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Synthesis and Structural Characterization of Neutral Hexacoordinate Silicon(IV) Complexes with SiO_2N_4 Skeletons

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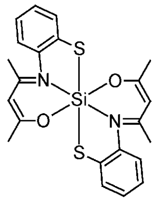
Abstract: A series of novel neutral hexacoordinate silicon(IV) complexes with SiO_2N_4 skeletons (compounds **4**–**8**) was synthesized and structurally characterized by single-crystal X-ray diffraction and solid-state NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si). The silicon(IV) complexes each contain two bidentate monoanionic O,N Schiff base ligands and two cyanato-*N* or thiocyanato-*N* ligands. Compounds **4**–**8** were prepared from $Si(NCO)_4$ or $Si(NCS)_4$, whereby the complex formation involved some unexpected chemical transformations of the ligands.

Keywords: coordination chemistry · hexacoordination · N,O ligands · silicon · X-ray diffraction

Introduction

In a series of recent publications, we have reported on the synthesis and structural characterization of the first pentacoordinate silicon(IV) complexes with Si–S bonds.[1] Quite recently, we have also demonstrated that hexacoordinate silicon(IV) complexes with Si–S bonds, such as compounds **1**–**3**, can be synthesized.[2] The neutral silicon(IV) complex **1** ($SiS_2O_2N_2$ skeleton), with its two tridentate dianionic S,N,O ligands, was obtained by treatment of tetra(cyanato-*N*)silane with two molar equivalents of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)propan-2-one and four molar equivalents of triethylamine. The derivatives **2** and **3** were obtained analogously. To our great surprise, totally different products were obtained when these syntheses were performed in the absence of triethylamine. Herein, we report on the synthesis and structural characterization of the neutral hexacoordinate silicon(IV) complexes **4**–**8**. The studies reported in this paper were performed in context with our systematic investigations on higher-coordinate silicon compounds (for recent publications, see reference [3]; in this context, see also references [4] and [5]). Preliminary results of the studies reported here have already been presented elsewhere.[6]



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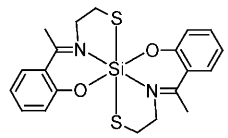

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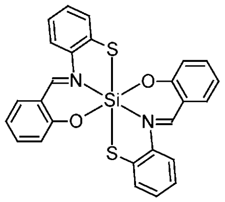

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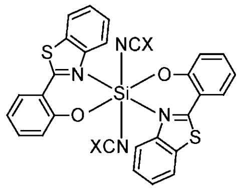
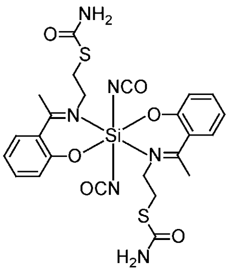


4: X = O
5: X = S



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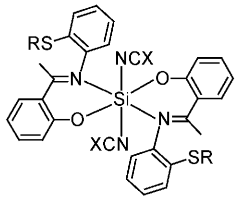

7: X = O, R = C(O)NH2
8: X = S, R = H

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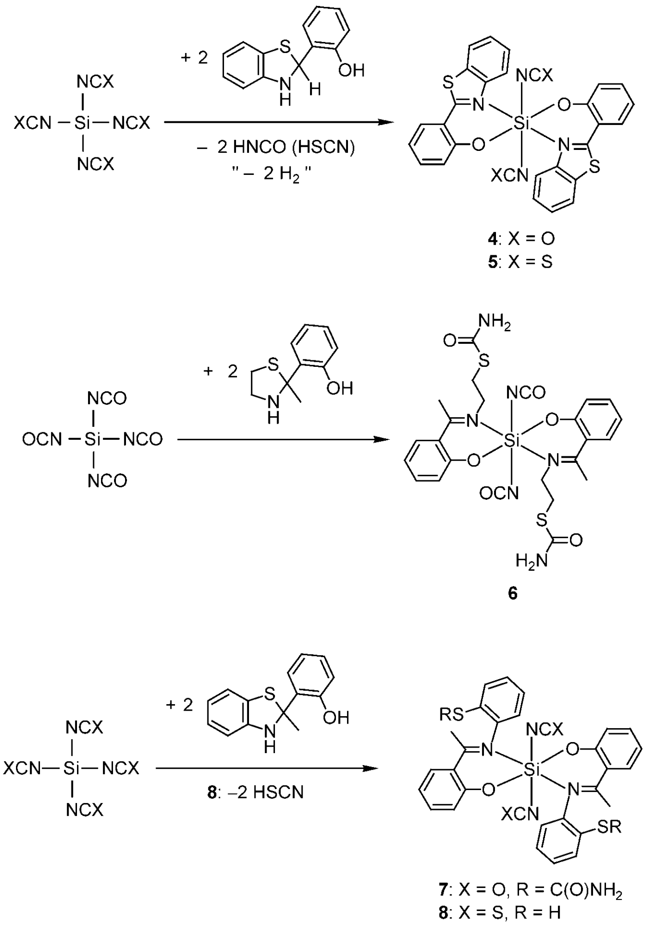
Results and Discussion

