2,5-Bis(di-*tert*-butylhydroxysilyl)furan as a Host Molecule for Potassium Fluoride, H_2O, NH_3 and $MeNH_2$

Uwe Klingebiel,*[a] Peter Neugebauer,[a] Ilka Müller,[a] Mathias Noltemeyer,[a] and Isabel Usón[a]

Keywords: Silicon / Furan / Host-guest complexes / Structure elucidation

2,5-Bis(di-*tert*-butylfluorosilyl)furan reacts with potassium hydroxide in a 1:2 molar ratio to give 2,5-bis(di-*tert*-butylhydroxysilyl)furan, $O(CRCH)_2$ [R = $SiOH(CMe_3)_2$ (**1**)]. Compound **1** is very selective in its adduct formation and forms host-guest complexes in the presence of KF [**1**·1/2KF (**2**)], H_2O [**1**·H_2O (**3**)], NH_3 [**1**·NH_3 (**4**)] and $MeNH_2$ [**1**·$2MeNH_2$ (**5**)]. The host-guest complexes are stable at room temperature. Compound **4** is the first neutral ammonia cage that is stable up to 100 °C. The crystal structures of **2**, **3**, **4** and **5** have been determined.

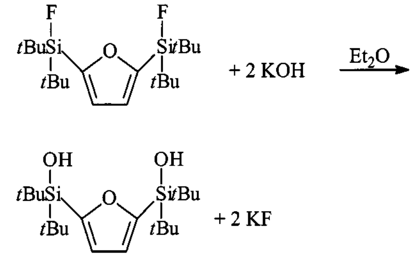
Introduction

Heterocycles such as furan undergo electrophilic aromatic substitution reactions very readily and regioselectively, with the 2-position being more reactive than the 3-position. On particular such reaction is metallation, particularly lithiation of a C−H group next to the oxygen atom. These lithium compounds are very reactive and combine with electrophiles such as fluorosilanes.[1] Recently, 2,5-bis(di-*tert*-butylfluorosilyl)furan was obtained from the reaction of dilithiated furan and $F_2Si(CMe_3)_2$ in a 1:2 molar ratio.[1] Fluorosilyl compounds are, like other halosilanes, excellent precursors for the synthesis of silylamines or silanols.[2] In view of the high acidity and the relatively high basicity of silanols[2] is to be expected that they will form strong hydrogen bonds both with themselves[2−5] and with other suitable species.[2] The association of silanols in solution has been discussed previously and a wide range of hydrogen-bonded structures has been found in the solid state.[2−5] The crystal structure of triphenylsilanol, for example, has 16 molecules in the unit cell, arranged as two sets of two independent tetrameric hydrogen-bonded units.[2,6] This tetrameric structure is retained in the adduct with ethanol, $(Ph_3SiOH)_4·EtOH$, which has a cyclic network of hydrogen bonds. Silanol is very selective in its adduct formation and also forms adducts with MeOH, DMSO and ethers.[2,7,8] Host-guest complexes between silanols and many organic liquids and solids are nicely summarized in ref. 2.

In this paper we describe the preparation of 2,5-bis(di-*tert*-butylhydroxysilyl)furan and its application as a host molecule for the gases NH_3 and $MeNH_2$, the liquid H_2O and the salt KF.

Results and Discussion

2,5-Bis(di-*tert*-butylfluorosilyl)furan[1] reacts with KOH in a 1:2 molar ratio to give 2,5-bis(di-*tert*-butylhydroxysilyl)furan.[1]



1

The reaction progress can be followed by ^{19}F NMR spectroscopy. Unreacted KF was separated by filtration and condensation of **1** into a cooled trap in vacuo (10^{-2} mbar) above 100 °C.

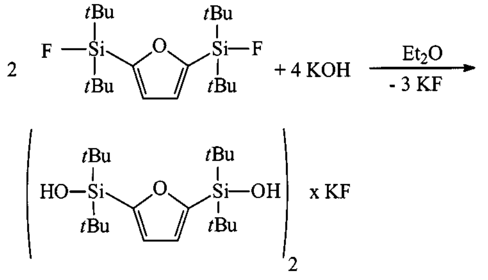
Attempts to crystallize **1** from the reaction mixture led to the isolation of the host-guest complex **2**, where two molecules of **1** coordinate one of KF.

