Bis(O—Si)-chelate difluorobis{[*N*-(1-phenylethyl)acetamido]methyl}silane: the first stable hexacoordinated silicon compound with two C,O-chelating ligands

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Bischelates L_2MHal_2 containing bidentate C,X-coordinating ligands L (X = N and O) belong to thoroughly studied compounds with hexacoordinated germanium and tin.[1] In the solid state, these compounds usually have a near-octahedral configuration with *trans*-C atoms, while coordinating X atoms and halogen atoms are *cis* to each other (X-ray diffraction data). However, their silicon analogs are virtually unknown.[2] Only compounds with N→Si coordination, namely, dichloro- and difluoro[bis(8-dimethylamino-1-naphthyl)]silanes[3] and difluoro(8-dimethylamino-1-naphthyl)(2-dimethylaminomethylphenyl)silane (**1**),[4] were reported. In difluoride **1**, the coordination environment of the Si atom is a "bicapped" tetrahedron (X-ray diffraction data).

Attempts to synthesize neutral hexacoordinated dichlorosilanes L_2SiCl_2 by reactions of *N*-trimethylsilyllactams and -amides with $(ClCH_2)_2SiCl_2$ (in the 2 : 1 ratio) gave unstable, easily hydrolyzable substances. The latter were treated with Me_3SiOTf or $HgCl_2$ with access for atmospheric moisture to form cation-anionic disiloxane complexes of pentacoordinated silicon, in which disilylium dications $[L_2SiOSiL_2]^{2+}$ are stabilized by O→Si coordination.[5]

Earlier,[6] we synthesized rather stable monochelate amidomethyl- and lactamomethyldifluorosilanes $LSiMeF_2$ by reactions of crude, easily hydrolyzable dichlorides $LSiMeCl_2$ with aqueous $NaHCO_3$ followed by *in situ* treatment of the resulting oligosiloxanes with BF_3 etherate. A similar strategy has been recently[7] used to obtain *in situ* dichlorosilane $(L^7)_2SiCl_2$ from *N*-trimethylsilylcaprolactam and $(ClCH_2)_2SiCl_2$ (L^n is a bidentate lactamomethyl *n*-membered C,O-chelating ligand). The resulting cation-anionic complex $[(L^7)_2SiF]^+BF_4^-$ (**2**) contains the pentacoordinated Si atom.

In this communication, another way of converting dichlorosilanes L_2SiCl_2 into more stable compounds is proposed. The method includes treatment of dichlorosilanes with alcohols in the presence of Et_3N followed by *in situ* reactions of the resulting dialkoxides $L_2Si(OAlk)_2$ with BF_3 etherate. In such a way, bis(O—Si)-chelate difluorobis{[*N*-(1-phenylethyl)acetamido]methyl}silane (**3**) was obtained in a moderate yield from *N*-[(*S*)-1-phenylethyl]-*N*-trimethylsilylacetamide[8] and MeOH. Compound **3** is the first representative of stable compounds of hexacoordinated silicon with two C,O-chelating ligands. According to X-ray diffraction data, the environment of the Si atom in a crystal of difluoride **3** is a slightly distorted octahedron, in which two monodentate ligands and two coordinating O atoms occupy *cis*-positions, while C atoms of the chelating ligands are *trans* to each other (Fig. 1).

The hexacoordinated Si atom in difluoride **3** is involved in two hypervalent O—Si—F fragments with the very weak coordination O—Si bond and the stronger covalent Si—F bond. Elongation of these bonds (especially the O—Si bond) with respect to the corresponding tetrahedral bonds is slightly lesser than in monochelate trigonal-bipyramidal fluoride $PhCH(Me)N[C(O)Me]CH_2SiMe_2F$ (the O—Si and Si—F distances in the hypervalent O—Si—F fragment of the latter are 2.15 and 1.67 Å, respectively).[8] At the same time, in the aforesaid difluoride **1** with analogous hypervalent N—Si—F bonds, the Si—F distances (1.602—1.616 Å) are close to standard values for a covalent bond, while the N—Si distances (2.59—2.81 Å) are much longer.[4]

Complete X-ray diffraction and dynamic NMR data for difluoride **3** will be published elsewhere.

