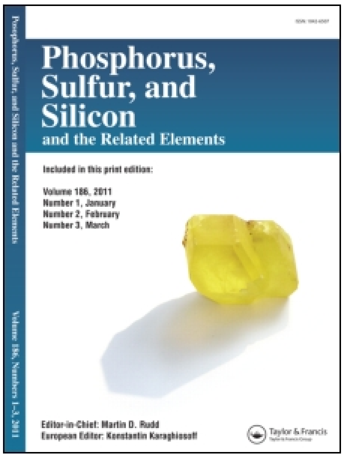


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Hexafluoropropylene Oxide-Alcohol: A Convenient System for Silica Dissolution

Sergey A. Lermontov[a]; Alena N. Malkova[a]; El'mira Kh. Lermontova[b]; Andrei V. Churakov[b]
[a] Russian Academy of Sciences, Institute of Physiologically Active Compounds, Chernogolovka, Moscow region, Russia [b] Russian Academy of Sciences, N. S. Kurnakov Institute of General and Inorganic Chemistry, Moscow, Russia

To cite this Article Lermontov, Sergey A. , Malkova, Alena N. , Lermontova, El'mira Kh. and Churakov, Andrei V.(2011) 'Hexafluoropropylene Oxide-Alcohol: A Convenient System for Silica Dissolution', Phosphorus, Sulfur, and Silicon and the Related Elements, 186: 1, 178 — 188

To link to this Article: DOI: 10.1080/10426507.2010.530324

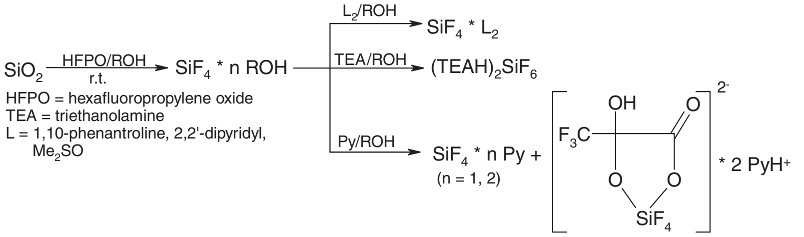
URL: http://dx.doi.org/10.1080/10426507.2010.530324

Phosphorus, Sulfur, and Silicon, 186:178–188, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2010.530324

HEXAFLUOROPROPYLENE OXIDE–ALCOHOL: A CONVENIENT SYSTEM FOR SILICA DISSOLUTION

Sergey A. Lermontov,[1] Alena N. Malkova,[1]
El'mira Kh. Lermontova,[2] and Andrei V. Churakov[2]
[1]Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka, Moscow region, Russia
[2]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia

GRAPHICAL ABSTRACT



Abstract *A new method of silica dissolution is described. It involves the formation of a stable $SiF_4 \cdot n$ ROH complex (**1**, **1a**) just from SiO_2 and anhydrous alcoholic HF generated in situ from commercially available hexafluoropropene oxide. Alcoholic SiF_4 complexes can be easily converted to different organosilicon compounds of the type SiF_4L_2 and $(LH)_2SiF_6$ [L = 1,10-phenantroline (**2a**), 2,2′-dipyridyl (**2b**), Me_2SO (**2c**), pyridine (**2d**), triethanolamine (**3a**)]. Different silica-containing compounds can be used in this strategy—silicagel, sand, alumosilicates, and even rice husk.*

Keywords Hexafluoropropene oxide; hydrogen fluoride; silica dissolution; silicon tetrafluoride

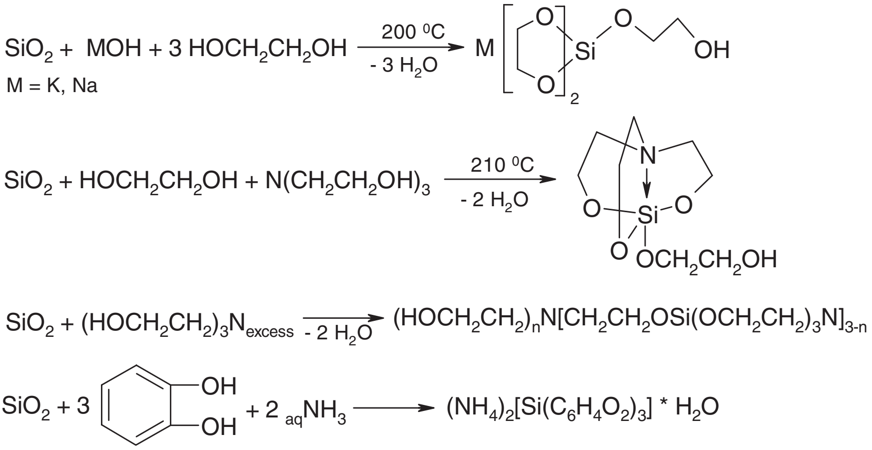
INTRODUCTION

Organosilicon chemicals are almost exclusively prepared from elemental silicon or silicon tetrachloride, obtained from the carbothermal reduction of silica at around 1200–1300°C.[1] The main problem with any industrial process based on silica as a starting material is the very strong Si—O bond (about 535 kJ/mol in SiO_2). The utilization of silica itself to produce silicon-containing compounds with the aim to exclude high-temperature processes has been the aim of a number of investigations. Only a few strategies of silica depolymerization and further dissolution are known to date. Silica dissolution in alkali

Received 28 May 2010; accepted 4 October 2010.