Heating **2** in vacuo (10^{-2} mbar) above 100 °C leads to the condensation of **1** into the cold trap. The reaction is not reversible: we didn't succeed in preparing **2** from **1** and KF, perhaps because of the insolubility of KF in organic solvents.

---

[a] Institut für Anorganische Chemie der Georg-August-Universität Göttingen,
Tammannstraße 4, 37077 Göttingen, Germany
Fax: (internat.) +49-(0)551/393-373
E-mail: uklinge@gwdg.de

1434−1948/02/0303−0717 $ 17.50+.50/0



2

Crystal Structure of 2

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of **1** and half a molecule of potassium fluoride in the asymmetric unit i.e. the potassium atom is coordinated by two disilanol molecules. In this dimer, the coordination sphere of the potassium is quite unusual: six oxygen atoms and one fluorine atom coordinate to the cation to form a distorted hexagonal pyramid with the fluorine atom, which forms hydrogen bonds with two hydroxyl groups, at the axial position (Figure 1).

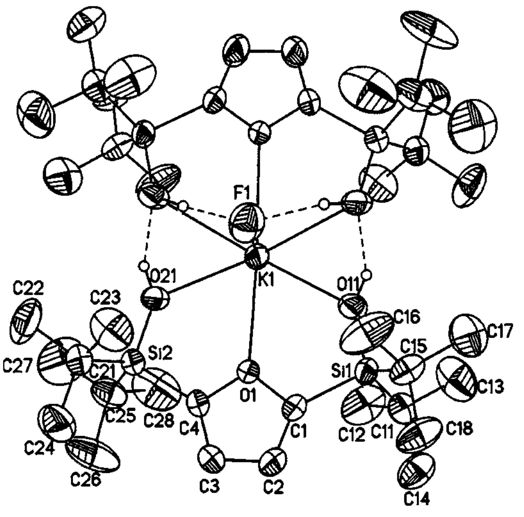
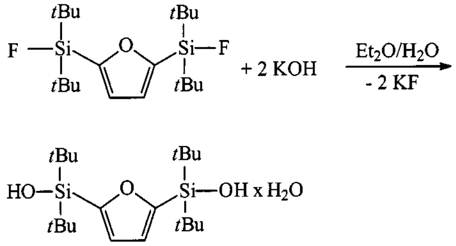


Figure 1. Structure of **2**

The potassium atom lies out of the base of the pyramid. This could be a result of the limited space in the dimer which does not allow the potassium and the fluoride atom to lie in the plane of the hydroxyl group. Another reason for the special arrangement of the potassium atom above the pyramid base could be the conflict between the attempts of the fluorine atom to build up hydrogen bonds and the minimum distance between the fluorine and potassium atoms.

As all oxygen atoms of the disilanol are coordinated to the potassium, the Si(1)−O(11) [Si(2)−O(21)] and the C(1)−O(1) [C(4)−O(1)] bonds are eclipsed. This induces stronger steric interactions between the methylene group C(2) and the *tert*-butyl substituents so that the Si(1)−C(1) and the Si(2)−C(4) bonds are lengthened.

Attempts to accelerate the formation of **1** by addition of water or to dissolve KF in order to purify **1** led to the formation of the host-guest complex **3**. Warming **3** in vacuo (10^{-2} mbar) up to 130 °C leads to the loss of water and reisolation of **1**. This process is reversible.



3

Crystal Structure of 3

In compound **3**, which crystallizes in the orthorhombic space group *F*dd2, one water molecule per disilanol molecule is incorporated in the crystal. One 2,5-bis(di-*tert*-butylsilyl)furan molecule and one water molecule form the asymmetric unit.

