Pages: 8



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Neutral Hexacoordinate Silicon(IV) Complexes with a Tridentate Dianionic O, N, X Ligand (X = O, N, S), Bidentate Monoanionic X, N Ligand (X = O, S), and Phenyl Ligand: Compounds with a SiO_3N_2C , $SiSO_2N_2C$, SiO_2N_3C , $SiSON_3C$, or SiS_2ON_2C Skeleton

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A series of neutral hexacoordinate silicon(IV) complexes (4a, 4b, 5a, 5b, 6a, and 6b) with a SiO_3N_2C , $SiSO_2N_2C$, SiO_2N_3C , $SiSON_3C$, or SiS_2ON_2C skeleton have been synthesized and structurally characterized by solid-state and solution NMR spectroscopy and single-crystal X-ray diffraction. These

Introduction

The past decade has witnessed great advances in the chemistry of higher-coordinate silicon.^[1] A huge variety of penta- and hexacoordinate silicon(IV) complexes with novel combinations of different ligand atoms (including soft ligand atoms such as sulfur, selenium, tellurium, and iodine) have been synthesized, structurally characterized, and studied for their reactivity. In this context, we have demonstrated the neutral pentacoordinate silicon(IV) complexes 1-3 to be particularly versatile precursors for the synthesis of new neutral penta- and hexacoordinate silicon(IV) complexes.^[2] In continuation of these investigations, we have now succeeded in synthesizing the neutral hexacoordinate silicon(IV) complexes 4a, 4b, 5a, 5b, 6a, and 6b. Compounds 4b, 5b, 6a, and 6b, with their novel sulfur-containing SiSO₂N₂C, SiSON₃C, or SiS₂ON₂C skeleton, are of particular interest because only very few hexacoordinate silicon(IV) complexes with sulfur ligand atoms have been described in the literature.^[2e,3-5] Compounds 4a/5a/6a and 4b/5b/6b represent O/NMe/S analogues, and 4a/4b, 5a/5b, and 6a/6b are O/S analogues. To gain information on the effects of the O/NMe/S (4a/5a/6a and 4b/5b/6b) and O/S exchange (4a/4b, 5a/5b, and 6a/6b) on the structures and NMR spectroscopic parameters, all these compounds were characterized by solid-state and solution NMR specstudies were performed with a special emphasis on comparing the respective O/NMe/S analogues **4a/5a/6a** and **4b/5b/ 6b** and the O/S pairs **4a/4b**, **5a/5b**, and **6a/6b** with respect to their structures and NMR spectroscopic parameters.

troscopy and single-crystal X-ray diffraction. The studies reported herein were performed as part of our ongoing systematic investigations into higher-coordinate silicon(IV) complexes.^[6,7]



Results and Discussion

Compounds 4a, 4b, 5a, 5b, 6a, and 6b were synthesized by treatment of the corresponding neutral pentacoordinate chlorosilicon(IV) complexes 1-3 with 8-(trimethylsilyloxy)quinoline (7) or 8-(trimethylsilylthio)quinoline (8) using acetonitrile as the solvent (Scheme 1). The products were isolated as colored crystalline solids (yield/color: 4a, 94%/ yellow; 4b·0.5CH₃CN, 79%/yellow; 5a, 99%/red; 5b·0.5CH₃CN, 74%/red; 6a·0.5CH₃CN, 74%/orange;

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6b•0.5CH₃CN, 88%/orange). 8-(Trimethylsilyloxy)quinoline (7) and 8-(trimethylsilylthio)quinoline (8) were synthesized by treatment of 8-hydroxy- and 8-mercaptoquinoline, respectively, with an excess of bis(trimethylsilyl)amine and were isolated as colorless liquids (yield: 7, 91%; 8, 74%).



Scheme 1. Synthesis of compounds 4a, 4b, 5a, 5b, 6a, and 6b.

Compounds 4a, 4b·0.5CH₃CN, 5a, 5b·CH₃CN, 6a, and 6b·0.5CH₃CN were structurally characterized by singlecrystal X-ray diffraction. The crystal data and experimental parameters used for the crystal structure analyses are given in Table S1 of the Supporting Information, and the molecular structures of 4a, 4b, 5a, 5b, 6a, and 6b in the crystal are shown in Figures 1, 2, 3, 4, 5, and 6, respectively; selected bond lengths and angles are given in the respective figure legends. Compound 6a contains two molecules in the asymmetric unit, which, as a first approximation, behave as mirror images.