Syntheses

Compounds **4**–**8** were synthesized according to Scheme 1, starting from tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane, and were isolated as crystalline solids (**7** was obtained as the acetonitrile solvates **7**·2CH_3CN[7] (preparative scale) and **7**·4CH_3CN (single crystals for X-ray diffraction studies) (yields: **4**, 48 %; **5**, 39 %; **6**, 71 %; **7**·2CH_3CN, 32 %; **8**, 62 %). In principle, all these yields could be improved by reducing the volume of solvent used in the synthesis; however, this was only possible at the expense of crystal quality owing to fast crystallization of the products. All attempts at recrystallization failed owing to their poor solubility in common organic solvents.

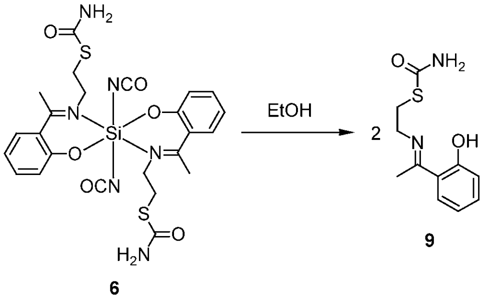


Scheme 1. Syntheses of compounds **4**–**8**.

Treatment of 2-(2,3-dihydrobenzothiazol-2-yl)phenol with tetra(cyanato-*N*)silane or tetra(thiocyanato-*N*)silane, in the absence of triethylamine, did not result in the formation of **3** ($SiS_2O_2N_2$ skeleton) as expected; instead, the silicon(IV) complexes **4** and **5** (SiO_2N_4 skeletons) were isolated. From a formal point of view, the formation of **4** (**5**) involves the elimination of HNCO (HSCN) and hydrogen. As a result of the (formal) hydrogen elimination, the bidentate monoanionic 2-(benzothiazol-2-yl)phenolato ligand is formed. The mechanism of this redox chemistry, which was not observed in the presence of triethylamine,[2] is unclear.[8]

Treatment of tetra(cyanato-*N*)silane with 2-(2-methyl-1,3-thiazolidin-2-yl)phenol resulted in another surprise: Again, the expected product **2** ($SiS_2O_2N_2$ skeleton) could not be obtained. Instead, the silicon(IV) complex **6** (SiO_2N_4 skeleton) was isolated. However, in contrast to the treatment of tetra(cyanato-*N*)silane with 2-(2,3-dihydrobenzothiazol-2-yl)phenol (→**4**), the analogous treatment with 2-(2-methyl-1,3-thiazolidin-2-yl)phenol (→**6**) did not involve hydrogen elimination. Rather we observed the formation of a thiocarbamate group as part of the ligand system. This result might be explained by the coordination of the ring-opened isomer of 2-(2-methyl-1,3-thiazolidin-2-yl)phenol (in this context, see reference [2]) as a bidentate monoanionic O,N ligand and addition of the resulting HNCO to the free SH group. Treatment of tetra(cyanato-*N*)silane with 2-(2-methyl-2,3-dihydrobenzothiazol-2-yl)phenol resulted in an analogous reaction (formation of **7**). However, when using tetra(thiocyanato-*N*)silane instead of tetra(cyanato-*N*)silane, compound **8** (with an SH group as part of the ligand system) was formed. Obviously, the resulting HSCN does not react with the ligand system, contrary to what is observed in the case of HNCO.

The unexpected formation of compounds **6** and **7** suggested this chemistry could be useful as a method for the synthesis of thiocarbamates. To test this approach, **6** was treated with ethanol to generate the free ligand of **6**, compound **9** (64 % yield, Scheme 2). Demonstrating that the reaction sequence $Si(NCO)_4$→**6**→**9** is a synthetic method for the synthesis of the thiocarbamate **9**, starting from 2-(2-methyl-1,3-thiazolidin-2-yl)phenol, future studies would be necessary to evaluate the scope and applicability of this method.



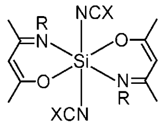
Scheme 2. Synthesis of compound **9**.