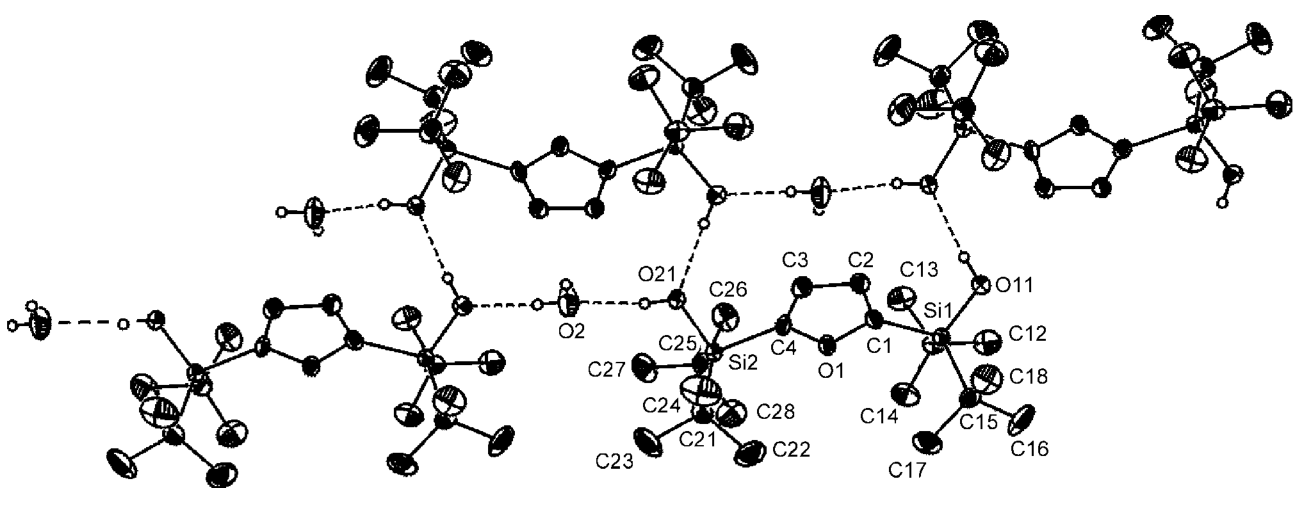


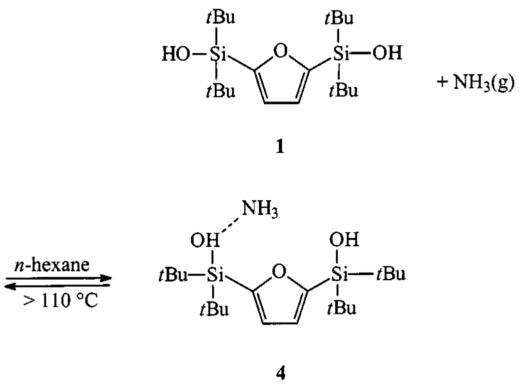
Figure 2. Structure of **3**

The disilanol molecules are arranged in zig-zag chains with hydrogen bonds between the hydroxyl groups. In these chains, a water molecule connects a monomer N, with monomer (N + 2), acting once as a hydrogen donor and once as an acceptor (Figure 2). One of the water hydrogen atoms is not involved in hydrogen bonding.

In order to minimize steric constraints, the distance between the *tert*-butyl groups at the silicon and the methylene groups of the furan is maximized. As a result, the Si(1)−O(11) [Si(2)−C(21)] and the C(1)−C(2) [C(4)−C(3)] bonds are arranged eclipsed. Due to this conformation, the oxygen atom that is part of the furan ring lies on the outer side of the zig-zag chain, and it does not form hydrogen bonds because of the shielding effect of the *tert*-butyl groups. In this way, the chains form tubes along the crystallographic *c*-axis with the hydrophobic groups on the outside and hydrophilic ones inside.

Ammonia and amines are well-known as ligands in complexes, where they generally undergo a formal Lewis acid-base interaction, with the nitrogen bound to the central metal atom or ion through its free electron pair.[10] The inclusion of gas molecules in salts or clathrates prepared under gas pressure or at low temperature has been reported,[11] although only one inclusion compound of dihydroxybinaphthyl containing ammonia and methanol as guest molecules is known.[12]

Having succeeded in isolating host-guest complexes of the bis(hydroxysilyl)furan **1** with the KF and water, we considered the possibility of the inclusion of gaseous amines such as NH_3 and $MeNH_2$. A solution of **1** in *n*-hexane was saturated with ammonia or methylamine at room temperature to give the host-guest compounds **4** or **5**, respectively. Compound **4** was obtained as colourless prisms with a melting point of 90 °C. TG and DTA studies show that **4** loses NH_3 above its melting point (90 °C), in two steps (at 100 °C and 110 °C), with reconversion of **1**.



