

Ionic structure of the bischelate dichlorosilane stabilized by O→Si coordination, the product of reaction of *N*-methyl-*N*-trimethylsilylacetamide with (ClCH₂)₂SiCl₂

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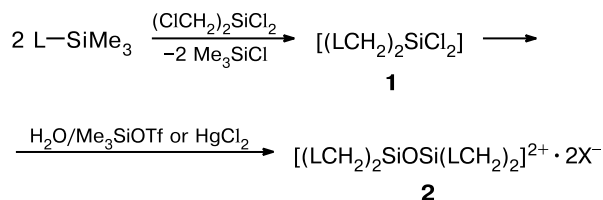
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In the chemistry of hypervalent silicon¹ and germanium² complexes, silylium ions and their Ge analogs stabilized by intraionic coordination have been intensively studied in recent years. Earlier, we showed that the thermodynamically controlled reactions of *N*-trimethylsilylamides and -lactams with (ClCH₂)₂GeCl₂ in the 2 : 1 ratio afford covalent bischelates (LCH₂)₂GeCl₂ (LCH₂ is a monoanionic bidentate *N*-methylacetamidomethyl or lactamomethyl C,O-chelating ligand) that include a hexacoordinated Ge atom in a nearly octahedral configuration.³ However, an analogous reaction with (ClCH₂)₂SiCl₂ yielded unstable, highly hydrolytically labile dichlorosilanes (LCH₂)₂SiCl₂ (**1**). Although their structures could not be precisely determined, the reactions of these compounds with Me₃SiOTf or HgCl₂ without protection against atmospheric moisture led to cation-anionic disiloxane complexes of pentacoordinated silicon **2** (Scheme 1) containing the disilylium dication $\{[(LCH_2)_2Si]_2O\}^{2+}$ stabilized by O→Si intraion coordination (X-ray diffraction data).⁴

Scheme 1



LH = AcNHMe, five-, six-, or seven-membered lactam;
X[−] = OTf[−], HgCl₃[−], 2 X[−] = HgCl₄^{2−}, 3 Cl[−] · [H₃O]⁺

In this communication, structural data for dichlorides **1** are presented for the first time with *N*-methylacetamide derivative **1a** as an example. The extremely hydrolytically labile dichloride **1a** was obtained as individual compound and characterized by X-ray diffraction data. It turned out that its structure corresponds to the

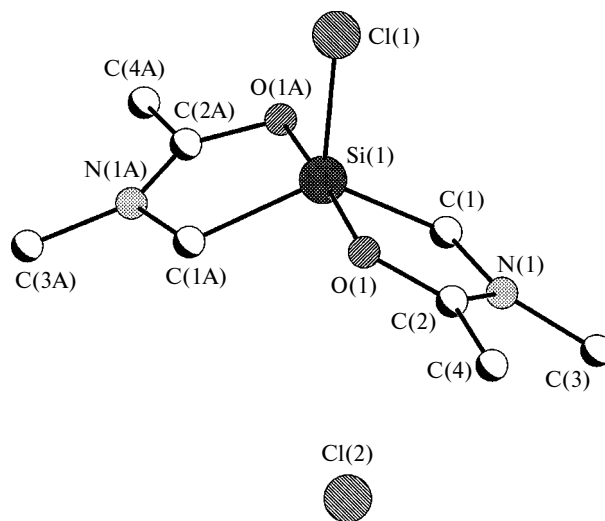


Fig. 1. Crystal structure of the cation-anionic complex **1a**. Hydrogen atoms are omitted. In the crystal, cation **1a** occupies a special position; the Si(1) and Cl(1) atoms lie on a twofold axis. The coordinates of the atoms additionally designated "A" were determined by the symmetry operation (*xy, x, −z*) for the independent part of the cation. The distances are Si(1)—Cl(1) 2.074(1) Å, Si(1)...Cl(2) 4.091(1) Å, and Si(1)—O(1) 1.847(2) Å; the bond angles are O(1)—Si—O(1A) 174.6(1)°, C(1)—Si—C(1A) 128.1(2)°, Cl(1)—Si—C(1) 116.0(1)°, and O(1)—Si(1)—Cl(1) 92.71(7)°.

cation-anionic complex $[(\text{AcN}(\text{Me})\text{CH}_2)_2\text{Si}(\text{Cl})]^+\text{Cl}^-$ (**1a**) containing a silylium ion stabilized by $\text{O} \rightarrow \text{Si}$ coordination rather than the covalent hexacoordinate dichlorosilane $[\text{AcN}(\text{Me})\text{CH}_2)_2\text{SiCl}_2$ (Fig. 1). In this structure, the Si atom is pentacoordinated and its configuration is a distorted trigonal bipyramid with axial O atoms and equatorial C and Cl atoms and a concave toward the chloride anion.

The Si—Cl bond in complex **1a** (2.07 Å) is shorter than a normal $\text{Si}^{\text{V}}\text{—Cl}$ bond. Its length is close to a standard value in tetrahedral silicon compounds (2.05 Å); the distance between the Si atom and the Cl anion is 4.09 Å. Complete X-ray diffraction data for complex **1a** will be published elsewhere.

Thus, primary products were found to have an ionic structure, which significantly complements the general scheme of formation of the cation-anionic disiloxane complexes $\{[(\text{LCH}_2)_2\text{Si}]_2\text{O}\}^{2+} \cdot 2\text{X}^-$ (X^- is the nonnucleophilic anion) usually isolated upon the reactions of *N*-trimethylsilylamides and -lactams with $(\text{ClCH}_2)_2\text{SiCl}_2$.⁴

Bis(O—Si)-chelate chlorobis[(*N*-methyl)acetamidomethyl]silylium chloride (1a). Dichlorobis(chloromethyl)silane (4.2 g, 0.021 mol) was added dropwise at 0 °C to a stirred solution of *N*-methyl-*N*-trimethylsilylacetamide (5.8 g, 0.04 mol) in 10 mL of dry CH_2Cl_2 . The day after, the reaction mixture with crystals of dichloride **1a** was sampled for X-ray diffraction analysis. The rest of the crystals were filtered off (4.9 g, 90%).

Their subsequent conversions into the stable complex $[\text{MeC}(\text{O})\text{N}(\text{Me})\text{CH}_2)_2\text{Si}(\text{F})^+\text{BF}_4^-$ with the aim of further identification will be described elsewhere.

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