Figure 1. Molecular structure of **4a** in the crystal (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–O1 1.7915(11), Si–O2 1.7702(11), Si–O3 1.7564(10), Si–N1 1.9329(13), Si–N2 2.0907(13), Si–C1 1.9107(15); O1–Si–O2 166.89(5), O1–Si–O3 91.26(5), O1–Si–N1 89.70(5), O1–Si–N2 82.72(5), O1–Si–C1 95.69(5), O2–Si–O3 92.23(5), O2–Si–N1 84.94(5), O2–Si–N2 85.21(5), O2–Si–C1 96.80(6), O3–Si–N1 171.10(5), O3–Si–N2 82.55(5), O3–Si–C1 92.31(5), N1–Si–N2 88.80(5), N1–Si–C1 96.40(6), N2–Si–C1 174.56(6).



Figure 2. Molecular structure of **4b** in the crystal of **4b**·0.5CH₃CN (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–S 2.2677(7), Si–O1 1.8007(13), Si–O2 1.7723(13), Si–N1 1.9308(15), Si–N2 2.0720(16), Si–C1 1.9323(19); S–Si–O1 92.27(5), S–Si–O2 90.45(5), S–Si–N1 171.68(5), S–Si–N2 84.26(5), S–Si–C1 91.84(6), O1–Si–O2 168.55(6), O1–Si–N1 90.81(6), O1–Si–N2 82.64(6), O1–Si–C1 95.47(7), O2–Si–N1 85.06(6), O2–Si–N2 86.57(6), O2–Si–C1 95.56(7), N1–Si–N2 88.48(6), N1–Si–C1 95.55(7), N2–Si–C1 175.58(8).



Figure 3. Molecular structure of **5a** in the crystal (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–O1 1.803(2), Si–O2 1.771(2), Si–N1 1.917(3), Si–N2 2.092(3), Si–N3 1.826(2), Si–C1 1.910(3); O1–Si–O2 90.35(10), O1–Si–N1 90.10(10), O1–Si–N2 82.72(9), O1–Si–N3 168.72(10), O1–Si–C1 93.05(11), O2–Si–N1 168.54(11), O2–Si–N2 82.00(10), O2–Si–N3 94.58(10), O2–Si–C1 93.56(11), N1–Si–N2 86.69(10), N1–Si–N3 83.07(11), N1–Si–C1 97.86(12), N2–Si–N3 87.91(10), N2–Si–C1 173.82(12), N3–Si–C1 96.75(12).

The silicon coordination polyhedra of 4a, $4b \cdot 0.5 CH_3 CN$, 5a, $5b \cdot CH_3 CN$, 6a, and $6b \cdot 0.5 CH_3 CN$ are best described as strongly distorted octahedra, with maximum deviations from the ideal angles of 90 and 180° ranging from 6.85(11) to 8.00(9)° and from 9.83(5) to 13.11(5)°, respectively. The structures of all the compounds studied are very similar,

/KAP1

Date: 31-03-14 17:03:10

Pages: 8



Figure 4. Molecular structure of **5b** in the crystal of **5b**·CH₃CN (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–S 2.2981(8), Si–O 1.8013(15), Si–N1 1.9097(18), Si–N2 2.1159(19), Si–N3 1.8365(18), Si–C1 1.929(2); S–Si–O 90.90(5), S–Si–N1 169.36(6), S–Si–N2 82.06(5), S–Si–N3 94.68(6), S–Si–C1 91.76(7), O–Si–N1 89.69(7), O–Si–N2 82.60(7), O–Si–N3 167.59(8), O–Si–C1 93.73(8), N1–Si–N2 87.49(7), N1–Si–N3 82.79(8), N1–Si–C1 98.80(9), N2–Si–N3 87.20(8), N2–Si–C1 172.73(9), N3–Si–C1 97.16(9).

with the tridentate O,N,O, N,N,O, and S,N,O ligands in *mer* positions. In all the structures, the imino nitrogen atoms of these tridentate ligands and the chalcogen atoms of the bidentate N,X ligands (X = O, S) occupy *trans* positions, and the nitrogen atoms of the N,X ligands and the carbon ligand atoms of the phenyl groups are also found in *trans* positions.

As can be seen from Table 1, neither the O/NMe/S nor O/S exchange significantly affects the bond lengths between the silicon coordination center and the respective ligand atoms. The Si–O(enolato) bond lengths are in the range 1.7785(14)–1.803(2) Å, and the Si–C bond lengths range from 1.910(3) to 1.9323(19) Å. The Si–N(imino) bond lengths are 1.9097(18)–1.935(3) Å, and the significantly longer Si–N(quinoline) atom distances are 2.033(3)–2.1159(19) Å. The respective Si–O [1.754(2)–1.771(2) Å] and Si–S [2.2677(7)–2.2981(8) Å] bond lengths of the bidentate *N*,*X* ligands (X = O, S) are also very similar. Likewise, the O/S exchange in the bidentate ligand does not influence the Si–O(phenolato) [1.7702(11) and 1.7723(13) Å] and Si–S [2.2704(9) and 2.2939(15)/2.2862(14) Å] bond lengths of