Crystal Structure of 4

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with one disilanol molecule and two ammonia molecules in the asymmetric unit. The hydroxyl groups of the disilanol monomers form hydrogen bonds with each other and with the ammonia molecules. Only two of the hydrogen atoms of each ammonia molecule participate in this hydrogen bonding (Figure 3). As in compound **2**, the Si1−O11 (Si2−O21) and the C1−O1 (C4−O1) bonds are eclipsed thus permitting formation of the dimer and causing the lengthening of the Si1−C1 (Si2−C4) bond.

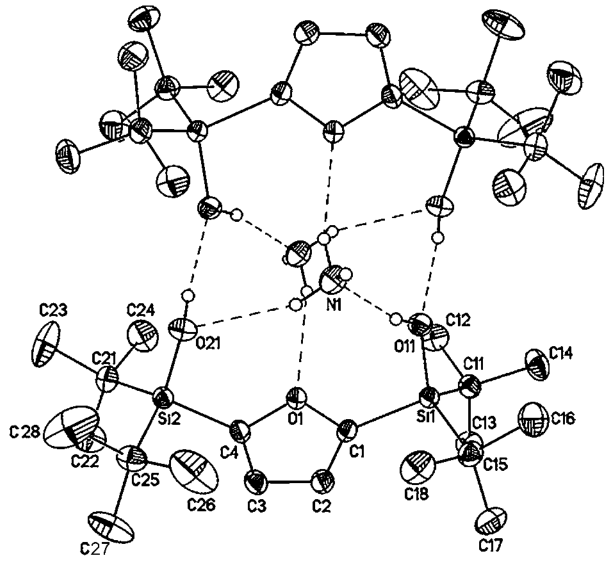
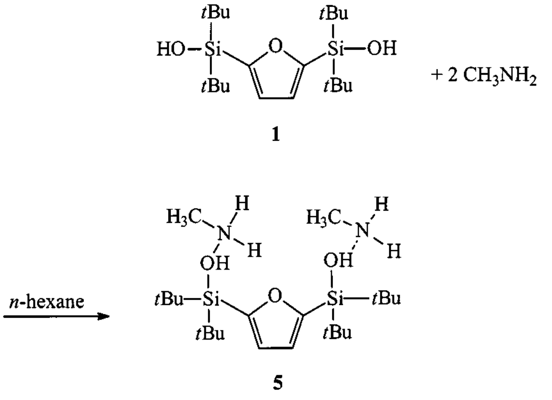


Figure 3. Structure of **4**

The host-guest complex **5**, obtained at room temperature, incorporates $MeNH_2$ in a molar ratio 1:2. It is far less stable than **4** and loses $MeNH_2$ when isolated from solution at room temperature.



Crystal Structure of 5

Crystals of compound **5**, which were not stable out of the mother liquor at room temperature, belong to the triclinic space group $P\bar{1}$. They contain one 2,5-bis(di-*tert*-butylsilyl)furan molecule and two methylamine molecules in the asymmetric unit (Figure). The disilanol monomers are connected to each other and the guest molecules through hydrogen bonds, forming a double chain. One of the methylamine molecules [$CH_3-N(1)H_2$] in the asymmetric unit connects opposite disilanol molecules through hydrogen bonds. The other one [$CH_3-N(2)H_2$] establishes these same contacts and an additional hydrogen bond to the next disilanol molecule along the chain. The hydrogen bonds