Address correspondence to Sergey A. Lermontov, Institute of Physiologically Active Compounds, Russian Academy of Sciences, Severny proezd 1, 142432, Chernogolovka, Moscow region, Russia. E-mail: lermon@ipac.ac.ru

metals hydroxides and in hydrogen fluoride are well known reactions affording inorganic silicates, H_2SiF_6, or gaseous SiF_4.[1] A method of SiO_2 depolymerization in alkaline alcohols with the formation of silicon chelates has been developed by different research groups[2–5] (Scheme 1). These procedures usually afford crystalline solvates, frequently containing water and/or glycol. This fact makes it difficult to use the products in organometallic synthesis.



Scheme 1

The main goal of our work was to find a method of silica dissolution that was satisfactory to the following conditions: (i) the method should not need high temperature and (ii) it should afford products suitable for organometallic synthesis or as a silicon source for the electronics industry.

RESULTS AND DISCUSSION

Dissolution of Silica

Silicon tetrafluoride reacts rapidly with water, forming H_2SiF_6 and SiO_2.[6] Unlike solutions of SiF_4 in lower alcohols, (C_1–C_4) are rather stable at least at ambient temperature.[6,7] It is assumed that solvates containing hexacoordinate silicon are formed (Figure 1).

Basing on these facts, we propose a new strategy for silica dissolution under very mild conditions. The strategy consists in the primary generation of anhydrous HF in an alcohol

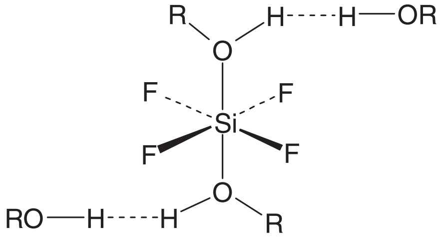
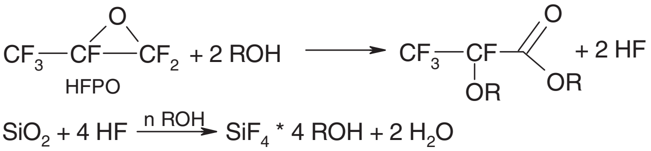


Figure 1 Structure of SiF_4–alcohol complex.

followed by the reaction with silica. The idea is based on the assumption that an excess of the alcohol will replace water from the coordination sphere of SiF_4, thus preventing its hydrolysis. Different compounds producing HF in the reaction with alcohols can be used for this strategy: SF_4,[8] perfluoroalkene oxides,[9,10] organic acid fluoroanhydrides,[11] and, of course, hydrogen fluoride itself.

We have found that the most convenient source of alcoholic HF in laboratory practice is hexafluoropropene oxide (HFPO), a commercially available and safe compound, which reacts rapidly with alcohols producing two moles of HF and an inert ester.[9,10] Silica and silica-containing compounds are easily dissolved in an alcoholic solution of HFPO giving SiF_4 complexes **1** and **1a**, which are stable at ambient temperature (Scheme 2).



1 , R = Me
1a , R = Et

Scheme 2

The dissolution reaction proceeds rapidly at room temperature when a stream of HFPO is passed through a SiO_2 suspension in the respective alcohol. We have found esters of 2-alkoxytetrafluoropropionic acid in the reaction mixture, thus confirming the primary reaction of HFPO with the alcohol. By a special experiment, we have prepared a solution of gaseous SiF_4 in anhydrous MeOH and have found that its ^{19}F NMR spectrum was identical with that of **1**.

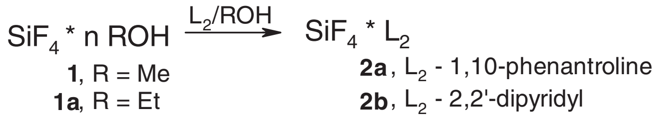
Different silica-containing compounds can be used as a silica source in this procedure: silicagel, sand, alumosilicates, and even rice husk. Rice husk is one of the most serious contaminants in rice-producing countries. Its annual worldwide production is about 100 million tons.[12] Rice husk is a rather unusual material: the SiO_2 content in it is approximately 20% (together with 75% organic matter—mainly cellulose and lignin—and 5% inorganic salts). Rice husk is hardly burned or milled, and it is very slowly decomposed in nature.[13] Several methods of its use as a silica source are known.[13–15] Usually these methods include controlled burning or anaerobic pyrolysis of rice husk (at 500–600°C) followed by a SiO_2/C mixture oxidation.