Compounds **4**–**6**, **7**·2CH_3CN, and **8** were characterized by elemental analyses (C, H, N, S), solid-state VACP/MAS NMR experiments (^{13}C, ^{15}N, ^{29}Si), and single-crystal X-ray diffraction studies (**7** was structurally characterized as the solvate **7**·4CH_3CN). Compound **9** was characterized by elemental analysis (C, H, N, S) and solution NMR spectroscopy (^{1}H, ^{13}C; solvent: $[D_6]DMSO$).

Crystal Structure Analyses

The crystal data and the experimental parameters for the crystal structure analyses of **4**–**6**, **7**·4 CH_3CN, and **8** are given in Table 1. The molecular structures in the crystal are shown in Figures 1–5; selected bond lengths and angles are given in the respective figure legends.

The Si-coordination polyhedra of **4**–**6**, **7**·4 CH_3CN, and **8** are slightly distorted octahedra, with the two NCX (X = O, S) ligands in *trans* positions. The two nitrogen atoms and the two oxygen atoms of the two bidentate O,N ligands each also occupy *trans* positions. The same stereochemistry has also been observed experimentally for the related compounds **10** and **11**, and the five possible stereoisomers of the model system **12** have been studied computationally.[3a] Except for in the case of **5**, the asymmetric units contain half a molecule. The Si–O distances of the compounds studied are in the range 1.7046(10)–1.7324(12) Å, and the Si–N (Si–NCX; X = O, S) distances range from 1.950(2) Å (1.8262(13) Å) to 1.9680(12) Å (1.8577(18) Å). All these



	X	R
10	O	Ph
11	S	Ph
12	O	Me

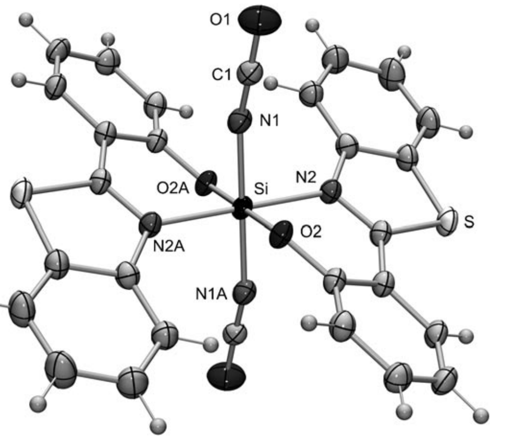


Figure 1. Molecular structure of **4** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O2 1.7324(12), Si-N1 1.8262(13), Si-N2 1.9668(14), N1-C1 1.1654(19), C1-O1 1.1898(19); O2-Si-O2A 179.999(1), O2-Si-N1 88.51(6), O2-Si-N1A 91.49(6), O2-Si-N2 89.31(6), O2-Si-N2A 90.69(6), N1-Si-N1A 180.00(9), N1-Si-N2 90.37(6), N1-Si-N2A 89.63(6), N2-Si-N2A 180.0, Si-N1-C1 158.77(13), N1-C1-O1 177.44(17).

Table 1. Crystallographic data for compounds **4**–**6**, **7**·4 CH_3CN, and **8**.

	4	**5**	**6**	**7**·4 CH_3CN	**8**
Empirical formula	$C_{28}H_{16}N_4O_4S_2Si$	$C_{28}H_{16}N_4O_2S_4Si$	$C_{24}H_{26}N_6O_6S_2Si$	$C_{40}H_{38}N_{10}O_6S_2Si$	$C_{30}H_{24}N_4O_2S_4Si$
Formula mass [g mol^{-1}]	564.66	596.78	586.72	847.01	628.86
T [K]	193(2)	173(2)	173(2)	173(2)	173(2)
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group (no.)	$P\bar{1}$ (2)	$C2/c$ (15)	$C2/c$ (15)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	7.1874(14)	15.2726(15)	14.529(3)	7.3210(15)	7.4107(11)
b [Å]	9.2835(19)	12.9228(11)	8.5317(17)	10.779(2)	9.6940(14)
c [Å]	9.983(2)	13.8134(13)	21.745(4)	14.706(3)	11.4629(17)
α [°]	74.20(3)	90	90	73.05(3)	66.980(16)
β [°]	70.09(3)	104.745(11)	101.58(3)	81.37(3)	74.052(17)
γ [°]	75.58(3)	90	90	72.82(3)	79.065(18)
V [Å^3]	593.6(2)	2636.5(4)	2640.5(9)	1058.0(4)	725.59(18)
Z	1	4	4	1	1
ρ_{calcd} [g cm^{-3}]	1.580	1.503	1.476	1.329	1.439
μ [mm^{-1}]	0.323	0.442	0.300	0.213	0.405
F_{000}	290	1224	1224	442	326
Crystal dimensions [mm]	0.5 × 0.3 × 0.2	0.5 × 0.5 × 0.4	0.5 × 0.3 × 0.1	0.5 × 0.5 × 0.4	0.4 × 0.4 × 0.3
2θ range [°]	4.62–54.58	5.52–56.08	5.56–56.00	5.60–56.06	4.58–56.16
Index ranges	$-9 \le h \le 9$ $-11 \le k \le 11$ $-12 \le l \le 12$	$-20 \le h \le 20$ $-17 \le k \le 16$ $-18 \le l \le 18$	$-19 \le h \le 19$ $-11 \le k \le 11$ $-28 \le l \le 28$	$-9 \le h \le 9$ $-14 \le k \le 14$ $-19 \le l \le 19$	$-9 \le h \le 9$ $-12 \le k \le 12$ $-15 \le l \le 15$
No. of collected reflections	5406	13734	19646	12766	8461
No. of independent reflections	2424	3147	3158	4715	3237
R_{int}	0.0411	0.0325	0.0546	0.0433	0.0467
No. of reflections used	2424	3147	3158	4715	3237
No. of parameters	178	180	179	277	191
S[a]	1.053	1.055	1.097	1.063	1.038
Weight parameters a/b[b]	0.0502/0.1661	0.0418/3.2876	0.0887/4.7061	0.0659/0.3049	0.0447/0.4871
$R1$[c] [$I > 2\sigma(I)$]	0.0340	0.0328	0.0585	0.0442	0.0405
$wR2$[d] (all data)	0.0909	0.0885	0.1747	0.1231	0.1056
Max./min. residual electron density [e Å^{-3}]	+0.276/−0.333	+0.509/−0.540	+1.355/−0.538	+0.341/−0.348	+0.292/−0.449

