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A Neutral Pentacoordinate Silicon(IV) Complex with a Monodentate Nitrato Ligand: Synthesis and Structural Characterization

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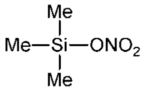
Summary: The neutral pentacoordinate nitratosilicon(IV) complex **7** *was synthesized by treatment of the corresponding chlorosilicon(IV) complex* **8** *with Me_3SiONO_2 (Cl/ONO_2 exchange). Compound* **7** *is the first higher-coordinate silicon compound with an Si−ONO_2 group that could be structurally characterized both in solution (^{1}H, ^{13}C, and ^{29}Si NMR) and in the solid state (VACP/MAS ^{13}C and ^{29}Si NMR, crystal structure analysis of* **7**$\cdot CH_2Cl_2$*).*

Only a few silicon compounds with an Si−ONO_2 moiety have been described in the literature, such as **1**,[1] **2**,[2] **3**,[3] **4**,[4] **5**,[5] and **6**[6]. To the best of our knowledge, the nitratosilane **3** (with a tetracoordinate silicon atom) is the only Si−ONO_2-containing compound that has been structurally characterized by single-crystal X-ray diffraction.[3] We have now succeeded in synthesizing a neutral pentacoordinate silicon(IV) complex with a monodentate nitrato ligand, compound **7**, and in characterizing its structure both in the solid state (^{13}C and ^{29}Si VACP/MAS NMR studies, crystal structure analysis of the solvate **7**$\cdot CH_2Cl_2$) and in solution (^{1}H, ^{13}C, and ^{29}Si NMR studies). The studies reported here were performed in context with our systematic investigations on higher-coordinate silicon compounds (for recent publications, see ref 7; for reviews dealing with higher-coordinate silicon compounds, see ref 8).


$Me_3Si{-}ONO_2$

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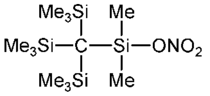
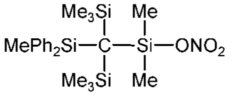
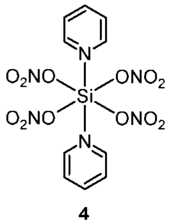

$(Me_3Si)_3C{-}SiMe_2{-}ONO_2$

2


$(Me_3Si)_2(MePh_2Si)C{-}SiMe_2{-}ONO_2$

3



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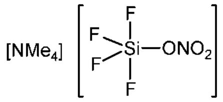

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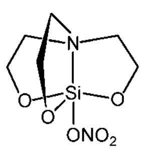

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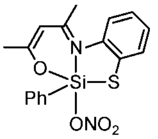
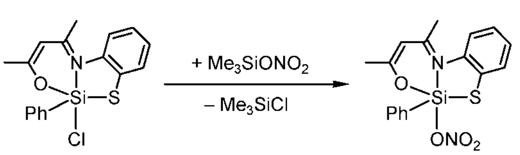


7

The pentacoordinate nitratosilicon(IV) complex **7** was synthesized according to Scheme 1 by treatment of the corresponding chlorosilicon(IV) complex **8**[9] with an excess of trimethyl(nitrato)silane (**1**), which was used as a freshly prepared solution in dichloromethane.[10]

Scheme 1



8 **7**

The synthesis of **7** was performed at 20 °C, and the product was isolated as the crystalline yellow solvate **7**$\cdot CH_2Cl_2$. The solvent of this solvate could be removed by heating to 40 °C in vacuo over a period of 3 h without significant decomposition. However, upon heating to 80 °C, compound **7** decomposed spontaneously (formation of a brown gas). Neat **7** could be stored at −20 °C under an argon atmosphere

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10.1021/om800676a CCC: $40.75

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of $7 \cdot CH_2Cl_2$

empirical formula	$C_{18}H_{18}Cl_2N_2O_4SSi$
formula mass, g mol^{-1}	457.39
collection *T*, K	193(2)
λ(Mo Kα), Å	0.71073
crystal system	orthorhombic
space group (no.)	*Pbca* (61)
a, Å	12.2777(14)
b, Å	16.159(3)
c, Å	20.531(3)
V, Å^3	4073.2(10)
Z	8
D(calcd), g cm^{-3}	1.492
μ, mm^{-1}	0.508
F(000)	1888
crystal dimensions, mm	0.5 × 0.4 × 0.2
2θ range, deg	5.18−58.20
index ranges	$-15 \le h \le 15$, $-22 \le k \le 22$, $-28 \le l \le 28$
no. of collected reflections	55964
no. of independent reflections	5245
R_{int}	0.0413
no. of reflections used	5245
no. of parameters	255
S^a	1.046
weight parameters *a*/*b*^{b}	0.0550/1.8181
$R1^c$ [$I > 2\sigma(I)$]	0.0381
$wR2^d$ (all data)	0.1030
max./min. residual electron density, e Å^{-3}	+0.708/−0.554

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

for some months, whereas at 20 °C, after a period of ca. two weeks, decomposition was observed (change of color from yellow to brown to black). The mechanism of this decomposition is unclear.