We have shown that up to 97% of silica could be extracted from rice husk using the described procedure. It is worth mentioning that the organic part of rice husk (cellulose and lignin) is not destroyed during SiO_2 extraction and can be further used as usual wood. This means that there exists a possibility to elaborate a process of full rice husk processing: silica extraction → fermentation → bioethanol and biobuthanol.

For the purposes of potential industrial application, we have dissolved silica gel and have extracted silica from rice husk by an alcoholic solution of inexpensive hydrogen fluoride. This procedure is not convenient for laboratory use because serious precautions are needed to prevent personnel from poisoning by the very hazardous hydrogen fluoride.

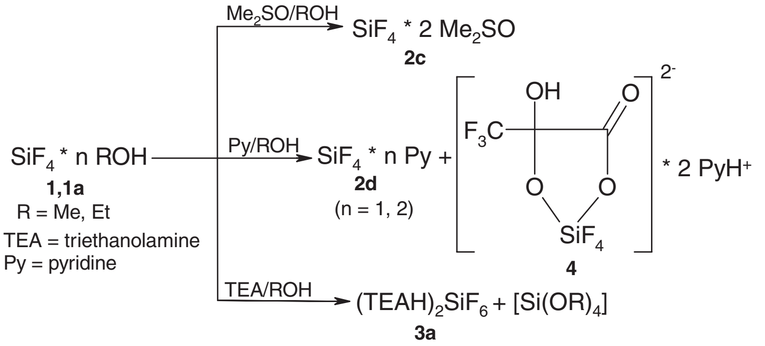
Properties of the Complexes Prepared

Complexes **1** and **1a** afford crystalline products after the reaction with tertiary amines (Scheme 3). Compounds **2** are formed immediately after addition of the ligand and are usually pure enough after filtration, washing, and drying. They are colorless, stable crystalline substances that are soluble in polar solvents like Me_2SO and DMF. The structures of both **2a** and **2b** were established by NMR spectroscopy and elemental analysis and were confirmed by X-ray diffraction.[16,17] The ^{19}F NMR spectra of **2a,b** show two triplets (A_2X_2 spin systems), confirming the formation of *cis*-complexes.



Scheme 3

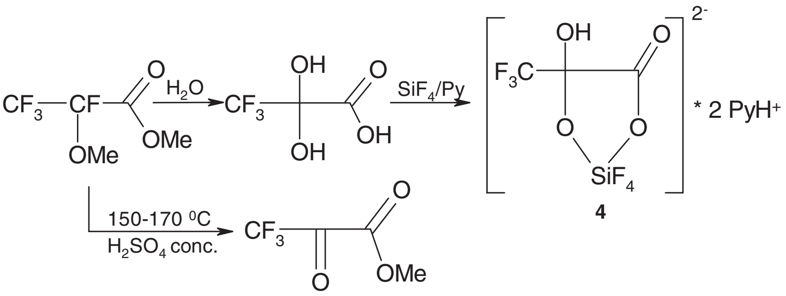
More complex mixtures of silicon-containing compounds are usually formed with nonchelating ligands (Scheme 4). Thus, dimethylsulfoxide gives a “normal” 1:2 adduct **2c**. In the case of triethanolamine (TEA), only hexafluorosilicate **3a** was formed as a Si-F-containing product. Our attempt to prepare pure compounds of type **2** or **3** from compound **1** and pyridine were unsuccessful. The reaction affords a mixture of products. The formation of **2d** is consistent with data in the literature for SiF_4-pyridine adducts—both types of products (1:2 and 1:1) are described.[18,19]



Scheme 4

We were able to obtain single crystals of a minor product **4**, which were suitable for X-ray diffraction. Compound **4** is a rare example of the hexacoordinate silicon anion with mixed oxygen—bonded and halogen ligands.[20] The organic part of this anion is a derivative of trifluoropyruvic acid hydrate, which is probably formed from hydrolysis of the methyl ester of 2-methoxytetrafluoropropionic acid by water present in the reaction mixture (Scheme 5).

The formation of compound **4** looks very unusual because a transformation of alkoxytetrafluoropropionic esters into trifluoropyruvic acid derivatives needs high temperature and strong acids as catalysts[10] (Scheme 5). In our case it proceeds at ambient temperature without any catalyst.