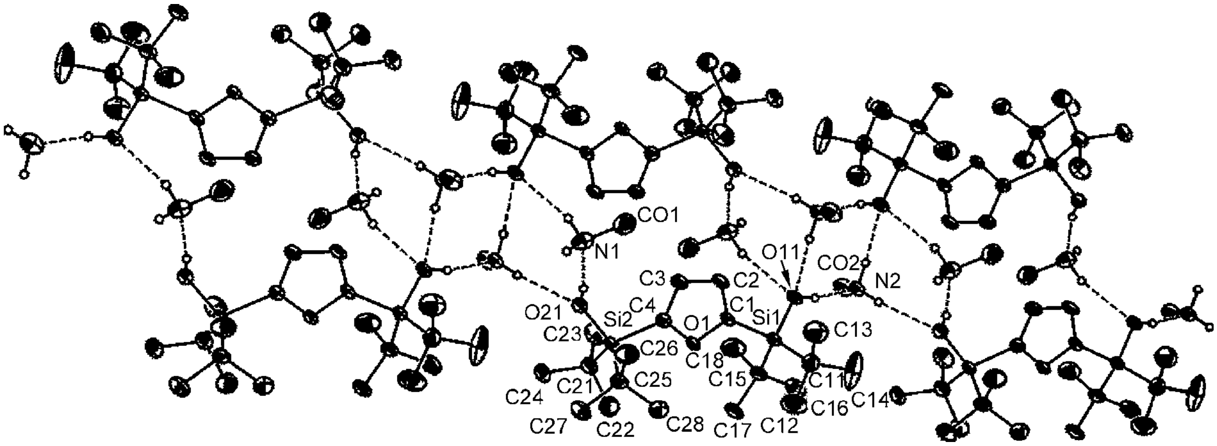


Figure 4. Structure of **5**

Table 1. Crystal data and data collections parameters for **2**, **3**, **4,** and **5**

	2	**3**	**4**	**5**
Empirical formula	$C_{40}H_{80}FKO_6Si_4$	$C_{20}H_{42}O_4Si_2$	$C_{40}H_{86}N_2O_6Si_4$	$C_{22}H_{50}N_2O_3Si_2$
Molecular weight	827.50	402.72	803.47	446.82
Temperature[K]	210(2)	150(2)	150(2)	133(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/c$	$Fdd2$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions [Å]	$a = 8.6035(12)$ $b = 23.927(8)$ $c = 12.6008(18)$ $\alpha = 90°$ $\beta = 104.771(13)°$ $\gamma = 90°$	$a = 23.872(9)$ $b = 32.482(3)$ $c = 12.834(3)$ $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$	$a = 12.8380(15)$ $b = 15.459(3)$ $c = 12.9418(15)$ $\alpha = 90°$ $\beta = 106.030(10)°$ $\gamma = 90°$	$a = 9.0380(18)$ $b = 12.529(3)$ $c = 13.712(3)$ $\alpha = 64.31(3)°$ $\beta = 80.20(3)°$ $\gamma = 88.36(3)°$
Volume [$Å^3$]	2508.2(10)	9951(4)	2468.6(6)	1377(5)
Z	2	16	2	2
Density (calculated) [Mg/m^3]	1.096	1.075	1.081	1.078
Absorption coefficient [mm^{-1}]	0.243	0.162	0.161	0.151
$F(000)$	904	3552	888	496
Crystal size [mm^3]	0.70 × 0.50 × 0.30	1.00 × 0.70 × 0.60	1.00 × 1.00 × 1.00	0.40 × 0.30 × 0.10
θ range for data collection	3.54 to 22.45°	3.55 to 24.95°	3.49 to 24.88°	2.29 to 25.99°
Reflections collected	4099	3373	8926	17419
Independent reflections	3234 [$R_{int} = 0.0436$]	3163 [$R_{int} = 0.0488$]	4275 [$R_{int} = 0.0663$]	5386 [$R_{int} = 0.058$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3234/4/268	3163/5/259	4275/4/ 267	5386/6/294
Goodness-of-fit on F^2	1.065	1.050	1.073	1.065
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0453$ $wR2 = 0.1031$	$R1 = 0.0369$ $wR2 = 0.0958$	$R1 = 0.0348$ $wR2 = 0.0884$	$R1 = 0.0659$ $wR2 = 0.1703$
R indices (all data)	$R1 = 0.0594$ $wR2 = 0.1148$	$R1 = 0.0390$ $wR2 = 0.0984$	$R1 = 0.0380$ $wR2 = 0.0907$	$R1 = 0.0808$ $wR2 = 0.1875$
Largest diff. peak and hole [$e \cdot Å^{-3}$]	0.259 and −0.202	0.272 and −0.189	0.274 and −0.228	0.836 and −0.736

formed by the first methylamine are longer than those formed by the4 ammonia molecule in compound **4**. The second methylamine molecule interacts more strongly with the disilanol than with the ammonia molecule (Table 2). The instability of the crystals of compound **5** could be a consequence of the formation of only two hydrogen bonds by one of the methylamine moieties instead of the three that are possible.

As in compound **2**, the Si(1)−O(11) and Si(2)−O(21) bonds are eclipsed to the C(1)−C(2) and C(4)−C(3) bonds, respectively, to avoid steric hindrance between the furan methylene groups and the *tert*-butyl groups. The difference between the Si(1)−O(11) and Si(2)−O(21) bond lengths is 0.01 Å, whereas the same bonds in compounds **2−4** are equal within the experimental error. As the oxygen atom O(11) is part of three hydrogen bonds and O(21) participates only in two hydrogen bonds, the Si(2)−O(21) bond is shorter than the corresponding Si(1)−O(11) bond.