Figure 5. Molecular structures of the two crystallographically independent molecules A and B in the crystal of 6a (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°] of molecule A (top): Si1-S1 2.2939(15), Si1-O1 1.798(3), Si1-O2 1.754(2), Si1-N1 1.913(3), Si1-N2 2.039(3), Si1-C1 1.930(3); S1-Si1-O1 169.88(9), S1-Si1-O2 90.30(9), S1-Si1-N1 85.57(9), S1-Si1-N2 87.48(9), S1-Si1-C1 95.44(11), O1-Si1-O2 92.38(11), O1-Si1-N1 90.51(12), O1-Si1-N2 83.15(11), O1-Si1-C1 94.24(13), O2-Si1-N1 171.82(11), O2-Si1-N2 83.17(11), O2-Si1-C1 91.66(13), N1-Si1-N2 89.59(12), N1-Si1-C1 95.76(13), N2-Si1-C1 174.08(13). Selected bond lengths [Å] and angles [°] of molecule B (bottom): Si2–S2 2.2862(14), Si2–O3 1.794(3), Si2–O4 1.759(2), Si2-N3 1.935(3), Si2-N4 2.033(3), Si2-C27 1.920(4); S2-Si2-O3 169.86(10), S2-Si2-O4 89.82(9), S2-Si2-N3 85.66(9), S2-Si2-N4 88.16(9), S2-Si2-C27 95.44(11), O3-Si2-O4 92.51(11), O3-Si2-N3 90.67(12), O3-Si2-N4 82.32(11), O3-Si2-C27 94.34(13), O4-Si2-N3 171.13(11), O4-Si2-N4 83.36(11), O4-Si2-C27 91.85(13), N3-Si2-N4 88.87(11), N3-Si2-C27 96.17(13), N4-Si2-C27 174.01(13).

Table 1. Selected bond lengths of compounds 4a, 4b, 5a, 5b, 6a, and 6b.

| Compound (ligands) | Si–O(enolato) [Å] | Si–N(imino) [Å] | Si-N(quinoline) [Å] | Si–C [Å] | Si–X (tridentate) [Å] (X = O, NMe, S) | Si–X (bidentate) [Å] (X = O, S) |
|---------------------------------------|-------------------|-----------------|---------------------|------------|--|------------------------------------|
| 4a (O,N,O, N,O) | 1.7915(11) | 1.9329(13) | 2.0907(13) | 1.9107(15) | 1.7702(11) | 1.7564(10) |
| 4b $(O, N, O, N, S)^{[a]}$ | 1.8007(13) | 1.9308(15) | 2.0720(16) | 1.9323(19) | 1.7723(13) | 2.2677(7) |
| 5a (N,N,O, N,O) | 1.803(2) | 1.917(3) | 2.092(3) | 1.910(3) | 1.826(2) | 1.771(2) |
| 5b (N,N,O, N,S) ^[b] | 1.8013(15) | 1.9097(18) | 2.1159(19) | 1.929(2) | 1.8365(18) | 2.2981(8) |
| 6a $(S,N,O, N,O)^{[c]}$ | 1.798(3)/ | 1.913(3)/ | 2.039(3)/ | 1.930(3)/ | 2.2939(15)/ | 1.754(2)/ |
| | 1.794(3) | 1.935(3) | 2.033(3) | 1.920(4) | 2.2862(14) | 1.759(2) |
| 6b (S,N,O, N,S) ^[d] | 1.7785(14) | 1.9276(18) | 2.0337(19) | 1.932(2) | 2.2704(9) | 2.2834(12) |

[a] Solvate 4b·0.5CH₃CN. [b] Solvate 5b·CH₃CN. [c] Data for two crystallographically independent molecules. [d] Solvate 6b·0.5CH₃CN.

Date: 31-03-14 17:03:10

7:03:10

/KAP1

Pages: 8



Figure 6. Molecular structure of **6b** in the crystal of **6b**·0.5CH₃CN (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–S1 2.2704(9), Si–S2 2.2834(12), Si–O 1.7785(14), Si–N1 1.9276(18), Si–N2 2.0337(19), Si–C1 1.932(2); S1–Si–S2 88.15(4), S1–Si–O 170.17(5), S1–Si–N1 86.02(6), S1–Si–N2 88.04(5), S1–Si–C1 94.50(7), S2–Si–O 93.28(6), S2–Si–N1 171.60(6), S2–Si–N2 84.26(7), S2–Si–C1 90.21(8), O–Si–N1 91.45(7), O–Si–N2 82.43(7), O–Si–C1 95.22(8), N1–Si–N2 89.49(8), N1–Si–C1 96.28(9), N2–Si–C1 173.84(8).

