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Interaction between Hydrofluorosilicic Acid and 1,10-Phenanthroline: Hydrolytic Stability of Chelate Complexes of Silicon Tetrafluoride with Bidentate N-Donors

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Abstract—Hexafluorosilicate (LH₂)SiF₆ and the *cis*-[SiF₄(L)] chelate complex characterized by ¹⁹F NMR are products of reaction between hydrofluorosilicic acid and 1,10-phenanthroline (L). XRD findings show that the structure of (LH₂)SiF₆ is stabilized by NH⋯F hydrogen bonds (N⋯F 2.618(4), 2.676(4) Å) and CH⋯F contacts. The relative resistance of the *cis*-[SiF₄(L)] complex to hydrolysis is associated with the chelate effect.

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The interaction between hydrofluosilicic acid (HFA) and organic bases is known to mainly give rise to onium salts of SiF₆²⁻ anion [1, 2]. Onium hexafluorosilicates are used in various areas [2]. They have recently been intensively studied as promising dental caries-protective and hyposensitive agents [3–9]. We found previously that the reaction between HFA and 2,2'-bipyridine yields hexafluorosilicate (2,2'-BipyH₂)SiF₆ as the main product with an impurity of the *cis*-[SiF₄(2,2'-Bipy)] complex, both of which were identified by X-ray diffraction analysis. The formation of a SiF₄ complex in the HFA–2,2'-Bipy–MeOH–H₂O system was appreciably sudden, since molecular complexes between silicon tetrafluoride and N-donors are distinguished by extremely low hydrolytic stability and their synthesis usually occurs via reaction between components in the gas phase or in anhydrous solvents [10, 11]. Gelmboldt et al. [8] suggested a correlation between formation of the *cis*-[SiF₄(2,2'-Bipy)] complex in aqueous solutions and the chelate effect of the bidentate ligand that stabilizes the structure of the *cis*-complex [12]. It was of interest to elucidate how common the tendency toward increasing hydrolytic stability of silicon tetrafluoride complexes with chelate-forming N-donor ligands found in [8] is. We report the results of studying the products of reaction between HFA and 1,10-phenanthroline (L), the chelate-forming ligand that is structurally similar to 2,2'-Bipy.

EXPERIMENTAL

Synthesis. 1,10-Phenanthroline (1.982 g, 0.01 mol) was dissolved in boiling methanol (25 mL); a 45% HFA solution (15 mL, 1 : 3 Phen : HFA mol/mol) was added. The reaction mixture was subjected to spontaneous evaporation at room temperature until the solvents were completely removed. The main product was extracted from the heterogeneous crystalline mass in the form of high-quality colorless transparent crystals; their composition was determined by elemental analysis. For (PhenH₂)SiF₆ (I) anal. calcd., %: Si, 8.66; N, 8.64; F, 35.15. Found, %: Si, 8.79; N, 8.61; F, 35.52.

EI mass spectrum was recorded on an MX-1321 spectrometer (the sample was injected directly into the ion source; ionization energy, 70 eV).

Mass spectrum of I: [ML]⁺ (*m/z* = 180, *I* = 100%), [ML–CN]⁺ (*m/z* = 154, *I* = 20%), [SiF₃]⁺ (*m/z* = 85, *I* = 40%).

¹⁹F NMR spectra were recorded on a Varian Gemini-200 spectrometer (188.14 MHz, CFCl₃ reference).

XRD analysis of complex I was carried out on an Xcalibur E diffractometer (room temperature, two-coordinate CCD sensor, graphite monochromator, MoK_α radiation).

Crystals I (C₁₂H₁₀F₆N₂Si, *M* = 324.31) crystallize in the triclinic system: *a* = 6.8358(6) Å, *b* = 9.7764(9) Å, *c* = 10.1932(9) Å, α = 73.739(8)°, β = 75.165(8)°, γ = 69.899(8)°, *V* = 604.40(9) Å³, spatial group *P* $\bar{1}$, *Z* = 2, ρ_{calc} = 1.782 mg/m³, μ = 0.266 mm⁻¹, *F*(000) = 328.