Comparison of the Crystal structures of 2, 3, 4, and 5

The crystallographic data of compounds **2** to **5** are summarized in Table 1 and selected bond lengths and angles are given in Table 2.

Table 2. Comparison of selected bond lengths [Å] and angles [°] of **2**, **3**, **4** and **5**

	2	**3**	**4**	**5**
Si1−O11	1.618(2)	1.653(2)	1.6350(11)	1.6349(18)
Si2−O21	1.623(2)	1.652(2)	1.6304(11)	1.6246(18)
Si1−C11	1.890(3)	1.896(3)	1.8974(16)	1.898(3)
Si1−C15	1.891(3)	1.888(3)	1.9006(16)	1.897(3)
Si2−C21	1.890(3)	1.899(3)	1.8917(16)	1.891(3)
Si2−C25	1.884(3)	1.894(3)	1.8935(16)	1.896(3)
Si1−C1	1.875(3)	1.860(3)	1.8803(15)	1.861(2)
Si2−C4	1.878(3)	1.871(3)	1.8830(15)	1.867(2)
O11−Si1−C1	106.13(13)	105.08(12)	107.54(6)	101.33(10)
O11−Si1−C11	107.67(14)	109.06(11)	106.38(7)	108.89(11)
O11−Si1−C15	109.61(13)	106.95(12)	108.23(6)	110.41(11)
C11−Si1−C15	117.39(14)	116.88(12)	118.41(7)	116.33(12)
C11−Si1−C1	107.54(15)	110.34(13)	109.48(7)	108.40(11)
C15−Si1−C1	107.93(15)	107.84(12)	106.37(7)	110.41(11)
O21−Si2−C4	106.04(12)	100.07(12)	107.46(6)	107.84(10)
O21−Si2−C21	109.11(13)	111.30(12)	110.84(7)	104.60(11)
O21−Si2−C25	107.42(15)	108.35(13)	103.38(7)	110.49(10)
C21−Si2−C25	118.34(15)	117.36(12)	118.22(7)	117.20(12)
C21−Si2−C4	107.51(15)	107.12(12)	108.65(7)	108.96(11)
C25−Si2−C4	107.78(16)	111.28(13)	107.75(7)	106.45(11)
K1−F1	2.843(6)			
K1−O1	2.948(3)			
K1−O11	2.695(3)			
K1−O21	2.659(3)			
N1−C01				1.458(4)
N2−C02				1.463(4)

The X-ray analyses of **2**, **3**, **4**, and **5** show that the arrangement of the 2,5-bis(di-*tert*-butylhydroxysilyl)furan, which is the central structural element of all four structures, is mainly influenced by the guest molecule. In the case of compounds **2** and **4** the molecules form dimers that are held together by hydrogen bonds. Additionally, ionic interactions occur between potassium and the oxygen atoms of the disilanol in compound **2**. Again, hydrogen bonds between the guest molecules and the disilanol connect the monomers in compounds **3** and **5** to form long chains. Due to the arrangement of the silane molecules either as chains or as dimers in the crystals, the conformations of the silanol groups are different depending on the guest molecule.

Nevertheless, the bond lengths and angles of the disilanol molecules are very similar. The angles between the *tert*-butyl substituents at the silicon atoms are not tetrahedral but about 118° (**2:**118.34°; **3:** 116.88°; **4:** 118.41°; **5:** 116.33°) in all four structures to minimize steric hindrance. The geometry of the furan ring in these structures is identical within experimental error. As the four structures are not isostructural and the fixation of the different guest molecules is unique. Interatomic distances concerning hydrogen bonds between the monomers and guest molecules of **2** to **5** are given in Table 3.