Table 2. Isotropic ²⁹Si chemical shifts of **4a**, **4b**, **5a**, **5b**, **6a**, and **6b** in the solid state (T = 22 °C) and in solution (T = 23 °C; solvent, CD₂Cl₂).

| Compound (ligands) | δ^{29} Si (solid state) [ppm] | δ^{29} Si (solution) [ppm] |
|------------------------|---|--------------------------------------|
| 4a (0,N,0, N,0) | -144.6 | -147.2 |
| 4b (0,N,0, N,S) | -140.0 ^[a] | -138.8 |
| 5a (N,N,0, N,0) | -146.9 | -144.0 |
| 5b (N,N,0, N,S) | -135.3 ^[b] | -135.8 |
| 6a (S,N,0, N,0) | -146.4 ^[c] | -141.7 |
| 6b (S,N,0, N,S) | -145.4 ^[d] | -141.6 |

[a] Solvate 4b·0.5CH₃CN. [b] Solvate 5b·0.5CH₃CN. [c] Solvate 6a·0.5CH₃CN. [d] Solvate 6b·0.5CH₃CN.

the tridentate ligand significantly, whereas the Si–NCH₃ distance [1.826(2) and 1.8365(18) Å] is slightly shortened by the O/S exchange.

Compounds 4a, 4b·0.5CH₃CN, 5a, 5b·0.5CH₃CN, 6a·0.5CH₃CN, and 6b·0.5CH₃CN were also studied by NMR spectroscopy in the solid state (15 N, 29 Si) as well as in solution (1 H, 13 C, 29 Si; solvent, CD₂Cl₂). The data obtained (see the Exp. Sect.) confirmed the identities of the compounds studied.

As can be seen from Table 2, the isotropic ²⁹Si chemical shifts of **4a**, **4b**, **5a**, **5b**, **6a**, and **6b** in the solid state and in solution are very similar (maximum deviation, $\Delta \delta^{29}$ Si = 3.8 ppm), which indicates that these neutral hexacoordinate silicon(IV) compounds also exist in solution. The ²⁹Si chemical shifts range from $\delta = -146.9$ to -135.3 ppm in the solid state ($\Delta \delta^{29}$ Si = 11.6 ppm) and from $\delta = -147.2$ to -135.8 ppm in solution ($\Delta \delta^{29}$ Si = 11.4 ppm). The data obtained do not reveal a clear effect of the O/NMe/S and O/S exchange in terms of a correlation between the ²⁹Si chemical shifts and the electronegativities of the respective ligand atoms.

Conclusions

With the synthesis of 4a, 4b, 5a, 5b, 6a, and 6b, we have succeeded in synthesizing a series of novel hexacoordinate silicon(IV) complexes that contain a tridentate dianionic O.N.O. N.N.O. or S.N.O ligand, a bidentate monoanionic N,X ligand (X = O, S), and a phenyl ligand. These compounds contain a SiO_3N_2C (4a), $SiSO_2N_2C$ (4b, 6a), SiO_2N_3C (5a), $SiSON_3C$ (5b), or SiS_2ON_2C (6b) skeleton. The three sulfur-containing skeletons have not previously been described in the literature. In this context it should be noted that only a few hexacoordinate silicon(IV) complexes with sulfur ligand atoms have been synthesized and characterized so far.^[2e,3-5] The studies reported herein again emphasize the high synthetic potential of the pentacoordinate chlorosilicon(IV) complexes 1-3 for the targeted synthesis of novel hexacoordinate silicon(IV) complexes, including those with soft sulfur ligand atoms.

As shown by crystal structure analyses, the silicon coordination polyhedra of the title compounds are distorted octahedra, with the tridentate O,N,O, N,N,O or S,N,O ligand in *mer* positions. The imino nitrogen atoms of these tridentate ligands and the chalcogen atoms of the bidentate N,X ligands (X = O, S) occupy *trans* positions, and the nitrogen atom of the N,X ligands and the carbon ligand atom of the phenyl group are also found in *trans* positions. In general, the structures of all the compounds studied are very similar, that is, neither the O/NMe/S nor the O/S exchange affects the structures significantly.

As demonstrated by solid-state and solution NMR spectroscopic studies, the title compounds also exist in solution, and it is likely that their structures in the solid state and in solution are very similar. Interestingly, the isotropic ²⁹Si chemical shifts of the title compounds are similar [solid state: $\delta = -146.9$ to -135.3 ppm; solution (CD₂Cl₂): $\delta = -147.2$ to -135.8 ppm] and show no systematic trend in terms of a clear correlation between the chemical shift and the electronegativity of the ligand atoms.