Scheme 5

Compound **4** crystallizes in the space group P-1. The diamond representation of the complex is given in Figure 2; selected bond lengths and bond angles are listed in Table 1. The coordination polyhedron of the silicon atom in complex **4** displays a slightly distorted octahedral geometry. All of the *cis* bond angles are close to 90° [86.3(7)–95.8(7)°], while *trans* angles are greater than 170° [174.0(1)–177.8(1)°]. The five-membered ring is almost planar, with atom O1 displaced from the least-squares plane by 0.180(3) Å. The O1—C1—C3—O2 torsion angle is 7.2(3)°.

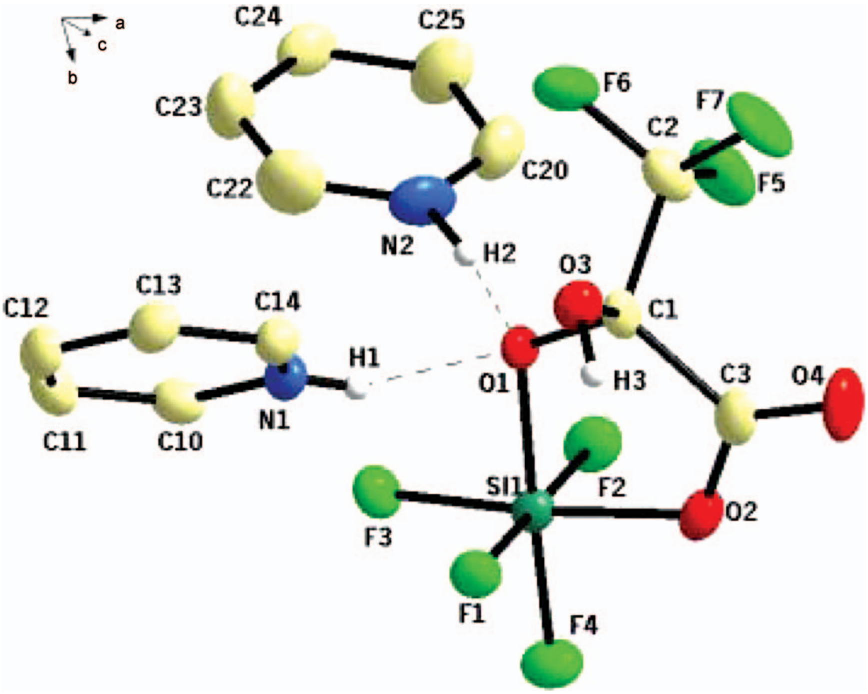


Figure 2 Crystal structure of **4** showing anion–cation interactions. Hydrogen atoms are omitted for clarity except those participating in hydrogen bonding. Thermal ellipsoids are given at the 50% probability level, except for H atoms, which have arbitrary radii. [Please see the color version of this figure online.]

Table 1 Selected bond lengths (Å) and angles (°) of 4

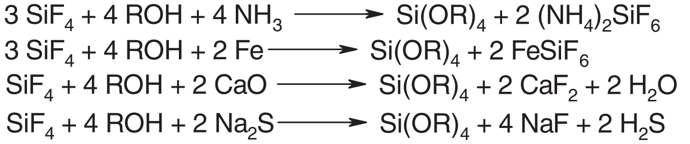
Bond length (Å)		Bond angle (°)	
Si1—F4	1.6497(14)	∠F2—Si1—F1	177.78(7)
Si1—F3	1.6576(14)	∠F4—Si1—O1	175.14(8)
Si1—F2	1.6678(14)	∠F3—Si1—O2	173.98(7)
Si1—F1	1.7137(14)		
Si1—O1	1.8017(15)		
Si1—O2	1.8135(17)		
O1—C1	1.385(3)		
O2—C3	1.303(3)		
O3—C1	1.402(3)		
O4—C3	1.212(3)		

The pyridinium counter ions are linked to a central dianion through N—H—O hydrogen bonds. Only one oxygen atom of the ligand is involved in both hydrogen bonds. Two centrosymmetrically related anions form dimers by O(3)—H(3)—F(1) hydrogen bond (Figure 3). The latter results in a noticeable elongation of the Si(1)—F(1) bond. The structural parameters of the hydrogen bonds are given in Table 2.

CONCLUSION

In summary, a novel, convenient strategy for the dissolution of silicon dioxide has been developed, which uses available reagents and proceeds at ambient temperature affording pure complexes of SiF_4. This procedure can make SiO_2 a good starting material for inorganic and organometallic synthesis.