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

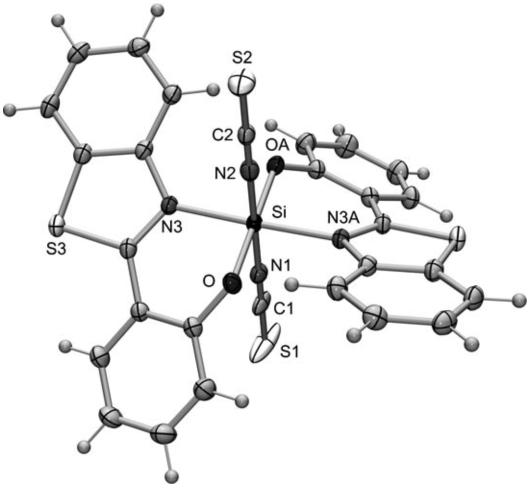


Figure 2. Molecular structure of **5** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O 1.7046(10), Si-N1 1.8577(18), Si-N2 1.8287(19), Si-N3 1.9680(12), N1-C1 1.162(3), N2-C2 1.170(3), C1-S1 1.607(2), C2-S2 1.605(2); O-Si-OA 179.87(8), O-Si-N1 90.07(4), O-Si-N2 89.93(4), O-Si-N3 90.07(5), O-Si-N3A 89.93(5), N1-Si-N2 180.0, N1-Si-N3 91.33(4), N1-Si-N3A 91.33(4), N2-Si-N3 88.67(4), N2-Si-N3A 88.67(4), N3-Si-N3A 177.34(7), Si-N1-C1 180.0, Si-N2-C2 180.0, N1-C1-S1 180.0, N2-C2-S2 180.0.

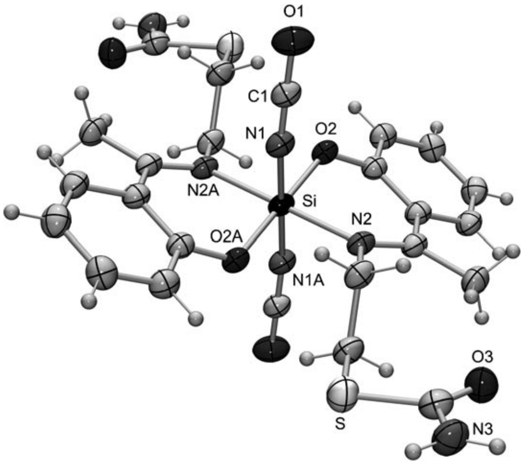


Figure 3. Molecular structure of **6** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O2 1.718(2), Si-N1 1.850(2), Si-N2 1.950(2), N1-C1 1.158(4), C1-O1 1.202(4); O2-Si-O2A 180.0, O2-Si-N1 88.74(10), O2-Si-N1A 91.26(10), O2-Si-N2 90.83(10), O2-Si-N2A 89.17(9), N1-Si-N1A 180.00(15), N1-Si-N2 89.63(10), N1-Si-N2A 90.36(10), N2-Si-N2A 179.999(1), Si-N1-C1 162.1(2), N1-C1-O1 178.1(3).

bond lengths are very similar to those found for structurally related hexacoordinate silicon(IV) complexes with SiO$_2$N$_4$ skeletons.[3a] The *trans*-X-Si-X (X = O, S) angles fit almost perfectly with the ideal 180° angle (maximum deviation, 2.66(7)°), and the *cis*-X-Si-X (X = O, S) angles show a maximum deviation of 1.87(8)° from the ideal 90° angle. The Si-N-C(X) (X = O, N) angles range from 158.77(13)° to 180.0°, and the N-C-X (X = O, N) angles range from 177.44(17)° to 180.0°.