Table 3. Interatomic distances concerning hydrogen bonds between the monomers and the guest molecules of compounds **2** to **5**

Compound **2**		
D−H···A	d(D···A)	<(DHA)
O(11)−H(11B)···O(21)#1	2.594(3)	147(8)
O(21)−H(21B)···O(11)#1	2.594(3)	142(8)
O(21)−H(21A)···F(1)#1	2.724(7)	170(7)
O(11)−H(11A)···F(1)#1	2.632(7)	172(8)
O(21)−H(21A)···O(1)	2.925(3)	110(6)
Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 2$		
Compound **3**		
O(11)−H(11)···O(21)#1	2.846(3)	171(3)
O(21)−H(21)···O(2)	2.759(4)	160(4)
O(2)−H(1)···O(11)#2	2.863(3)	175(4)
Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2, -y, z + 1/2$; #2 $x, y, z - 1$		
Compound **4**		
O(11)−H(11)···N(1)	2.6539(18)	165(3)
N(1)−H(2)···O(21)	3.2326(19)	153(2)
N(1)−H(3)···O(1)#1	3.3228(18)	162(2)
O(21)−H(21)···O(11)#1	2.6935(16)	166(2)
Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z + 2$		
Compound **5**		
O(11)−H(11)···N(2)	2.667(3)	169(3)
O(21)−H(21)···N(1)	2.723(3)	169(3)
N(1)−H(2)···O(11)#1	3.265(3)	165(3)
N(2)−H(3)···O(11)#2	3.130(3)	169(2)
N(2)−H(4)···O(21)#3	3.116(3)	170(3)
Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z$; #2 $-x + 1, -y + 2, -z$; #3 $x, y + 1, z$		

Experimental Section

All experiments were performed under N_2. The NMR spectra were recorded in $CDCl_3$ with $SiMe_4$ as internal references. The mass spectrum of **1** was obtained with a Finnigan MAT 8200.

2,5-Bis(di-*tert*-butylhydroxysilyl)furan (1): 2,5-Bis(di-*tert*-butylfluorosilyl)furan (3.9 g, 0.01 mol) was added to a suspension of KOH (1.1 g, 0.02 mol) in Et_2O (200 mL) and the resulting mixture was stirred for 24 h. Separation of KF by filtration and condensation of the raw product into a cooled trap in vacuo (10^{-2} mbar) gave **1**. Yield: 98% (3.8 g), m.p. 95 °C. ^1H NMR ($CDCl_3$): δ = 1.04 (s, 36 H, CH_3), 1.63 (br. s, 2 H, OH), 6.78 (s, 2 H, 3-H, 4-H). ^{13}C NMR: δ = 20.00 [s, $C(CH_3)_3$], 27.29 [s, $C(CH_3)_3$], 121.16 (s, 3-H, 4-C), 161.0 (s, 2-C, 5-C). ^{29}Si NMR: δ = 1.08 (s). MS (EI): *m*/*z* (%) = 384 (15) $[M]^+$, 327 (100) $[M - C_4H_9]^+$. $C_{20}H_{40}O_3Si_2$ (384.70): calcd. C 62.96, H 10.48; found C 63.15, H 10.64.

2,5-Bis(di-*tert*-butylhydroxysilyl)furan Potassium Fluoride Adduct (2): The synthesis of **2** was performed analogously to the synthesis of **1**. Compound **2** crystallized out of the reaction mixture at room temperature. Yield: 35% (1.4 g), m.p. > 260 °C (decomposition). $C_{40}H_{80}FKOSi_4$ (827.51): calcd. C 58.54, H 9.74; found C 59.02, H 10.05.

2,5-Bis(di-*tert*-butylhydroxysilyl)furan-hydrate (3): The synthesis of **3** was performed analogously to the synthesis of **2** in aqueous KOH solvent (5% H_2O in Et_2O). Compound **3** crystallized from the reaction solvent. Yield: 61% (2.5 g), m.p. 90 °C. $C_{20}H_{42}O_2Si_2$ (402.72): calcd. C 61.15, H 10.51; found C 61.02, H 10.38.

2,5-Bis(di-*tert*-butylhydroxysilyl)furan-ammoniate (4): A solution of **1** (1.9 g, 0.005 mol) in *n*-hexane (150 mL) was saturated with ammonia. Compound **4** crystallized as colourless prisms from the reaction mixture. Yield: 65% (2.6 g), m.p. 90 °C. $C_{20}H_{43}NO_3Si_2$ (401.73): calcd. C 60.29, H 10.79; found C 60.51, H 11.02.

2,5-Bis(di-*tert*-butylbutylhydroxysilyl)furan-methylamine (5): The synthesis of **5** was performed similarly to the synthesis of **4**, with $MeNH_2$ instead of NH_3. Yield: 20% (0.9 g). $C_{22}H_{50}N_2O_3Si_2$ (446.82): calcd. 59.14, H 11.28; found C 58.85, H 11.01.