Table 1. Bond lengths (d) and bond angles (ω) for **I**

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$
Si(1)–F(1)	1.651(3)	Si(1)–F(4)	1.717(3)
Si(1)–F(3)	1.663(3)	Si(1)–F(5)	1.6908(17)
Si(1)–F(6)	1.6709(18)	Si(1)–F(2)	1.701(3)
N(1)–C(1)	1.325(4)	N(2)–C(12)	1.324(4)
N(1)–C(5)	1.370(4)	N(2)–C(6)	1.359(4)
Angle	ω, deg	Angle	ω, deg
F(1)Si(1)F(3)	91.86(16)	F(5)Si(1)F(2)	86.79(11)
F(1)Si(1)F(6)	91.55(11)	F(1)Si(1)F(4)	179.47(13)
F(3)Si(1)F(6)	91.25(11)	F(3)Si(1)F(4)	88.22(16)
F(1)Si(1)F(5)	91.64(11)	F(6)Si(1)F(4)	88.97(12)
F(3)Si(1)F(5)	92.33(11)	F(5)Si(1)F(4)	87.83(11)
F(6)Si(1)F(5)	175.12(10)	F(2)Si(1)F(4)	88.51(19)
F(1)Si(1)F(2)	91.41(18)	F(6)Si(1)F(2)	89.44(11)
F(3)Si(1)F(2)	176.64(18)	C(12)N(2)C(6)	123.6(3)
C(1)N(1)C(5)	122.9(3)		

A total of 3567 reflections were recorded; the number of independent reflections was 2355. The final refined data: $R_1 = 0.0530$, $wR_2 = 0.1275$ for 1720 reflections with $I > 2\sigma(I)$; $R_1 = 0.0718$, $wR_2 = 0.1529$ for all reflections.

The structure was solved and refined using the SHELX97 software package [13]. Four equatorial fluorine atoms in the SiF_6^{2-} anion randomly occupy two positions with population of 0.889(6) and 0.111(6). All the non-hydrogen atoms were refined in the anisotropic approximation. Some bond lengths and bond angles for **I** are summarized in Table 1; the geometric parameters of hydrogen bonds are listed in Table 2. The crystallographic data for **I** were deposited into the Cambridge Structural Database (CCDC no. 1053167).

RESULTS AND DISCUSSION

Figure 1a shows the formula units of **I**: the diprotonated 1,10-phenanthroline cation and anion SiF_6^{2-} . Positions of hydrogen atoms bound to nitrogen atoms were determined from difference Fourier syntheses. The fact of protonation of nitrogen atoms is clearly manifested as an increase in CNC angles in aromatic cycles up to $122.9(3)^\circ$ – $123.6(3)^\circ$. Anion SiF_6^{2-} in structure **I** has a distorted octahedron geometry (Si–F lying within 1.651(3)–1.717(3) Å). The cation and anion in **I** are linked by two $\text{NH}\cdots\text{F}$ hydrogen bonds oriented according to the chelate type (Fig. 1a). Weak $\text{CH}\cdots\text{F}$ interactions also make additional contribution to the stabilization of structure **I** (Fig. 1b).

Unlike for the HFA–2,2'-Bipy–MeOH–H₂O system [8], we were unable to extract crystals of the second possible reaction product, the *cis*-[SiF₄(Phen)] complex (**II**) suitable for use in XRD analysis, from the HFA–Phen–MeOH–H₂O reaction solution. The possibility of formation of the chelate complex **II** as one of the products of interaction in the HFA–Phen–MeOH–H₂O system was studied by ¹⁹F NMR. The ¹⁹F NMR spectrum of the products of the reaction between HFA and Phen in chloroform (Fig. 2), in addition to the signal from SiF_6^{2-} anion ($\delta_{\text{F}} = -127.89$ ppm), features two triplet signals of different intensities (A_2B_2 spin system, $\delta(\text{F}_A) = -124.88$ ppm, $\delta(\text{F}_B) = -149.51$ ppm, $J(\text{F}_A\text{F}_B) = 17.8$ Hz) that belong to the chelate complex **II** (**I** : **II** ~ 3 : 1 mol/mol) according to [14]. Interestingly, the ¹⁹F NMR spectrum of these products in an aqueous solution has a qualitatively similar shape; that is, the chelate structure of **II** is relatively stable in aqueous solution as well.