Experimental Section

General Procedures: All syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. The solutionstate 1H, 13C, and 29Si NMR spectra were recorded at 23 °C by using a Bruker Avance 500 NMR spectrometer (¹H, 500.1 MHz; 13 C, 125.8 MHz; 29 Si, 99.4 MHz) with CD₂Cl₂ as the solvent. Chemical shifts were determined relative to internal CHDCl₂ (¹H, δ = 5.32 ppm), CD₂Cl₂ (¹³C, δ = 53.8 ppm), or external TMS (²⁹Si, $\delta = 0$ ppm). Assignment of the ¹³C NMR spectroscopic data was supported by DEPT 135 and 13C,1H correlation experiments. Solidstate ¹⁵N and ²⁹Si VACP/MAS NMR spectra were recorded at 22 °C by using a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO₂ (diameter, 7 mm) containing around 300 mg of sample [15N, 40.6 MHz; 29Si, 79.5 MHz; external standard, TMS $(^{29}\text{Si}, \delta = 0 \text{ ppm})$ or glycine $(^{15}\text{N}, \delta = -342.0 \text{ ppm})$; spinning rate, 5 kHz; contact time, 3 (¹⁵N) or 5 ms (²⁹Si); 90° ¹H transmitter pulse length, 3.6 µs; repetition time, 4–7 s].

Synthesis of 4a: Compound 7 (316 mg, 1.45 mmol) was added in a single portion at 20 °C to a stirred solution of 1 (457 mg,

Date: 31-03-14 17:03:10

Pages: 8

www.eurjic.org

1.39 mmol) in acetonitrile (60 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h and then at -20 °C for a further 24 h. The resulting solid was isolated by filtration, washed with *n*-pentane (10 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 4a in 94% yield (572 mg, 1.30 mmol) as a yellow crystalline solid. ¹H NMR (CD₂Cl₂, 500.1 MHz): $\delta = 1.77$ (s, 3 H, CCH₃), 2.46 (s, 3 H, CCH₃), 5.18 (s, 1 H, CCHC), 6.49-6.52, 6.70-6.74, 6.91-6.96, 7.13-7.16, 7.18-7.21, 7.27-7.36, 7.58-7.65, 8.17-8.20, 8.27-8.31 (m, 15 H, C₆H₄, C₆H₅, C₉H₆NO) ppm. ¹³C NMR $(CD_2Cl_2, 125.8 \text{ MHz}): \delta = 24.4 (CCH_3), 24.9 (CCH_3), 103.0$ (CCHC), 111.7, 114.4, 115.8, 117.8, 120.6, 121.6, 126.7 (2 C), 126.9, 128.0, 129.4, 130.8, 133.0, 134.5 (2 C), 135.1, 138.9, 141.7, 149.8, 154.3, 155.3 (C₆H₄, C₆H₅, C₉H₆NO), 170.5 [C(N)CH₃], 179.7 [C(O)CH₃] ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): δ = -147.2 ppm. ¹⁵N VACP/MAS NMR: $\delta = -186.6$ [C(N)CH₃], -122.8 (C_9H_6NO) ppm. ²⁹Si VACP/MAS NMR: $\delta = -144.6$ ppm. C₂₆H₂₂N₂O₃Si (438.56): calcd. C 71.21, H 5.06, N 6.39; found C 71.0, H 5.2, N 6.5.

Synthesis of 4b·0.5CH₃CN: Compound 8 (810 mg, 3.47 mmol) was added in a single portion at 20 °C to a stirred solution of 1 (1.14 g, 3.46 mmol) in acetonitrile (70 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h. The resulting solid was isolated by filtration, washed with n-pentane (20 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 4b·0.5CH₃CN in 79% yield (1.30 g, 2.74 mmol) as a yellow crystalline solid. ¹H NMR (CD₂Cl₂, 500.1 MHz): $\delta = 1.94$ (s, 3 H, CCH₃), 1.97 (s, 1.5 H, N=CCH₃), 2.38 (s, 3 H, CCH₃), 5.25 (s, 1 H, CCHC), 6.40–6.44, 6.67–6.72, 6.86-6.91, 7.16-7.20, 7.23-7.30, 7.43-7.51, 7.52-7.56, 7.75-7.79, 8.23-8.26, 8.51-8.55 (m, 15 H, C_6H_4 , C_6H_5 , C_9H_6NS) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): $\delta = 2.0$ (N=CCH₃), 24.1 (CCH₃), 25.1 (CCH₃), 103.7 (CCHC), 116.9 (N≡CCH₃), 115.6, 117.9, 120.5, 120.6, 120.7, 126.9 (2 C), 127.0, 128.1, 128.5, 128.7, 129.8, 132.8, 133.2 (2 C), 139.0, 141.1, 142.6, 146.1, 151.9, 155.0 (C₆H₄, C₆H₅, C₉H₆NS), 171.1 [C(N)CH₃], 180.2 [C(O)CH₃] ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): δ = -138.8 ppm. ¹⁵N VACP/MAS NMR: $\delta = -176.0 [C(N)CH_3], -127.3 (N \equiv CCH_3), -120.8$ (C_9H_6NS) ppm. ²⁹Si VACP/MAS NMR: $\delta = -140.0$ ppm. C₂₇H_{23 5}N_{2 5}O₂SSi (475.15): calcd. C 68.25, H 4.99, N 7.37, S 6.75; found C 68.5, H 5.1, N 7.5, S 6.7.