Upon dissolution of **7** in CD_2Cl_2 at 20 °C, decomposition was observed within some hours. Nevertheless, the ^1H, ^{13}C, and ^{29}Si NMR spectra of **7** could be measured. However, after a short time under MAS conditions at 22 °C, compound **7** decomposed spontaneously in the rotor of the solid-state NMR spectrometer. Therefore, it was not possible to measure a ^{15}N NMR spectrum, and we could only perform ^{13}C and ^{29}Si VACP/MAS NMR experiments with a limited number of scans.

The isotropic ^{29}Si chemical shift obtained in the solid state (δ −89.1) confirms the existence of a pentacoordinate silicon atom and is very similar to that measured in solution (CD_2Cl_2, δ −86.2), indicating similar structural features of **7** in the solid state and in solution. This is also supported by other solid-state and solution NMR data (see Experimental Section).

The crystal structure analysis of $\mathbf{7} \cdot CH_2Cl_2$ (Table 1, Figure 1) revealed a somewhat distorted trigonal-bipyramidal Si-coordination polyhedron, with an axial O2−Si−N1 angle of 163.23(6)° and maximum deviations from the ideal 90° and 120° angles of 10.19(6)° and 9.24(5)°, respectively. The Si−S, Si−O1, Si−N1, and Si−C1 distances of $\mathbf{7} \cdot CH_2Cl_2$ differ only slightly from those observed for **8**.[9] As expected, the equatorial Si−O1 bond (1.6807(11) Å) is significantly shorter than the axial Si−O2 bond (1.8323(12) Å). The latter $Si-ONO_2$ bond distance is significantly longer than the $Si-ONO_2$ bond distance of the tetracoordinate silicon compound **3** (1.728(5) Å), and the $SiO-NO_2$ bond of $\mathbf{7} \cdot CH_2Cl_2$ (1.3584(18) Å) is somewhat shorter than the $SiO-NO_2$ bond of **3** (1.380(9) Å).[3] The other geometric parameters of the ONO_2 moieties of **3** and $\mathbf{7} \cdot CH_2Cl_2$ are very similar.

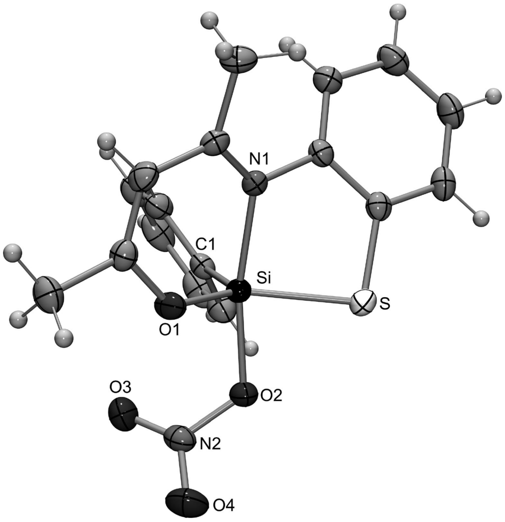

Figure 1. Molecular structure of **7** in the crystal of $\mathbf{7} \cdot CH_2Cl_2$ (probability level of displacement ellipsoids, 50%). Selected bond lengths (Å) and angles (°): Si−S 2.1720(6), Si−O1 1.6807(11), Si−O2 1.8323(12), Si−N1 1.9634(13), Si−C1 1.8722(16), O2−N2 1.3584(18), O3−N2 1.2170(19), O4−N2 1.2133(19); S−Si−O1 129.24(5), S−Si−O2 81.99(4), S−Si−N1 86.28(4), S−Si−C1 114.40(5), O1−Si−O2 86.67(6), O1−Si−N1 91.56(6), O1−Si−C1 116.28(6), O2−Si−N1 163.23(6), O2−Si−C1 100.19(6), N1−Si−C1 95.55(6), Si−O2−N2 121.42(9), O2−N2−O3 118.64(13), O2−N2−O4 115.19(14), O3−N2−O4 126.13(15).