In our opinion, the most interesting application of SiF_4 complexes is their conversion to tetraalkoxysilanes. Several methods for the synthesis of tetraalkoxysilanes $Si(OR)_4$ from tetrafluorosilane are patented[21–25] (Scheme 6).



$$3\,SiF_4 + 4\,ROH + 4\,NH_3 \longrightarrow Si(OR)_4 + 2\,(NH_4)_2SiF_6$$
$$3\,SiF_4 + 4\,ROH + 2\,Fe \longrightarrow Si(OR)_4 + 2\,FeSiF_6$$
$$SiF_4 + 4\,ROH + 2\,CaO \longrightarrow Si(OR)_4 + 2\,CaF_2 + 2\,H_2O$$
$$SiF_4 + 4\,ROH + 2\,Na_2S \longrightarrow Si(OR)_4 + 4\,NaF + 2\,H_2S$$

Scheme 6

When performed on an industrial scale, these processes can become the basis for the use of SiO_2 as a starting material in organosilicon chemistry.

The developed method of silica dissolution can also be useful for the extraction of silica from different silicon-containing compounds including serious agricultural contaminants such as rice husk.

EXPERIMENTAL

^1H and ^{19}F NMR spectra were recorded with a Bruker DPX-200 spectrometer at 200 MHz and 188 MHz, respectively. Chemical shifts are given relative to TMS (^1H) and $CFCl_3$ (^{19}F) as external standards.

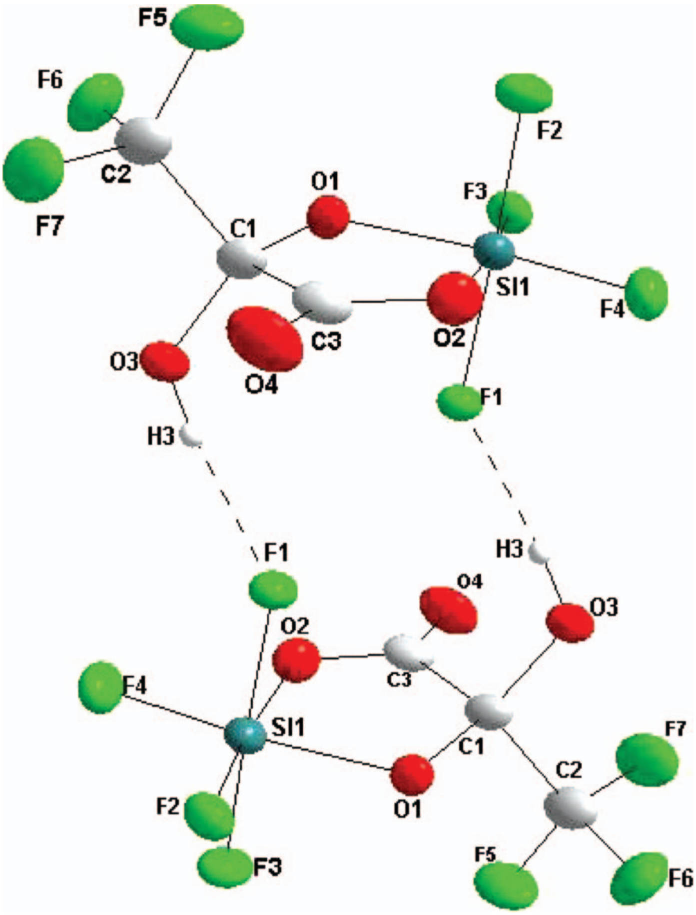


Figure 3 Centrosymmetric dimers in the structure of **4**. Hydrogen atoms are omitted for clarity except those participating in hydrogen bonding. The pyridine rings are not shown for clarity. Thermal ellipsoids are given at the 50% probability level, except for H atoms, which have arbitrary radii. [Please see the color version of this figure online.]

Hexafluoropropene oxide (HFPO) was a commercial product from Kirovo-Chepetsk chemical plant (Russia) (99.7% purity). Silica gel (Chemapol, L 100/250) was dried at 150°C during 2 h before a reaction. Rice husk was obtained from one of south Russia rice mills and was washed with aqueous HCl according to the method of Liou et al.[26]

Table 2 Hydrogen bonding interactions in the compound 4(Å, °)

	d(D—H)	d(H . . . A)	d(D . . . A)	∠(D—H . . . A)
O3—H3 . . . F1$^{\mathrm{i}}$	0.82(3)	1.81(3)	2.626(2)	174(3)
N1—H1 . . . O1$^{\mathrm{ii}}$	0.79(3)	2.24(3)	2.984(3)	156(3)
N2—H2 . . . O1$^{\mathrm{iii}}$	0.97(5)	1.86(5)	2.814(3)	168(4)

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $x-1, y, z-1$; (iii) $x-1, y, z$.

2,2′-Dipyridyl (Lancaster), 1,10′-phenanthroline (Chemapol), triethanolamine (Merck), *N*-pyridine oxide (Aldrich), anhydrous methanol (Aldrich, 0.05% water content), and ethanol (Aldrich, 0.1% water content) were used as purchased. Other solvents and reagents were purified and dried by standard procedures.

Anhydrous SiF_4 was prepared from a SiO_2/Na_2SiF_6 mixture by treatment with concentrated sulfuric acid.