Synthesis of 5a: Compound 7 (1.05 g, 4.83 mmol) was added in a single portion at 20 °C to a stirred solution of 2 (1.37 g, 4.00 mmol) in acetonitrile (70 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h and then at -20 °C for a further 24 h. The resulting solid was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 5a in 99% yield (1.79 g, 3.96 mmol) as a red crystalline solid. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 1.76 (s, 3 H, CCH₃), 2.26 (s, 3 H, CCH₃), 2.37 (s, 3 H, NCH₃), 5.10 (s, 1 H, CCHC), 6.02–6.07, 6.40– 6.46, 6.84-6.90, 7.10-7.15, 7.16-7.26, 7.53-7.58, 7.60-7.65, 8.18-8.22, 8.23–8.27 (m, 15 H, C_6H_4 , C_6H_5 , C_9H_6NO) ppm. ¹³C NMR $(CD_2Cl_2, 125.8 \text{ MHz}): \delta = 24.0 (CCH_3), 24.8 (CCH_3), 30.9$ (NCH₃), 103.4 (CCHC), 108.4, 111.4, 112.7, 114.3, 120.3, 121.5, 126.4 (2 C), 126.5, 127.8, 129.3, 130.4, 130.5, 135.1 (2 C), 135.2, 138.0, 140.6, 148.8, 150.4, 154.5 (C₆H₄, C₆H₅, C₉H₆NO), 170.6 [C(N)CH₃], 180.7 [C(O)CH₃] ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): δ = -144.0 ppm. ¹⁵N VACP/MAS NMR: δ = -288.0 (NCH₃), -185.3 [C(N)CH₃], -118.7 (C₉H₆NO) ppm. ²⁹Si VACP/ MAS NMR: δ = -146.9 ppm. C₂₇H₂₅N₃O₂Si (451.60): calcd. C 71.81, H 5.58, N 9.30; found C 71.8, H 5.6, N 9.4.

Synthesis of 5b·0.5CH₃CN: Compound 8 (1.03 g, 4.41 mmol) was added in a single portion at 20 °C to a stirred solution of 2 (1.37 g, 4.00 mmol) in acetonitrile (70 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h. The resulting solid was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 5b·0.5CH₃CN in 74% yield (1.44 g, 2.95 mmol) as a red crystalline solid. ¹H NMR (CD₂Cl₂, 500.1 MHz): $\delta = 1.94$ (s, 3 H, CCH₃), 1.97 (s, 1.5 H, N=CCH₃), 2.32 (s, 3 H, CCH₃), 2.49 (s, 3 H, NCH₃), 5.23 (s, 1 H, CCHC), 5.93-5.97, 6.37-6.43, 6.75-6.81, 7.03-7.07, 7.12-7.20, 7.38-7.44, 7.48-7.52, 7.73-7.77, 8.10-8.14, 8.41-8.45 (m, 15 H, C₆H₄, C₆H₅, C_9H_6NS) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): $\delta = 2.0$ (N≡CCH₃), 23.6 (CCH₃), 25.0 (CCH₃), 32.7 (NCH₃), 103.9 (CCHC), 116.5 $(N \equiv CCH_3)$, 109.2, 113.2, 120.1, 120.3, 120.6, 126.6, 126.7 (2 C), 127.9, 128.1, 128.3, 134.0 (2 C), 137.1, 139.4, 140.1, 142.7, 145.0, 148.9, 149.7, 151.8 (C₆H₄, C₆H₅, C₉H₆NS), 170.5 [C(N)CH₃], 181.4 [C(O)CH₃] ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): $\delta = -135.8$ ppm. ¹⁵N VACP/MAS NMR:^[8] $\delta = -283.1$ (NCH₃), -187.9 [C(N)CH₃], -114.1 (C₉H₆NS) ppm. ²⁹Si VACP/ MAS NMR:^[8] δ = -135.3 ppm. C₂₈H_{26.5}N_{3.5}OSSi (488.29):^[9] calcd. C 68.89, H 5.47, N 10.04, S 6.57; found C 69.1, H 5.5, N 9.4, S 7.1.

