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Bis(O—Si)-chelate fluorobis(2-oxohexahydroazepinomethyl)silylium tetrafluoroborate, a cation-anionic complex containing a silylium ion stabilized by O→Si coordination

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Reactions of dichlorodi(lactamomethyl)germanes $[L^{(n)}]_2GeCl_2$ (L is a bidentate lactamomethyl C,O-chelating ligand; n = 5—7, the size of the lactam ring) with lithium salts LiX or silanes Me_3SiX (X = I, OTf, or ClO_4) occur, as a rule, without complications yielding the substitution products of a nucleophile for the halogen atom, *viz.*, monochlorides $L^{(n)}]_2Ge(Cl)X$, whose C and O atoms and monodentate ligands are in *trans* positions with respect of each other according to X-ray diffraction analysis data.[1] In the solid state, the monochlorides mentioned above are complexes of six-coordinate germanium with the covalent Ge—Cl bond and essentially ionic character of the X→Ge bond. These complexes display rather high electric conductivity in CH_2Cl_2, which suggests the presence of germylium ions $\{[L^{(n)}]_2Ge(Cl)\}^+$ in solutions stabilized by O→Ge coordination.[1]

On the contrary, dichlorodi(lactamomethyl)silanes $[L^{(n)}]_2SiCl_2$ readily hydrolyzable with the atmospheric moisture react with Me_3SiOTf and $HgCl_2$ yielding disiloxane-type cation-anionic complexes with disilylium* dications $\{[L^{(n)}]_2SiOSi[L^{(n)}]_2\}^{2+}$ stabilized by intraionic coordination interaction O→Si.[2]

Recently,[3] we have reported on the synthesis of rather stable five-coordinate (amidomethyl)- and (lactamomethyl)methyldifluorosilanes starting from the corresponding labile, readily hydrolyzable dichlorides by the reaction of crude dichlorides with an aqueous solution of $NaHCO_3$ and subsequent treatment of the resulting intermediate oligosiloxanes without isolation with BF_3 etherate.[3]

Here we report on the first results of application of the analogous method for the transformation of dichlorosilanes $[L^{(n)}]_2SiCl_2$ into more stable compounds. In the case of caprolactam derivative $[L^{(7)}]_2SiCl_2$ obtained *in situ* from *N*-trimethylsilylcaprolactam and $(ClCH_2)_2SiCl_2$, the reaction unexpectedly gave cation-anionic complex $\{[L^{(7)}]_2SiF\}^+BF_4^-$ (**1**). According to X-ray diffraction data (Fig. 1), the resulting cationic complex of five-coordinate silicon contains the silylium ion with the covalent Si—F bond stabilized by O→Si coordination.

The configuration of the central coordination unit of complex **1** is a distorted trigonal bipyramid open towards

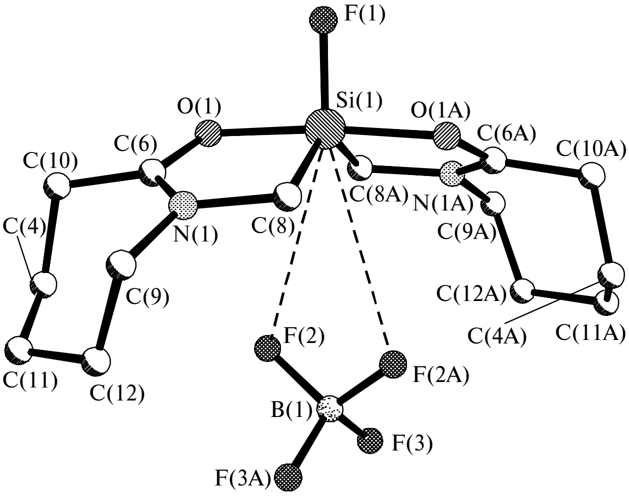

Fig. 1. The cation-anion pair in the crystal of **1**. H atoms are omitted. The bond lengths are: Si(1)—F(1) 1.600(1), Si(1)—O(1) and Si(1)—O(1A) 1.836(1) Å; the Si...F(2) and Si...F(2A) distances are 3.644(2) Å; the O(1)—Si(1)—O(1A) bond angle is 174.7(1)°.

