both s). Found (%): C, 38.67; H, 4.92; N, 3.16. $C_{13}H_{20}BCl_2F_2NO_2Si_2$. Calculated (%): C, 39.21; H, 5.06; N, 3.52. Crystals of compound **6** suitable for X-ray diffraction study were withdrawn directly from the reaction mixture.

Hydrolysis of 2-(difluoroboroxy)-*N*,*N*-bis(fluorodimethylsilylmethyl)benzamide (5). A sample of tetrafluoride **5** (0.3 g, 0.82 mmol) was stored in the presence of atmospheric moisture for half year, during which the melting point increased to 159—163 °C. After recrystallization of the product from benzene, disilamorpholine **3** was isolated in a yield of 0.2 g (71%), m.p. 165—168 °C (benzene); a mixed sample was characterized by m.p. 165—168 °C.

X-ray diffraction study of compounds 4, 5, and 6. The crystallographic parameters and principal details of X-ray diffraction study for compounds **4**, **5**, and **6** are given in Table 4. X-ray diffraction data sets were collected on Bruker Smart CCD 1000 (**4** and **5**) and Syntex P2$_1$ (**6**) diffractometers (Mo-Kα radiation). The structures of **4**, **5**, and **6** were solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were revealed from difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (version 5.10).[25]

Processing of the data from high-precision X-ray diffraction experiment and quantum-chemical calculations. The experimental electron density distribution in the crystal of compound **6** was determined by the multipole refinement of the X-ray diffraction data using the XD program package.[26] The refinement was carried out against F using 6461 reflections ($I > 4\sigma(I)$, $\theta_{\mathrm{max}} = 45°$). For all nonhydrogen atoms, the coordinates, thermal parameters, and multipole parameters up to the octupole level ($l = 3$) were refined, except for the O, Si and Cl atoms for which the multipole populations were refined up to hexadecapoles ($l = 4$). For the C(1) and C(2) atoms of the Me groups, the local C_{3v} symmetry was assigned. Before the refinement, the C—H distances were normalized to 1.07 Å, which corresponds to neutron diffraction data.[14] For the H atoms, only the dipole populations ($l = 1$) were refined, whereas the coordinates and thermal parameters were kept fixed. The maximum number of parameters involved in the multipole refinement was 528. The results of the multipole refinement were as follows: $R = 0.0337$, $wR = 0.0488$, GOF = 1.073 based on 6461 reflections with $I > 4\sigma(I)$. All calculations with full geometry optimization were performed using the Gaussian 98W program suite

Table 4. Main details of X-ray diffraction study and crystallographic parameters for compounds **4**, **5**, and **6**

Parameter	**4**	**5**	**6**
Molecular formula	$C_{13}H_{20}BF_2NO_3Si_2$	$C_{13}H_{20}BF_4NO_2Si_2$	$C_{13}H_{20}BCl_2F_2NO_2Si_2$
Molecular weight	343.29	365.29	398.19
T/K	110(2)	110(2)	148(2)
a/Å	8.3912(3)	9.3504(6)	7.435(3)
b/Å	10.3590(4)	9.5759(6)	9.292(3)
c/Å	19.0837(7)	11.2693(7)	14.140(5)
α/deg	90	112.238(1)	72.24(2)
β/deg	96.402(1)	91.401(1)	83.69(3)
γ/deg	90	109.811(1)	81.23(3)
V/Å^3	1648.5(1)	865.09(9)	917.4(6)
d_{calc}/g cm^{-3}	1.383	1.402	1.442
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2
2θ$_{\mathrm{max}}$/deg	63	60.0	90
F(000)	720	380	412
Scanning technique	ω	ω	θ/2θ
Number of measured reflections	18451	7326	9185
Number of independent reflections (R_{int})	5092 (0.059)	4889 (0.070)	8554 (0.032)
Number of observed reflections with $I > 2\sigma(I)$	3963	3935	7370
Number of parameters in refinement	279	288	288
Absorption coefficient/cm^{-1}	2.45	2.49	5.08
R_1 ($I > 2\sigma(I)$)	0.0434	0.0459	0.0446
wR_2	0.1264	0.1294	0.1320

(release A7)[27] employing the MPW1PW91 hybrid functional and the 6-311G(d) basis set. The topological analysis of the electron density distribution, which was extracted from the calculated data, was carried out using the EXTREME program.[28]

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