Synthesis of 6a·0.5CH₃CN: Compound 7 (870 mg, 4.00 mmol) was added in a single portion at 20 °C to a stirred solution of 3 (1.26 g, 3.64 mmol) in acetonitrile (60 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h. The resulting solid was isolated by filtration, washed with n-pentane (40 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 6a·0.5CH₃CN in 74% yield (1.28 g, 2.69 mmol) as an orange crystalline solid. ¹H NMR $(CD_2Cl_2, 500.1 \text{ MHz}): \delta = 1.75 \text{ (s, 3 H, } CCH_3), 1.97 \text{ (s, 1.5 H,}$ N=CCH₃), 2.40 (s, 3 H, CCH₃), 5.33 (s, 1 H, CCHC), 6.91-7.03, 7.12-7.20, 7.21-7.24, 7.27-7.31, 7.57-7.62, 7.77-7.81, 8.12-8.15, 8.25–8.28 (m, 15 H, C_6H_4 , C_6H_5 , C_9H_6NO) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): δ = 2.0 (N=CCH₃), 24.63 (CCH₃), 24.64 (CCH_3) , 105.2 (CCHC), 116.9 $(N \equiv CCH_3)$, 112.0, 114.7, 121.2, 122.4, 123.1, 126.1 (2 C), 126.4, 126.9, 129.5, 130.2, 130.7, 134.7, 135.4 (2 C), 139.1, 139.9, 140.5, 141.4, 152.6, 153.7 (C₆H₄, C₆H₅, C₉H₆NO), 173.6 [C(N)CH₃], 181.2 [C(O)CH₃] ppm. ²⁹Si NMR $(CD_2Cl_2, 99.4 \text{ MHz}): \delta = -141.7 \text{ ppm}.$ ¹⁵N VACP/MAS NMR: $\delta =$ -173.6 [C(N)CH₃], -127.8 (N≡CCH₃), -122.5 (C₉H₆NO) ppm. ²⁹Si VACP/MAS NMR: $\delta = -146.4 \text{ ppm. } C_{27}H_{23.5}N_{2.5}O_2SSi (475.15):$ calcd. C 68.25, H 4.99, N 7.37, S 6.75; found C 68.4, H 5.0, N 7.3, S 6.7.

Synthesis of 6b·0.5CH₃CN: Compound 8 (830 mg, 3.56 mmol) was added in a single portion at 20 °C to a stirred solution of 3 (1.23 g, 3.56 mmol) in acetonitrile (70 mL), and the reaction mixture was then stirred at this temperature for 1 min. The resulting clear solution was kept undisturbed at 20 °C for 16 h. The resulting solid was isolated by filtration, washed with n-pentane (15 mL), and dried in vacuo (20 °C, 1 h, 0.01 mbar) to give 6b·0.5CH₃CN in 88% yield (1.54 g, 3.14 mmol) as an orange crystalline solid. ¹H NMR $(CD_2Cl_2, 500.1 \text{ MHz}): \delta = 1.91 \text{ (s, 3 H, } CCH_3), 1.97 \text{ (s, 1.5 H,}$ $N \equiv CCH_3$), 2.33 (s, 3 H, CCH₃), 5.36 (s, 1 H, CCHC), 6.84–6.96, 7.06-7.20, 7.40-7.50, 7.72-7.78, 8.20-8.24, 8.36-8.40 (m, 15 H, C_6H_4 , C_6H_5 , C_9H_6NS) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): $\delta =$ 2.1 (N≡CCH₃), 24.6 (CCH₃), 24.9 (CCH₃), 105.8 (CCHC), 119.7 $(N \equiv CCH_3)$, 121.0, 122.4 (2 C), 123.0, 124.8, 126.3 (2 C), 126.6, 127.2, 128.6, 128.7, 129.4, 130.2, 134.2 (2 C), 137.1, 141.4, 141.8, 146.2, 149.7, 155.0 (C₆H₄, C₆H₅, C₉H₆NS), 173.9 [C(N)CH₃], 181.4 $[C(O)CH_3]$ ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): $\delta = -141.6$ ppm. ¹⁵N VACP/MAS NMR: $\delta = -176.0 [C(N)CH_3], -124.2 (N \equiv CCH_3),$ www.eurjic.org



–119.8 (C₉H₆NS) ppm. ²⁹Si VACP/MAS NMR: δ = –145.4 ppm. C₂₇H_{23.5}N_{2.5}OS₂Si (491.22): calcd. C 66.02, H 4.82, N 7.13, S 13.06; found C 66.1, H 4.8, N 7.0, S 13.0.