The structure of difluoride **3** was confirmed by IR spectra (Specord IR-75, KBr cuvette) and ^1H, ^{13}C, and ^{29}Si NMR spectra (Varian XL-400; 400.1, 100.6, and 79.5 MHz, respectively; 20 °C). Its specific rotation value was determined on a VNIIEKIPRODMASh A1-EPO polarimeter (0.5-dm cuvettes).

Molecule **3** as a whole is chiral and contains two additional chiral centers, namely, C atoms. Because the latter

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 251—253, January, 2004.

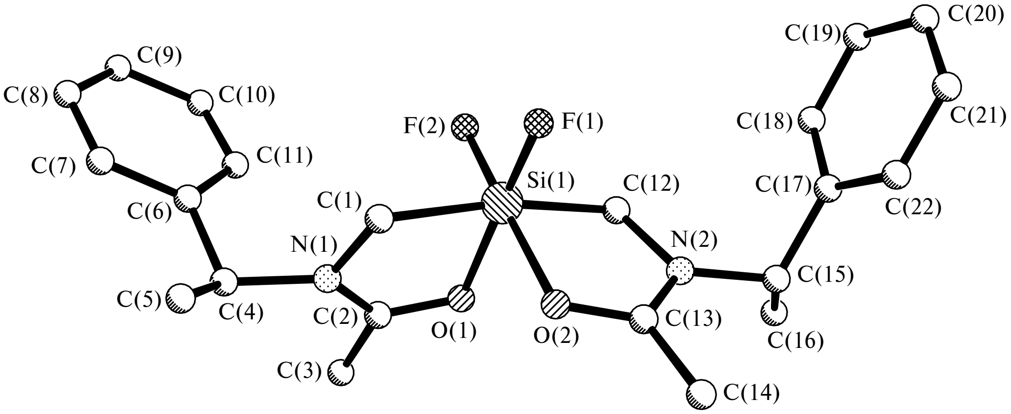

Fig. 1. Crystal structure of difluoride **3**. Hydrogen atoms are omitted; Si(1)—F(1) 1.660(2) Å, Si(1)—F(2) 1.670(2) Å, Si(1)—O(1) 1.932(2) Å, and Si(1)—O(2) 1.937(2) Å; the angles O(1)—Si(1)—F(1), O(2)—Si(1)—F(2), C(1)—Si(1)—C(12) are 173.1(1), 173.9(1), and 169.9(1)°, respectively.

have equal (*S*)-configuration, the number of possible diastereomers is reduced to two. For this reason, the ^{1}H and ^{13}C NMR spectra of compound **3** show two sets of signals of approximately equal integrated intensity, which correspond to two diastereomers. In the ^{1}H NMR spectra, signals for the NCH_2 group appear as two overlapped distorted broadened quartets of the AB system, one of their components being registered as a triplet with $^3J_{H,F}$. Spin-spin coupling between F atoms and the NCH_2 group is also manifested in the ^{13}C NMR spectrum. The upfield shift of signals for the diastereomers in the ^{29}Si NMR spectrum ($\delta \sim -129.1$, see below) indicates that the Si atom in solution is hexacoordinated. For complex **2** containing a pentacoordinated Si atom, the signal for the Si atom appears at δ −57.9.[7]