SiO_2 Dissolution: General Procedure

Anhydrous MeOH (10 mL) and silica gel (0.6 g, 0.01 mol) were placed in a polytetrafluoroethylene (PTFE) flask equipped with a PTFE gas-injection tube, and HFPO (3.32 g, 0.02 mol, determined from the weight increase) was introduced with magnetic stirring at room temperature. The reaction was slightly exothermic. When HFPO addition was complete, the reaction mixture was stirred for 1 h (the whole amount of silica gel was dissolved). Then a solution of 0.01 mol of 1,10-phenanthroline or 2,2′-bipyridyl in anhydrous MeOH (5 mL) was added. A precipitate was formed immediately, which was stored for 1 h, separated by filtration, washed with MeOH, and dried in vacuo.

The ^{19}F NMR spectrum of the filtrate after evaporation of the solvent contained the signals of $CF_3CF(OCH_3)COOCH_3$: $\delta = -80.5$ (d, $^3J_{FF} = 3$ Hz, 3F, CF_3), -133.5 (m, 1F), which coincided with those of the separately prepared ester.[10]

The reaction in dry ethanol produced compound **1a**.

Compound **2a** was isolated from a Me_2SO/MeOH mixture, 69% yield, mp > 230°C. The ^{1}H NMR spectrum (DMSO-d_6) contained two sets of signals corresponding to the 1,10-phenanthroline ligand in a 1.5:1 intensity ratio: $\delta = 8.0$ (m, 2H), 8.2 (s, 2H), 8.6 (m, 2H), 9.2 (m, 2H); $\delta = 8.2$ (m, 2H), 8.4 (s, 2H), 9.0 (m, 2H), 9.3 (m, 2H). ^{19}F NMR (DMSO-d_6): $\delta = -118.3$ (t, $^2J_{FF} = 18.4$ Hz, 2F, SiF_2; $J_{SiF} = 164$ Hz), -143.1 (t, $^2J_{FF} = 18.4$ Hz, 2F, SiF_2; $J_{SiF} = 146$ Hz), -135.0 (broad). Anal. Calcd for $C_{12}H_8N_2SiF_4$: C, 50.69; H, 2.84; F, 26.73. Found: C, 50.67; H, 2.79; F, 26.67%. Single crystals suitable for X-ray diffraction were obtained from the Me_2SO/MeOH mixture. X-ray analysis revealed that compound **2a** crystallized isostructurally to a substance described earlier in the literature.[16] Compound **2a** was also obtained from **1a** in 76% yield.

Compound **2b** was isolated from a Me_2SO/MeOH mixture, 74% yield, mp > 230°C. ^{1}H NMR spectrum (DMSO-d_6) contained signals corresponding to the 2,2′-bipyridyl ligand: $\delta = 8.0$ (m, 2H), 8.5 (m, 2H), 8.6 (m, 2H), 9.0 (m, 2H). ^{19}F NMR (DMSO-d_6): $\delta = -118.7$ (t, $^2J_{FF} = 14.4$ Hz, 2F, SiF_2; $J_{SiF} = 160$ Hz), -142.0 (t, $^2J_{FF} = 13.0$ Hz, 2F; SiF_2, $J_{SiF} = 161$ Hz). Anal. Calcd. for $C_{10}H_8N_2SiF_4$: C, 46.14; H, 3.09; F, 29.20. Found: C, 46.08; H, 3.06; F, 29.35%. Single crystals suitable for X-ray diffraction were obtained from the Me_2SO/MeOH mixture. X-ray analysis revealed that compound **2b** crystallized isostructurally to a substance described earlier in the literature.[17]

Dissolution of Sand

Compound **2a** was synthesized from washed sand according to the above procedure in 40% yield after 20 h of stirring (unreacted sand was separated by filtration).

Dissolution of Zeolite

Compound **2a** was prepared from 1 g of zeolite 4A ($Na_{12}[(AlO_2)_{12}/(SiO_2)_{12}] \cdot 27\ H_2O$, dried at 300°C during 6 h) in 74% yield after 25 h of stirring (unreacted zeolite was separated by filtration).

Extraction of SiO_2 from Rice Husk

Rice husk [3 g, containing approximately 0.6 g (0.01 mol) of SiO_2] were stirred for 4 h with a solution of 3.32 g (0.02 mol) of HFPO in anhydrous MeOH (20 mL) at room temperature. The organic part of rice husk was separated by filtration, and a solution of 1,10-phenanthroline (0.01 mol) in anhydrous MeOH (5 mL) was added to the filtrate. Compound **2a** was obtained in 73% yield.

A sample of organic part of rice husk was burnt at 500°C in a steam of air, revealing that 97% of SiO_2 was extracted.