Synthesis of 7: A mixture of 8-hydroxyquinoline (9.29 g, 64.0 mmol) and bis(trimethylsilyl)amine (130 mL) was heated under reflux for 2 h. The mixture was then cooled to 20 °C, the solvent was removed in vacuo, and the residue was purified by distillation in vacuo (102–104 °C/0.04 mbar) to give 7 in 91% yield (12.7 g, 58.4 mmol) as a colorless liquid. ¹H NMR (CD₂Cl₂, 500.1 MHz): $\delta = 0.36$ (s, 9 H, SiCH₃), 7.15–7.20, 7.36–7.41, 7.42–7.45, 8.11–8.15, 8.84–8.88 (m, 6 H, C₉H₆NO) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): $\delta = 1.18$ (SiCH₃), 118.0, 120.8, 121.7, 127.3, 130.2, 136.0, 142.3, 148.9, 152.8 (*C*₉H₆NO) ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): $\delta = 20.0$ ppm. C₁₂H₁₅NOSi (217.34): calcd. C 66.32, H 6.96, N 6.44; found C 66.0, H 7.0, N 6.9.

Synthesis of 8: A mixture of 8-mercaptoquinoline hydrochloride (4.83 g, 24.4 mmol) and bis(trimethylsilyl)amine (50 mL) was heated under reflux for 3 h. The mixture was then cooled to 20 °C, the solvent was removed in vacuo, and the residue was purified by distillation in vacuo (106 °C/0.08 mbar) to give **8** in 74% yield (4.21 g, 18.0 mmol) as a colorless liquid. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 0.33 (s, 9 H, SiCH₃), 7.39–7.45, 7.68–7.72, 7.89–7.92, 8.13–8.17, 8.94–8.97 (m, 6 H, C₉H₆NS) ppm. ¹³C NMR (CD₂Cl₂, 125.8 MHz): δ = 2.0 (SiCH₃), 121.7, 126.5, 127.0, 129.4, 134.6, 135.0, 136.8, 148.5, 149.9 (C₉H₆NS) ppm. ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): δ = 16.8 ppm. C₁₂H₁₅NSSi (233.41): calcd. C 61.75, H 6.48, N 6.00, S 13.74; found C 61.5, H 6.5, N 6.1, S 13.8.

Crystal Structure Analyses: Suitable single crystals of **4a**, **4b**·0.5CH₃CN, **5a**, **5b**·CH₃CN, and **6b**·0.5CH₃CN were obtained as described in the synthesis protocols. Suitable single crystals of **6a** were obtained by slow cooling of a saturated solution in tetrahydrofuran from 65 to 20 °C. 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 (**4a**, **4b**·0.5CH₃CN, and **6a**; graphite-monochromated Mo- K_a radiation, $\lambda = 0.71073$ Å) or Bruker Nonius KAPPA APEX II (**5a**, **5b**·CH₃CN, and **6b**·0.5CH₃CN; graphite-monochromated Mo- K_a radiation, $\lambda = 0.71073$ Å)]. All structures were solved by direct methods (SHELXS-97)^[10] and refined by full-matrix leastsquares methods on F^2 for all unique reflections (SHELXL-97).^[10] SHELXLE was used as refinement GUI.^[11] For the CH hydrogen atoms, a riding model was employed.

CCDC-976253 (for 4a), -976254 (for 4b·0.5CH₃CN), -976255 (for 5a), -976256 (for 5b·CH₃CN), -976257 (for 6a), and -976258 (for 6b·0.5CH₃CN) 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.

Supporting Information (see footnote on the first page of this article): Crystallographic data for compounds 4a, 4b·0.5CH₃CN, 5a, 5b·CH₃CN, 6a, and 6b·0.5CH₃CN.

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Hexacoordinate Silicon

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Neutral Hexacoordinate Silicon(IV) Complexes with a Tridentate Dianionic O,N,XLigand (X = O, N, S), Bidentate Monoanionic X,N Ligand (X = O, S), and Phenyl Ligand: Compounds with a SiO_3N_2C , $SiSO_2N_2C$, SiO_2N_3C , $SiSON_3C$, or SiS_2ON_2C Skeleton

Keywords: Chalcogens / Coordination modes / Main group elements / Silicon / Tridentate ligands



A series of neutral hexacoordinate silicon(IV) complexes have been synthesized and structurally characterized by NMR spectroscopy and single-crystal X-ray diffraction. These studies were performed with a special emphasis on comparing the respective O/NMe/S analogues 4a/5a/6a and 4b/5b/6b and the O/S pairs 4a/4b, 5a/ 5b, and 6a/6b with respect to their structures and NMR spectroscopic parameters.