In conclusion, compound **7** is the first higher-coordinate silicon(IV) complex with an $Si-ONO_2$ group that could be structurally characterized both in the solid state and in solution. Neat **7** is relatively stable at 20 °C but decomposes spontaneously upon heating to ca. 80 °C. In solution (CD_2Cl_2), compound **7** already decomposes at 20 °C within a few hours. Except for the detection of 2-methyl-1,3-benzothiazole and acetone, all attempts to determine the nature of the decomposition products failed so far. Thus, the decomposition mechanism in solution and in the solid is totally unclear.

Experimental Section

General Procedures. The syntheses were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and were stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed glass capillaries. The ^1H, ^{13}C, and ^{29}Si solution NMR spectra were recorded at 23 °C on a Bruker Avance 500 NMR spectrometer (^1H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz) using CD_2Cl_2 as the solvent. Chemical shifts (ppm) were determined relative to internal $CHDCl_2$ (^1H, δ 5.32), internal CD_2Cl_2 (^{13}C, δ 53.8), or external TMS (^{29}Si, δ 0). Solid-state ^{13}C and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter, 7 mm) containing ca. 300 mg of sample (^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz; external standard, TMS (δ 0); spinning rate, 6.5−7 kHz; contact time, 2 ms (^{13}C) or 5 ms (^{29}Si); 90° ^1H transmitter pulse length, 3.6 μs; repetition time, 4 s). Compound **8** was synthesized according to ref 9.

Compound 7. A mixture of chlorotrimethylsilane (330 mg, 3.04 mmol) and silver nitrate (516 mg, 3.04 mmol) was stirred at 20 °C for 30 min under exclusion of light. Dichloromethane (2 mL) was added to the reaction mixture, and the resulting clear solution was separated from the solid with a syringe. This freshly prepared solution of trimethyl(nitrato)silane in dichloromethane was added in one portion at 20 °C under exclusion of light to a stirred solution of **8** (600 mg, 1.73 mmol) in dichloromethane (8 mL), and the reaction mixture was kept undisturbed at 20 °C for 2 h and then at −20 °C for a further 24 h. The resulting yellow crystalline solid was isolated by filtration, washed with *n*-pentane (6 mL), and dried in vacuo (0.01 mbar, 40 °C, 3 h). Yield: 480 mg (1.29 mmol, 74%); mp 82 °C (dec).^{1}H NMR: δ 2.21 (d, $^4J_{H,H} = 0.4$ Hz, 3 H, OCCH_3), 2.39 (s, 3 H, NCCH_3), 5.83 (q, $^4J_{H,H} = 0.4$ Hz, 1 H, CC*H*C), 6.98−7.02, 7.12−7.16, 7.19−7.22, 7.26−7.30, and 7.39−7.42 (m, 9 H, SC_6H_4N, SiC_6H_5). ^{13}C NMR: δ 23.8 (OCCH$_3$), 23.9 (NCCH$_3$), 104.9 (C*C*HC), 123.6, 124.7, 127.9 (2 C), 128.7, 128.8, 130.3, 132.0, 133.3 (2 C), 135.7, and 137.1 (SC_6H_4N, SiC_6H_5), 171.8 (*C*N or *C*O), 172.3 (*C*N or *C*O). ^{29}Si NMR: δ −86.2. ^{13}C VACP/MAS NMR: δ 23.4 (CCH$_3$), 27.0 (CCH$_3$), 105.4 (C*C*HC), 124.7, 128.6, 129.3, 130.9, 132.6, 133.1, 135.1, and 137.2 (SC_6H_4N, SiC_6H_5), 172.8 (*C*N or *C*O), 174.4 (*C*N or *C*O). ^{29}Si VACP/MAS NMR: δ −89.1. Anal. Calcd for $C_{17}H_{16}N_2O_4SSi$ (372.48): C, 54.82; H, 4.33; N, 7.52; S, 8.61. Found: C, 53.1; H, 4.1; N, 7.1; S, 8.5.[11]

Crystal Structure Analysis. A suitable single crystal of **7**·CH_2Cl_2 was isolated directly from the reaction mixture. The crystal was mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). The structure was solved by direct methods.[12] The non-hydrogen atoms were refined anisotropically.[13] A riding model was employed in the refinement of the C*H* hydrogen atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-704277. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information Available: A CIF file, giving crystallographic data for **7**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Owing to the low stability of **7**, the results obtained in the elemental analyses deviate from the calculated values. A similar observation has been reported for compound **4** (ref 4).

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