Use of Alcoholic Solution of HF

Dissolution of SiO_2. Anhydrous MeOH (10 mL) and silica gel (0.6 g, 0.01 mol) were placed in a PTFE flask equipped with a PTFE gas-injection tube, and gaseous HF (0.8 g, 0.04 mol, determined from the weight increase) was introduced with magnetic stirring at room temperature. The reaction was slightly exothermic. After HF addition was complete, the reaction mixture was stirred during 1 h. During this time, the whole amount of silicagel was dissolved. Then a solution of 0.01 mol of 1,10-phenanthroline in anhydrous MeOH (5 mL) was added. A precipitate was immediately formed, stored for 1 h, separated by filtration, washed with MeOH, and dried in vacuo. Compound **2a** was obtained in 57% yield.

Extraction of SiO_2 from rice husk. Anhydrous MeOH (20 mL) and rice husk [3 g, containing approximately 0.6 g (0.01 mol) of SiO_2] were placed in a PTFE flask equipped with a PTFE gas-injection tube and gaseous HF (0.8 g, 0.04 mol, determined from the weight increase) was introduced with magnetic stirring at room temperature. The reaction was slightly exothermic. After HF addition was complete, the reaction mixture was stirred during 5 h. The organic part of rice husk was filtered off, and a solution of 0.005 mol of 1,10-phenanthroline in anhydrous MeOH (5 mL) was added to the filtrate. A precipitate was immediately formed, stored for 1 h, separated by filtration, washed with MeOH, and dried in vacuo. Compound **2a** was obtained in 49% yield.

Preparation of SiF_4L_2 with Nonchelating Ligands

A solution of 0.02 mol of Me_2SO, triethanolamine, or pyridine in anhydrous MeOH (5 mL) was added to a solution of **1**, prepared from SiO_2 (0.6 g, 0.01 mol). A precipitate was usually formed immediately, stored for 1 h, separated by filtration, washed with MeOH, and dried in vacuo. Compound **2c** was soluble in MeOH, and after removal of the solvent, it was purified by crystallization from toluene, 74% yield, mp 101–104°C. Anal. Calcd. for $C_4H_{12}S_2O_2SiF_4$: C, 18.45; H, 4.65; F; 29.19. Found: C, 17.85; H, 5.32; F; 29.13%. ^1H NMR (CD_3CN): $\delta = 2.9$ (s, 6H, CH_3S), 7.0 (s, 1H, SOH). ^{19}F NMR (CD_3CN): $\delta = -137.5$ (s). Alternatively, compound **2c** was prepared as described in the literature[18] by passing SiF_4 (0.0035 mol), prepared from conc. H_2SO_4 and **1**, through a solution of Me_2SO (0.6 g, 0,007 mol) in benzene (5 mL). A precipitate was immediately formed. The reaction mixture was stored for 1 h, the precipitate was separated by filtration, washed with benzene, and dried in vacuo. ^1H and ^{19}F NMR spectra and the melting point of both samples of **2c** were identical.

Compound **3a** was isolated from MeOH, 71% yield, mp 100–101°C. ^1H NMR (D_2O): $\delta = 3.4$ (t, $^3J_{HH} = 5.2$ Hz, 2H, NCH_2), 3.9 (t, $^3J_{HH} = 5.0$ Hz, 2H, OCH_2). ^{19}F NMR (D_2O):

$\delta = -127.5$; $J_{\mathrm{SiF}} = 108$ Hz. Anal. Calcd for $C_{12}H_{32}N_2O_6SiF_6$: C, 32.57; H, 7.29; F, 25.76. Found: C, 32.07; H, 7.36; F, 25.14%. Alternatively, compound **3a** was prepared as described in the literature[27] by passing SiF_4 (0.01 mol), prepared from conc. H_2SO_4 and **1**, through a solution of triethanolamine (2.98 g, 0,02 mol) in anhydrous MeOH (5 mL). A precipitate was immediately formed, the reaction mixture was stored for 1 h, the precipitate was separated by filtration, washed with MeOH, and dried in vacuo. ^1H and ^{19}F NMR spectra and the melting point of both samples of **3a** were identical.

Compound **2d** was isolated from MeOH, 1.92 g yield. Anal. Calcd for $C_{10}H_{12}N_2SiF_4$ ($SiF_4 \cdot 2$ py): C, 45.79; H, 3.84; F, 28.98. Anal. Calcd for $C_5H_5NSiF_4$ ($SiF_4 \cdot$ py): C, 32.78; H, 2.75; F, 41.49. Found: C, 37.53; H, 3.61; F, 35.53%. The elemental analysis data reveal that the composition of isolated **2d** is between that of $SiF_4 \cdot 2$ py and of $SiF_4 \cdot$ py. The ^1H NMR spectrum (DMSO-d_6) contained signals corresponding to the pyridine ligand: $\delta =$ 7.9 (m, 2H), 8.4 (m, 1H), 8.9 (m, 2H). ^{19}F NMR (DMSO-d_6): $\delta = -133.9$; $J_{\mathrm{SiF}} = 107$ Hz.