These data support the scheme of interaction between HFA and chelate-forming N-donor ligand **L** in an aqueous–organic environment that involves both formation of the expected product of acid–base

Table 2. Parameters of hydrogen bonds in **I**

D–H \cdots A	H \cdots A, Å	D \cdots A, Å	DHA angle, deg	Symmetry operations for atom A
N(1)–H(1N) \cdots F(2)	1.72(4)	2.618(4)	153(3)	x, y, z
N(2)–H(2N) \cdots F(4)	1.91(5)	2.676(4)	147(4)	x, y, z
C(3)–H(3) \cdots F(1)	2.34	3.248(4)	165	$2 - x, 1 - y, 1 - z$
C(1)–H(1) \cdots F(3)	2.25	3.143(4)	162	$x + 1, y, z$
C(8)–H(8) \cdots F(3)	2.57	3.156(4)	121	$x + 1, y, z - 1$
C(12)–H(12) \cdots F(3)	2.49	3.192(5)	133	$-x, 2 - y, 1 - z$
C(2)–H(2) \cdots F(5)	2.43	3.104(4)	129	$x + 1, y, z$
C(10)–H(10) \cdots F(6)	2.34	3.117(3)	141	$x, y, z - 1$
C(11)–H(11) \cdots F(6)	2.44	3.138(4)	132	$-x, 2 - y, 1 - z$

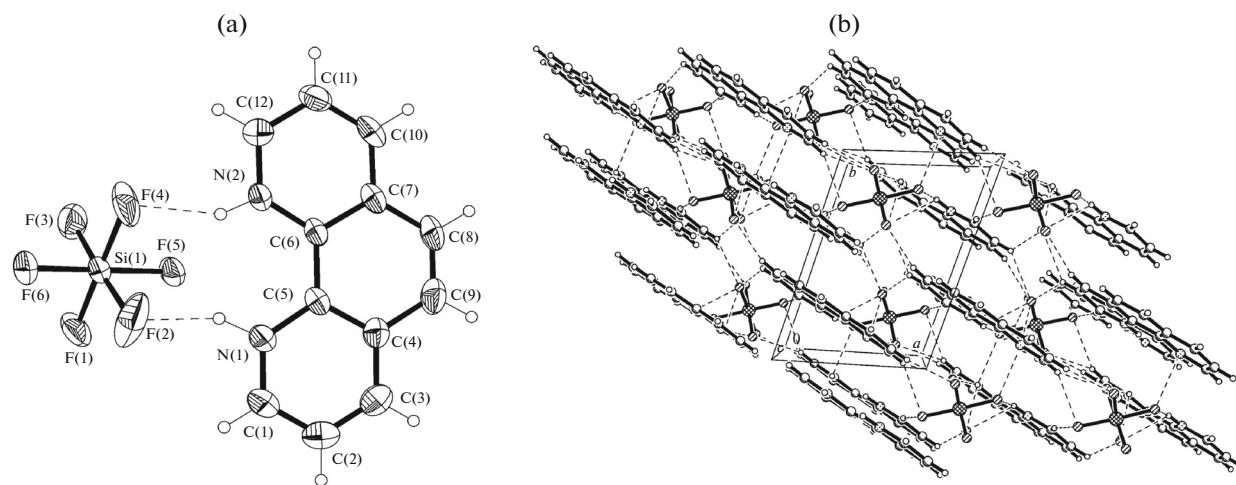


Fig. 1. (a) Structural units of crystal I: anion SiF_6^{2-} and cation PhenH_2^{2+} ; (b) packing of structural units in crystal I (projection along axis c).