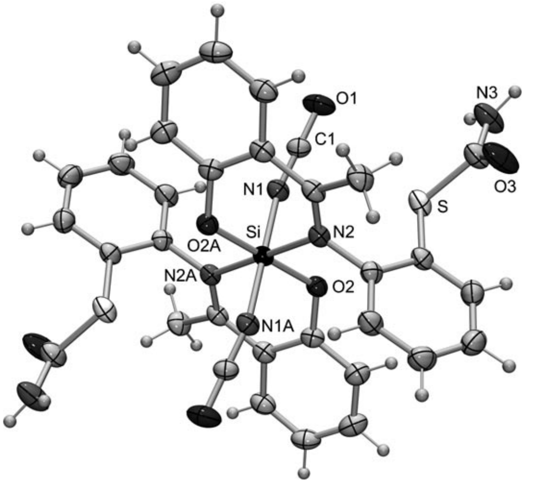


Figure 4. Molecular structure of **7** in the crystal of **7**·4CH$_3$CN (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O2 1.7220(12), Si-N1 1.8269(16), Si-N2 1.9606(14), N1-C1 1.172(2), C1-O1 1.191(2); O2-Si-O2A 180.0, O2-Si-N1 88.41(6), O2-Si-N1A 91.59(6), O2-Si-N2 90.36(6), O2-Si-N2A 89.64(6), N1-Si-N1A 180.00(7), N1-Si-N2 88.93(6), N1-Si-N2A 91.07(6), N2-Si-N2A 180.00(5), Si-N1-C1 159.33(13), N1-C1-O1 177.84(18).

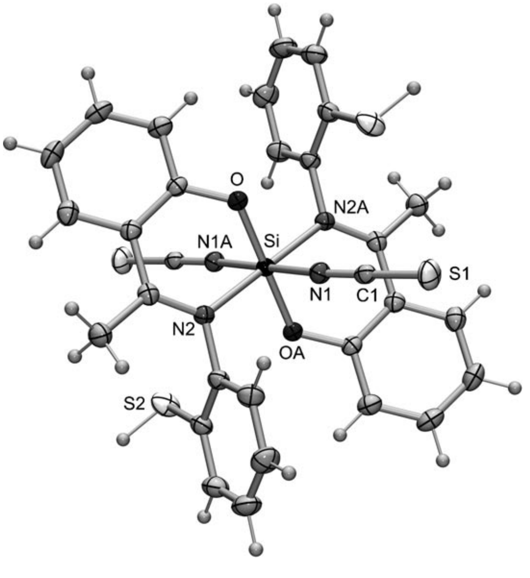


Figure 5. Molecular structure of **8** in the crystal (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si-O 1.7096(15), Si-N1 1.8465(17), Si-N2 1.9519(16), N1-C1 1.174(3), C1-S1 1.606(2); O-Si-OA 180.0, O-Si-N1 88.13(8), O-Si-N1A 91.87(8), O-Si-N2 90.27(7), O-Si-N2A 89.73(7), N1-Si-N1A 180.0, N1-Si-N2 89.68(7), N1-Si-N2A 90.32(7), N2-Si-N2A 179.999(1), Si-N1-C1 165.90(16), N1-C1-S1 178.8(2).

Some structural features of compound **5** differ from those observed for **4**, **6**, **7**·4CH$_3$CN, and **8**. Noteworthy are the two different Si−N(CS) bond lengths (1.8287(19) and 1.8577(18) Å) and the linear S-C-N-Si-N-C-S moiety of **5**,[9] as the Si-N-C(X) and N-C-X (X = O, S) angles of all the other compounds studied differ from the 180° angle (Si-N-C(X), 158.77(13)–165.90(10)°; N-C-X, 177.44(17)–178.8(2)°).