A single crystal of compound **4** was prepared by a slow evaporation of methanol from the mother liquid. Its structure was established by X-ray diffraction.

X-Ray Structure Determination

Experimental intensities were collected on a Bruker Smart Apex II diffractometer using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å, ω-scan). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL-97)[28] with anisotropic displacement parameters for all nonhydrogen atoms (Table 3).

All hydrogen atoms were found from difference Fourier synthesis and refined isotropically. Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-683674. Copies of the data can be obtained free of charge upon

Table 3 Crystal structure and data refinement parameters

Compound	**4**
Empirical formula	$C_{13}H_{13}F_7N_2O_4Si$
Formula weight	422.34
Crystal system/space group	*P*-1
a/Å	8.8583(17)
b/Å	10.062(2)
c/Å	10.163(2)
α/°	71.698(3)
β/°	69.623(3)
γ/°	72.258(3)
V/Å^3	786.5(3)
Z	2
D $_{\mathrm{calc}}$ (g/cm^3)	1.783
μ (mm^{-1})	0.254
Temp (K)	150(2)
Theta range for collection	$2.19 < \theta < 26.99$
Reflections collected	5831
Independent reflections	3327 [Rint = 0.0418]
R indices (all data)	0.0610; 0.1040

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

1. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; (Wiley-Interscience: New York, 1982); vol. 20, pp. 752–755.
2. Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardy, P.; Kampf, J.; Uhm, J. *Nature* **1991**, *353*, 642.
3. Laine, R. M.; Cheng, H. *New J. Chem.* **1999**, *23*, 1181.
4. Kemmitt, T.; Henderson, W. *Aust. J. Chem.* **1998**, *51*, 1031.
5. Barnum, D. W. *Inorg. Chem.* **1972**, *11*, 1424.
6. Gel'mbol'dt, V. O.; Ennan, A. A. *Koord. Khim. (Russ.)* **1983**, *9*, 579.
7. Guertin, J. P.; Onyszchuk, M. *Can. J. Chem.* **1963**, *41*, 1477.
8. Boswell, G. A.; Ripka, W. C.; Scribner, R. M.; Tullok, C. W. *Org. React.* **1973**, *21*, 1.
9. Sianesi, D.; Pasetti, A.; Tarli, F. *J. Org. Chem.* **1966**, *31*, 2312.
10. Dolenský, B.; Kvičala, J.; Paleček, J.; Paleta, O. *J. Fluorine Chem.* **2002**, *115*, 67.
11. Lermontov, S. A.; Malkova, A. N. *Russ. Chem. Bull.* **2007**, *56*, 435.
12. Yalcin, N.; Sevinc, V. *Ceram. Int.* **2001**, *27*, 219.
13. Sun, L.; Gong, K. *Ind. Eng. Chem. Res.* **2001**, *40*, 5861.
14. Kennedy, L. J.; Vijaya, J. J.; Sekaran, G. *Ind. Eng. Chem. Res.* **2004**, *43*, 1832.
15. Chandrasekhar, S.; Satyanarayana, K. G.; Pramada, P. N.; Raghavan, P.; Gupta, T. N. *J. Mater. Sci.* **2003**, *38*, 3159.
16. Chehlov, A. N.; Tkachev, V. V.; Lermontov, S. A. *J. Struct. Chem. (Russ.)* **2003**, *44*, 1080.
17. Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402.
18. Muetterties, E. L. *J. Am. Chem. Soc.* **1960**, *82*, 1082.
19. Bain, V. A.; Killean, R. C. G.; Webster, M. *Acta Cryst.* **1969**, *B25*, 156.
20. Denmark, S. E.; Fan, Y.; Eastgate, M. D. *J. Org. Chem.* **2005**, *70*, 5235.
21. Scheel, K. C.; Schmidt, H. W. West Germany Patent DE 946893, August 9, 1956.
22. Scheel, K. C. West Germany Patent DE 1002748, July 25, 1957.
23. Jenkner, H.; Koster, A.; Scheel, K. C. West Germany Patent DE 955236, January 3, 1957.
24. Maclelland Pollock, J. British Patent GB 901676, July 25, 1962.
25. Maclelland Pollock, J. British Patent GB 866766, May 3, 1961.
26. Liou, T.-H.; Chang, F.-W.; Lo, J.-J. *Ind. Eng. Chem. Res.* **1997**, *36*, 568.
27. Ennan, A. A.; Gavrilova, L. A.; Kirichenko, I. N. *Zh. Neorg. Khim. (Russ.)* **1974**, *19*, 3264.
28. Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures; University of Gottingen, Gottingen, Germany, 1997.