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* According to IUPAC recommendation, the name "silylium ions" has been adopted for R_3Si^+ trivalent positive ions, which were previously named as silicenium, siliconium, or silylenium ions.

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the BF_4^- anion. (The full data from the X-ray-diffraction analysis of complex **1** will be published later.)

The cation-anionic complex $[L^{(7)}]_2Ge(F)BF_4$ (Ref. 4) formed in the reaction of $AgBF_4$ with $[L^{(7)}]_2GeCl_2$ is a Ge analog of compound **1**. Its geometric parameters are close to those for **1** with account of corrections for the higher electrophilicity of the central Si atom.

It is of note that the cationic complexes of five-coordinate silicon reported thus far containing two Si—C bonds at the central atom (except for the disiloxane disilylium ions mentioned above) are stabilized through N→Si coordination (see Refs. 5, 6).

The structure of complex **1** was confirmed by the data from IR spectroscopy (Specord IR-75, KBr cell) and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy (Bruker AM-300; 300.1, 62.9, and 59.6 MHz, respectively; 20 °C) spectroscopy data. The signal for the NCH_2 group in the ^1H NMR spectrum is registered as two triplets with the spin-spin coupling constant with the F atom. Spin-spin coupling between the F atom and the NCH_2 group is also observed in the ^{13}C NMR spectrum. The ^{29}Si chemica shift (δ −57.9) is the evidence of the five-coordinate Si atom in solution. In the case of analogous cationic five-coordinate complexes with N→Si coordination, the signal for the Si atom is registered in the δ range −40 to −60 (Refs. 5,6).

Bis(O—Si)-chelate fluorobis(2-oxoperhydroazepinomethyl)silylium tetrafluoroborate (1). Dichlorobis(chloromethyl)silane (1.98 g, 0.01 mol) was added dropwise to a solution of *N*-trimethylsilylcaprolactam (3.70 g, 0.02 mol) in CH_2Cl_2 (5 mL) at 0 °C. After 2 h, chloroform (60 mL) and an aqueous solution of $NaHCO_3$ (50 mL) were added to the reaction mixture. The next day, the organic layer was separated, solvents were removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 (6 mL). The resulting solution was treated with $BF_3 \cdot Et_2O$ (2.9 g, 0.02 mol), and the reaction mixture was heated up to complete evaporation of CH_2Cl_2 and Et_2O. The residue was treated with dry methanol (10 mL) and extracted with hot acetonitrile (10 mL). Evaporation of the solvent *in vacuo* gave 1.8 g (47%) of **1**, m.p. 217—220 °C (benzene—acetonitrile, 5 : 1). IR (DMSO, ν/cm^{-1}): 1617, 1505 (NCO). ^1H NMR ($CDCl_3$), δ: 1.5—2.1 (m, 12 H, H(4), H(5), H(6)); 2.62 (m, 4 H, H(3)); 2.85 and 3.34 (both t, 4 H, $SiCH_2$, $^2J_{HH}$ = $^3J_{HF}$ = 17 Hz); 3.67 (m, 4 H, H(7)). ^{13}C NMR ($CDCl_3$), δ: 29.46 (C(3)); 21.74 (C(4)); 25.30 (C(5)); 31.75 (C(6)); 52.07 (C(7)); 38.75 (d, NCH_2, $^2J_{CF}$ = 35.6 Hz); 180.53 (C=O). ^{29}Si NMR ($CDCl_3$), δ: −57.9 (d, $^1J_{SiF}$ = 247.6 Hz). Found (%): C, 43.33; H, 6.42; N, 7.49. $C_{14}H_{24}BF_5N_2O_2Si$. Calculated (%): C, 43.54; H, 6.26; N, 7.25.

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