NMR Studies

Compounds **4**–**6**, **7**·2 CH_3CN, and **8** were studied by solid-state VACP/MAS NMR spectroscopy (^{13}C, ^{15}N, ^{29}Si). The isotropic ^{29}Si chemical shifts obtained in these studies (**4**, $\delta = -201.9$ ppm; **5**, $\delta = -204.0$ ppm; **6**, $\delta = -206.1$ ppm; **7**·2 CH_3CN, $\delta = -205.7$ ppm; **8**, $\delta = -207.1$ ppm)[10] are very similar and are in the same range as those found for structurally related silicon(IV) complexes with SiO_2N_4 skeletons that also contain two bidentate O,N Schiff base ligands and two cyanato-*N* or thiocyanato-*N* ligands.[3a] Thus, the ^{29}Si NMR data obtained confirms the identities of **4**–**8**. The solid-state ^{13}C and ^{15}N NMR data are also compatible with the structures determined by single-crystal X-ray diffraction. Owing to the poor solubility of **4**–**6**, **7**·2 CH_3CN, and **8** in common organic solvents, no solution-state NMR experiments could be performed.

Conclusions

With the synthesis of compounds **4**–**6**, **7**·2 CH_3CN, and **8**, a series of novel neutral hexacoordinate silicon(IV) complexes with SiO_2N_4 skeletons has been made accessible. All compounds contain two bidentate monoanionic O,N Schiff base ligands and two monodentate monoanionic cyanato-*N* or thiocyanato-*N* ligands. The formation of **4**–**8** was totally unexpected and is still not fully understood: When performing the syntheses in the presence of triethylamine, the expected neutral hexacoordinate silicon(IV) complexes with $SiS_2O_2N_2$ skeletons are formed (compounds **1**–**3**),[2] whereas in the absence of triethylamine, the sulfur atoms do not act as ligand atoms, that is, the ligands used for the syntheses do not behave as tridentate dianionic S,N,O ligands.[11] Instead, in the course of the formation of **4**–**7**, the ligands undergo further reactions (**4** and **5**, formal hydrogen elimination; **6** and **7**, formal addition of HNCO) and behave as bidentate monoanionic O,N ligands. In the case of **8**, the ligand undergoes no additional transformations and behaves as a bidentate monoanionic O,N ligand as well. Future studies to analyze the course of the reactions that lead to the formation of **4**–**8** in more detail are necessary. Furthermore, the synthetic potential of the ligand transformations (which has been demonstrated exemplarily by the synthesis of **9**) has to be evaluated.

Experimental Section

General procedures: All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ^1H and ^{13}C solution NMR spectra were recorded at 23 °C on a Bruker Avance 500 NMR spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz) using $[D_6]$DMSO as the solvent. Chemical shifts (ppm) were determined relative to internal $[D_5]$DMSO (^1H, $\delta = 2.49$ ppm) or $[D_6]$DMSO (^{13}C, $\delta = 39.5$ ppm). Assignment of the ^{13}C NMR data was supported by DEPT 135 and $^{13}C,^1H$ correlation experiments. Solid-state ^{13}C, ^{15}N, and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom-layer rotors of ZrO_2 (diameter 7 mm) containing ca. 200–300 mg of sample (^{13}C, 100.6 MHz; ^{15}N, 40.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (^{13}C, ^{29}Si; $\delta = 0$ ppm) or glycine (^{15}N, $\delta = -342.0$ ppm); spinning rate, 5–6 kHz; contact time, 2 ms (^{13}C), 3–5 ms (^{15}N), or 5 ms (^{29}Si); 90° ^1H transmitter pulse length, 3.6 μs; repetition time, 4 s). The precursors $Si(NCO)_4$ and $Si(NCS)_4$ were synthesized according to reference [12]. The ligands were synthesized according to reference [13]; for analytical data, see reference [2].

Silicon(IV) complex **4**: Tetra(cyanato-*N*)silane (171 mg, 872 μmol) was added in a single portion at 20 °C to a stirred solution of 2-(2,3-dihydrobenzothiazol-2-yl)phenol (400 mg, 1.74 mmol) in acetonitrile (25 mL), and the reaction mixture was then kept undisturbed at 20 °C for 2 days. The resulting solid was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **4** in 48 % yield (235 mg, 416 μmol) as a yellow crystalline product; m.p. 224–225 °C. ^{13}C VACP/MAS NMR: $\delta = 117$–127 (br signal with intensity maxima at 118.9, 121.1, and 124.6), 129.1, 134.9, 147.0, and 156.8 (SC_6H_4N, OC_6H_4C), 172.6 ppm (C=N), NCO signal not detected; ^{15}N VACP/MAS NMR: $\delta = -316.5$ (NCO), -142.6 ppm (C=N); ^{29}Si VACP/MAS NMR: $\delta = -201.9$ ppm; elemental analysis (%) calcd for $C_{28}H_{16}N_4O_4S_2Si$ (564.68): C 59.56, H 2.86, N 9.92, S 11.36; found: C 59.6, H 3.1, N 10.1, S 11.4.