X-ray Crystallographic Study: Crystals were mounted on a glass fibre in a rapidly cooled perfluoropolyether.[12] Data for compounds **3** and **4** were collected at 150(2) K, and data for compound **2** were collected at 210(2) K. The diffraction data of compounds **3** and **4** were collected on a Stoe AED2 four circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å).

The diffraction data of compound **5** were collected on a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area-detector at 133(2) K, with graphite-monochromated Mo-K_α radiation. The small, air-sensitive, plate-shaped crystals of **5** showed weaker diffraction than those of compounds **2**−**4**. This accounts for the somewhat higher values of the *R* factors obtained.

The structures were solved by direct methods using SHELXS-97[14] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the methyl groups of the *tert*-butyl ligands and the hydrogen atoms on the methylene groups of the furan ring were included in the model at geometrically calculated positions and refined using a riding model. The positions of the hydrogen atoms of the hydroxyl groups were located in the difference electron density map and the O−H bond lengths were restrained to be about 0.84 Å for compounds **3**, **4** and **5** and about 0.83 Å for compound **2**.

The structure of compound **3** is racemically twinned in the space group *Fdd*2.

In compound **2**, the position of the host molecule KF is only half occupied. Because of that the potassium fluoride molecule in the dimer is allowed to occupy one of two symmetry-related positions. As the formation of the hydrogen bonds depends on the orientation of the KF in the dimer, two half-occupied positions for the hydrogen atoms were refined as described above with an occupancy of 50%.

The unusual coordination sphere of the potassium atom (coordinated to the disilanol molecule and the fluorine atom, with the potassium above the base of a hexagonal pyramid) indicated the presence of a solvent molecule coordinated to the cation. However, residual electron density was not found near the cation and the packing of the dimers in the crystal does not allow enough space for additional ligands at the potassium.

CCDC-166872 (**2**), CCDC-166871 (**3**), CCDC-166873 (**4**) and CCDC-166874 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Fonds der Chemischen Industrie for financial support of this work.

---

[1] P. Neugebauer, U. Klingebiel, M. Noltemeyer, *Z. Naturforsch. B, Chem. Sci.* **2000**, *55*, 913.

[2] P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 14.

[3] L. King, A. C. Sullivan, *Coord. Chem. Rev.* **1999**, *6*, 1.

[4] U. Klingebiel, S. Schütte, D. Schmidt-Bäse, *The Chemistry of Inorganic Ring Systems* (Ed.: R. Steudel) Elsevier, Amsterdam, **1992**.

[5] R. Murugavel, M. Bhattacharjee, H. W. Roesky, *Appl. Organomet. Chem.* **1999**, *13*, 227.

[6] H. Puff, K. Braun, H. Reuter, *J. Organomet. Chem.* **1991**, *409*, 119.

[7] S. A. Bourne, L. R. Nassimbeni, K. Skobridis, E. Weber, *J. Chem. Soc., Chem. Commun.* **1991**, 228.

[8] E. Weber, K. Skobridis, I. Goldberg, *J. Chem. Soc., Chem. Commun.* **1989**, 1195.

[9] E. A. Babaian, M. Huff, F. A. Tibbals, D. C. Hrneir, *J. Chem. Soc., Chem. Commun.* **1990**, 306.

[10] C. Stanley, E. Livingstone, *Compr. Inorg. Chem.* **1973**, *3*, 1330.

[11] J. L. Atwood, J. E. D. Davies, D. D. Mac Nicol, *Inclusion Compounds, Vol. 1*, Academic Press Inc., London Ltd., **1984.**

[12] F. Toda, K. Tanaka, M. C. Wong, T. C. W. Mak, *Chem. Lett.* **1987**, 2069. D. J. Chadwick, C. Willbe, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 887.

[13] T. Kottke, D. Stalke, *J. Appl. Cryst.* **1993**, *26*, 615.

[14] SHELXS-97, Program for structure solution. Release 97−2. © G. M. Sheldrick, **1986−1997**.

[15] SHELXL-97, Program for structure refinement. Release 97−2. © G. M. Sheldrick, **1986−1997**.

Received August 23, 2001
[I01326]