Bis(O—Si)-chelate difluorobis{[*N*-(*S*)-(1-phenylethyl)acetamido]methyl}silane (3). Dichloro[bis(chloromethyl)]silane (1.98 g, 0.01 mol) was added dropwise to a stirred solution of *N*-[(*S*)-1-phenylethyl]-*N*-trimethylsilylacetamide[8] (4.78 g, 0.02 mol) in 10 mL of $CHCl_3$ while cooling the reaction mixture with ice water. After one day, the solvent was removed *in vacuo*, and the residual caramel of crude dichlorobis{[*N*-(*S*)-(1-phenylethyl)acetamido]methyl}silane was dissolved in a mixture of MeOH (7 mL) and benzene (8 mL). Then Et_3N (6 g, 0.06 mol) was added dropwise with stirring, and the reaction mixture was refluxed for 2 h. After one day, the precipitate of $Et_3N \cdot HCl$ that formed was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in 30 mL of $CHCl_3$ and washed with water (2×20 mL). The organic layer was dried over calcined $CaCl_2$, concentrated *in vacuo*, and dissolved in 5 mL of CH_2Cl_2, and $BF_3 \cdot Et_2O$ (1.13 g, 0.008 mol) was added. The reaction mixture was heated for 0.5 h until the mixture of CH_2Cl_2 and Et_2O was completely distilled off. Acetonitrile (20 mL) was added to the residue, the solution was decanted, and the solvent was removed *in vacuo*. The dark brown residue was refluxed with 100 mL of benzene, and the solution was poured into 300 mL of heptane. After one day, the solvent was decanted, and the residual oil was crystallized by adding ether, and the crystals were filtered off to give difluoride **3** (1.8 g, 43%), m.p. 183.5—184.5 °C (water—MeCN, 2 : 1), $[\alpha]_D^{20}$ −81.3 (*c*, CH_2Cl_2, 35 mg mL^{-1}). Found (%): C, 63.08; H, 6.74; N, 6.70. $C_{22}H_{28}F_2N_2O_2Si$. Calculated (%): C, 63.13; H, 6.74; N, 6.69. IR ($CHCl_3$), ν/cm^{-1}: 1580, 1510 (NCO). ^{1}H NMR ($CDCl_3$), δ: 1.63, 1.68 (both s, 12 H, MeC(O)); 2.26, 2.28 (both br.s, 12 H, $\underline{Me}$CH); 2.42, 2.45 (both dt, 8 H, NCH_2, $^2J_{H,H}$ = 13.3 Hz, $^3J_{H,F}$ = 14.7 Hz); 5.09 (q, 4 H, CH); 7.25—7.45 (m, 20 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 17.80 ($\underline{Me}$CH); 18.98, 19.39 (MeC(O)); 35.37, 35.59 (t, $^2J_{C,F}$ = 51.1 Hz); 56.62 (CH); 125.88, 125.94 (C_m); 127.45 (C_p); 128.63, 128.80 (C_o); 139.60, 140.54 (C_i); 172.28 (C=O). ^{29}Si NMR ($CDCl_3$), δ: −129.1 (br.t, $^1J_{Si,F}$ = 260.6 Hz).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 01-03-32216).

References

1. Yu. I. Baukov and S. N. Tandura, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol. **2**, Ed. Z. Rappoport, Wiley, London, 2002, 961.
2. D. Kost and I. Kalikhman, in *The Chemistry of Organic Silicon Compounds*, Eds. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, 1339.
3. C. Breliere, R. J. P. Corriu, G. Royo, W. W. C. Wong Chi Man, and J. Zwecker, *Organometallics*, 1990, **9**, 2633.
4. C. Breliere, F. Carre, R. J. P. Corriu, M. Poirier, G. Royo, and J. Zwecker, *Organometallics*, 1989, **8**, 1831.
5. Yu. E. Ovchinnikov, S. A. Pogozhikh, I. V. Razumovskaya, A. G. Shipov, E. P. Kramarova, S. Yu. Bylikin, Vad. V. Negrebetsky, and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 997 [*Russ. Chem. Bull.*, 1998, **47**, 967 (Engl. Transl.)].
6. E. P. Kramarova, A. G. Shipov, Vad. V. Negrebetsky, and Yu. I. Baukov, *Zh. Obshch. Khim.*, 1997, **67**, 1403 [*Russ. J. Gen. Chem.*, 1997, **67** (Engl. Transl.)].
7. E. P. Kramarova, S. A. Pogozhikh, A. G. Shipov, Vad. V. Negrebetsky, S. N. Tandura, A. N. Shumskii, S. A. Artamkin, S. Yu. Bylikin, Yu. E. Ovchinnikov, and Yu. I. Baukov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 315 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 331].
8. Yu. I. Baukov, Yu. E. Ovchinnikov, A. G. Shipov, E. P. Kramarova, Vad. V. Negrebetsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 399.

Received November 26, 2003;
in revised form December 29, 2003