Silicon(IV) complex **5**: Tetra(thiocyanato-*N*)silane (350 mg, 1.34 mmol) was added in a single portion at 20 °C to a stirred solution of 2-(2,3-dihydrobenzothiazol-2-yl)phenol (616 mg, 2.69 mmol) in THF (60 mL), and the reaction mixture was then stirred at 20 °C for 5 min. The undissolved solid was filtered off and discarded, and the filtrate was kept undisturbed at 20 °C for 2 days. The resulting solid was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **5** in 39 % yield (315 mg, 528 μmol) as a yellow crystalline product; m.p. > 250 °C (decomp.). ^{13}C VACP/MAS NMR: $\delta = 117.5$, 120.3, 122.3 (2 C), 124.1, 128.3 (3 C), 132.3, 139.6, 146.9, and 155.2 (SC_6H_4N, OC_6H_4C), 173.5 ppm (C=N), NCS signal not detected; ^{15}N VACP/MAS NMR: no signals detected; ^{29}Si VACP/MAS NMR: $\delta = -204.0$ ppm; elemental analysis (%) calcd for $C_{28}H_{16}N_4O_2S_4Si$ (596.81): C 56.35, H 2.70, N 9.39, S 21.49; found: C 56.4, H 2.9, N 9.3, S 21.4.

Silicon(IV) complex **6**: Tetra(cyanato-*N*)silane (202 mg, 1.03 mmol) was added in a single portion at 20 °C to a stirred solution of 2-(2-methyl-1,3-thiazolidin-2-yl)phenol (400 mg, 2.05 mmol) in a mixture of acetonitrile (20 mL) and THF (10 mL), and the reaction mixture was then kept undisturbed at 20 °C for 4 days. The resulting solid was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **6** in 71 % yield (430 mg, 733 μmol) as a pale yellow crystalline product; m.p. > 175 °C (decomp.). ^{13}C VACP/MAS NMR: $\delta = 19.7$ (CH_3), 27.6 (NCH_2CH_2S), 53.1 (NCH_2CH_2S), 118.9, 120.5 (2 C), 128.2, 136.7, and 158.9 (OC_6H_4C), 172.7 ($C(O)NH_2$ or C=N), 176.5 ppm ($C(O)NH_2$ or C=N), NCO signal not detected; ^{15}N VACP/MAS NMR: $\delta = -315.3$ (NCO), -273.0 ($C(O)NH_2$), -141.6 ppm (C=N); ^{29}Si VACP/MAS NMR: $\delta = -206.1$ ppm; elemental analysis (%) calcd for $C_{24}H_{26}N_6O_6S_2Si$ (586.72): C 49.13, H 4.47, N 14.32, S 10.93; found: C 49.3, H 4.6, N 14.3, S 10.9.

Silicon(IV) complex **7**·2 CH_3CN: Tetra(cyanato-*N*)silane (202 mg, 1.03 mmol) was added in a single portion at 20 °C to a stirred solution of 2-(2-methyl-2,3-dihydrobenzothiazol-2-yl)phenol (501 mg, 2.06 mmol) in acetonitrile (12 mL), and the reaction mixture was then kept undisturbed at 20 °C for 4 days. The resulting solid was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **7**·2 CH_3CN in 32 % yield (255 mg, 333 μmol) as a colorless crystalline product; m.p. 152–153 °C. ^{13}C VACP/MAS NMR: $\delta = 2.7$ (CH_3CN), 21.6 (CH_3), 119.4, 121.4 (2 C), 128.6 (3 C), 132.0 (2 C), 137.1, 138.4, 150.2, and 160.2 (SC_6H_4N, OC_6H_4C), 166.9 ($C(O)NH_2$ or C=N), 181.1 ppm ($C(O)NH_2$ or C=N), CH_3CN and NCO signals not detected;

^{15}N VACP/MAS NMR: $\delta = -315.4$ (NCO), -275 (br, C(O)NH$_2$), -132.0 ppm (C=N), CH$_3$CN signal not detected; ^{29}Si VACP/MAS NMR: $\delta = -205.7$ ppm; elemental analysis (%) calcd for $C_{36}H_{32}N_8O_6S_2Si$ (764.92): C 56.53, H 4.22, N 14.65, S 8.38; found: C 56.3, H 4.2, N 14.4, S 8.4.