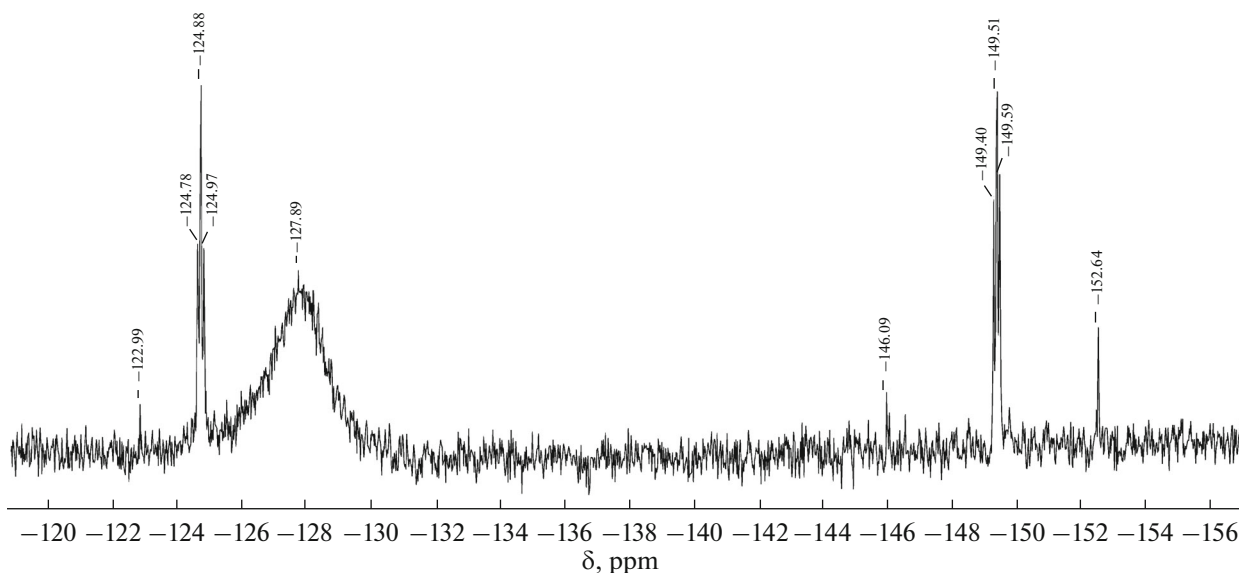
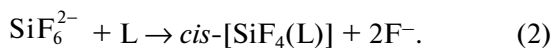
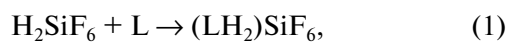
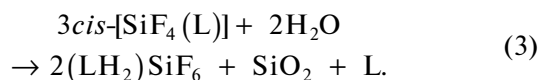


Fig. 2. ^{19}F NMR spectrum of the products of interaction between HFA and Phen in chloroform.

interaction (1) and the chelate complex (2) first proposed in [8]:



The chelate complex exhibits some resistance to hydrolysis in aqueous–organic and aqueous environments; i.e., the expected mild transformation of **II** to **I** via scheme 3 is not observed:



In particular, the *cis*- $[\text{SiF}_4(2,2'\text{-Bipy})]$ complex is also detected in the crystal mixture after recrystallization of the products of reaction between HFA and 2,2'-Bipy from an aqueous solution [8]. Let us emphasize that formation of the *cis*- $[\text{SiF}_4(\text{L})]$ chelate complex was detected previously when studying the interaction between HFA and various potential chelating ligands: piperazine [15], 1,2-phenylenediamine [16], tetramethyl ethylenediamine [17], 2-aminopyridine [18], and 3,5-diamino-1,2,4-triazole [19]. The possible reason is that ionic heterofluorosilicates, which were the major reaction products and most prone to form high-quality crystals, were extracted and studied in all cases.

Hence, the results of this study confirm the relative resistance of *cis*-[SiF₄(L)] chelate complexes to hydrolysis and the possibility of their formation as side products during the synthesis of hexafluorosilicates via reaction between HFA and bidentate N-donors, which needs to be taken into account when designing the corresponding experiments. To summarize, let us mention that the above-demonstrated experimental evidence for the hydrolysis resistance of the *cis*-[SiF₄(Phen)] complex is supported by quantum-chemical calculations [20] that attest to the stabilization of the *cis*-structure of the phenanthroline complex with bidentately coordinated molecular ligand due to the chelate effect.

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