Silicon(IV) complex **8**: Tetra(thiocyanato-*N*)silane (300 mg, 1.15 mmol) was added in a single portion at 20 °C to a stirred solution of 2-(2-methyl-2,3-dihydrobenzothiazol-2-yl)phenol (561 mg, 2.31 mmol) in acetonitrile (60 mL), and the reaction mixture was then stirred for 5 min. The undissolved solid was filtered off and discarded, and the filtrate was kept undisturbed at 20 °C for 3 days. The resulting solid was isolated by filtration, washed with diethyl ether (10 mL), and then dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **8** in 62 % yield (450 mg, 716 μmol) as a yellow crystalline product; m.p. > 140 °C (decomp.). ^{13}C VACP/MAS NMR: $\delta = 21.4$ (CH$_3$), 120.1 (2 C), 122.6, 126.3, 129.6 (2 C), 131.2 (3 C), 140.7, 145.0, and 159.4 (SC$_6$H$_4$N, OC$_6$H$_4$C), 180.6 ppm (C=N), NCS signal not detected; ^{15}N VACP/MAS NMR: $\delta = -139.0$ ppm (C=N), NCS signal not detected; ^{29}Si VACP/MAS NMR: $\delta = -207.1$ ppm; elemental analysis (%) calcd for $C_{30}H_{24}N_4O_2S_4Si$ (628.90): C 57.30, H 3.85, N 8.91, S 20.40; found: C 57.4, H 3.9, N 8.8, S 20.2.

9: A suspension of **6** (400 mg, 682 μmol) in a mixture of THF (5 mL) and ethanol (5 mL) was stirred at 20 °C for 3 h. The solvent was removed under reduced pressure, and the remaining solid was dissolved in boiling ethanol (9 mL). The resulting hot mixture was filtered, and the filtrate was kept undisturbed at −20 °C for 24 h. The resulting solid was isolated by filtration and dried in vacuo (0.01 mbar, 20 °C, 2 h) to give **10** in 64 % yield (209 mg, 877 μmol) as a yellow crystalline product; m.p. 143–145 °C. ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.34$ (s, 3 H, CH$_3$), 3.08 (t, ^3J(H,H) = 6.6 Hz, 2 H, SC*H*$_2$CH$_2$N), 3.71 (t, ^3J(H,H) = 6.6 Hz, 2 H, SCH$_2$C*H*$_2$N), 6.75–6.79 (m, 2 H, H-4/H-6, OC$_6$H$_4$C), 7.24–7.29 (m, 1 H, H-5, OC$_6$H$_4$C), 7.63–7.66 (m, 1 H, H-3, OC$_6$H$_4$C), 7.4–7.8 (br m, 2 H, NH$_2$), 15.91 ppm (s, 1 H, OH); ^{13}C NMR ([D$_6$]DMSO): $\delta = 14.7$ (CH$_3$), 29.7 (S*C*H$_2$CH$_2$N), 49.2 (SCH$_2$*C*H$_2$N), 117.0 and 117.8 (C-4/C-6, OC$_6$H$_4$C), 119.1 (C-2, OC$_6$H$_4$C), 128.8 (C-3, OC$_6$H$_4$C), 132.3 (C-5, OC$_6$H$_4$C), 162.9 (C-1, OC$_6$H$_4$C), 166.6 (C=N or C(O)NH$_2$), 172.9 ppm (C=N or C(O)NH$_2$); elemental analysis (%) calcd for $C_{11}H_{14}N_2O_2S$ (238.31): C 55.44, H 5.92, N 11.76, S 13.46; found: C 54.7, H 5.9, N 11.8, S 13.4.

Crystal structure analyses: Suitable single crystals of **4**–**6**, **7**·4CH$_3$CN, and **8** were isolated directly from the respective reaction mixtures. The crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). All structures were solved by direct methods.[14] The non-hydrogen atoms were refined anisotropically.[15] A riding model was employed in the refinement of the CH hydrogen atoms. CCDC 713792 (**4**), 713793 (**5**), 713794 (**6**), 713795 (**7**·4 CH$_3$CN), and 713796 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[7] The composition of this solvate is based on the elemental analysis.

[8] The synthesis of **5** was also performed in dichloromethane leading to a similar yield and indicating that the formation of the oxidized product does not depend on the solvent.

[9] Only in the case of **5**, the S-C-N-Si-N-C-S moiety lies on a crystallographic twofold axis. As can be seen from the thermal parameters, the N1-C1-S1 moiety could be slightly disordered, which consequently would result in a deviation of the Si-N1-C1 angle from 180°.

[10] Owing to ^{29}Si,^{14}N coupling, the ^{29}Si VACP/MAS NMR spectra of **4**–**6**, **7**·2 CH$_3$CN, and **8** are characterized by broad and slightly structured signals.

[11] One could speculate that the SH sulfur atom of the ring-opened form of the reagents can only coordinate to the silicon center in the presence of triethylamine; in the absence of the amine, the SH group may exist as it is or undergo further reactions. However, there is no experimental evidence for this assumption.

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