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X-ray structural study of 3 : 1 solvate of 1-chlorosilatrane with MeCN

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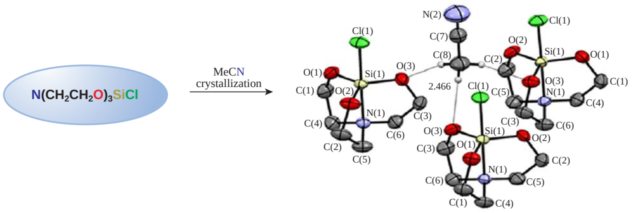
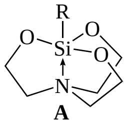
The single-crystal X-ray study of $ClSi(OCH_2CH_2)_3N$ showed the formation of a cluster of three silatrane molecules with one acetonitrile molecule featuring hypercoordinated Si atoms in a trigonal-bipyramidal coordination environment with O atom in the equatorial plane. A number of solid-phase structural parameters and the conformation of the five-membered rings of 1-chlorosilatrane were thus clarified.



Keywords: silatranes, pentacoordination, Si–Hal bond, Si···N interaction, five-membered rings, X-ray diffraction analysis, crystal solvate, acetonitrile.

Silatranes (5-aza-2,8,9-trioxa-1-silabicyclo[3.3.3]undecanes) represent a unique class of pentacoordinate silicon compounds with the general structure **A**. Their widely varying physicochemical properties[1–3] and diverse biological activities[4–6] are determined by the nature of the axial substituent R at the silicon atom. 1-Halosilatranes $RSi(OCH_2CH_2)_3N$ (R = F, Cl, Br, I) were synthesized more than 40 years ago, and their structure was proven by multinuclear NMR spectroscopy.[7] The molecular structures of 1-fluorosilatrane[8,9] and 1-chlorosilatrane[10] were determined by X-ray diffraction. However, several problems regarding the structure and properties of these compounds remain unresolved. First, in the crystals the length of the Si←N dative bond of 1-fluorosilatrane [2.042(1) Å at 298 K,[8] 2.050(2) Å at 210 K,[9] 2.056(3) Å at 100 K[9]] is greater than that in 1-chlorosilatrane (2.023 Å).[10] These results are contradictory to the established correlations between the length of the Si←N dative bond and the Taft inductive constant of the substituent R ($l = 2.20–0.063\sigma^*_R$),[10] as well as its Sanderson electronegativity ($l = 3.021X_R^{-0.257}$).[9] A few different explanations of this fact given suffer from their weaknesses.[11–14] It should be noted that some geometric parameters of 1-chlorosilatrane determined in the X-ray experiment are questionable.[13,14] Apparently, the quality of the crystal in experiment[10] was not high enough when the *R*-factor was 6.50,[10] which is greater than the permissible value (5%) guaranteeing reasonable accuracy of structural parameters.[15] Therefore, the goal of our work was to clarify the geometric parameters of molecule of 1-chlorosilatrane. In the present paper its synthesis and results of X-ray study are reported.



A

1-Chlorosilatrane was synthesized by treatment of tris(2-trimethylsiloxyethyl)amine with tetrachlorosilane in thoroughly dried chloroform (Scheme 1). We modified the Lukevics procedure[16] used for the synthesis of [^{15}N]-1-chlorosilatrane. The reaction was carried out in an evacuated Schlenk flask, which made it possible to increase the temperature of the reaction mixture to 85 °C. The structure of the compound obtained was confirmed by ^{1}H, ^{13}C, IR spectra and elemental analysis. Note that these spectral characteristics lie in the range of the characteristic values of 1-chlorosilatrane.[7]

$$(Me_3SiOCH_2CH_2)_3N + SiCl_4 \xrightarrow[-\,Me_3SiCl]{i} ClSi(OCH_2CH_2)_3N$$

Scheme 1 *Reagents and conditions*: i, $CHCl_3$, 85 °C, 4 h.

A single crystal of 1-chlorosilatrane for the X-ray diffraction analysis was obtained in a Schlenk flask using acetonitrile as a solvent. The results of the X-ray study indicate the existence of 1-chlorosilatrane in the crystal in the form of solvate with acetonitrile (Figure 1).[†] The unit cell contains six molecules of 1-chlorosilatrane and two molecules of MeCN. 1-Chlorosilatrane is very poorly soluble in organic solvents, but its ^{1}H NMR spectrum in DMSO-d_6 contains signal for acetonitrile traces (see Online Supplementary Materials, Figure S3). A long-term evacuation of the sample to remove acetonitrile led to the crystal destruction. The molecule of 1-chlorosilatrane/MeCN solvate in the crystal is characterized by C_3 symmetry of the molecular core. Its framework consists of three five-membered rings connected to each other by bridging Si and N atoms. The main geometric parameters of 1-chlorosilatrane solvate and previously reported[10] data on X-ray experiment are given in Table 1.

[†] *Crystallographic data for 1-chlorosilatrane*. $3(C_6H_{12}ClNO_3Si)\cdot C_2H_3N$ ($M = 670.17$), hexagonal, $P6_3$, at 293 K, $a = 14.6357(7)$ and $c = 8.037(6)$ Å, $V = 1491(4)$ Å^3, $Z = 2$, $d_{calc} = 1.493$ g cm^{-3}, μ(MoKα) = 0.482 mm^{-1}, $F(000) = 705$. 11 325 reflections were measured and 2240 independent reflections ($R_{int} = 0.0668$) were used in a further refinement. The refinement converged to $wR_2 = 0.087$ and GOF = 0.9630 for all independent reflections [$R_1 = 0.039$ was calculated against F for 1442 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker D8 Venture diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL.[15]

CCDC 2182235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

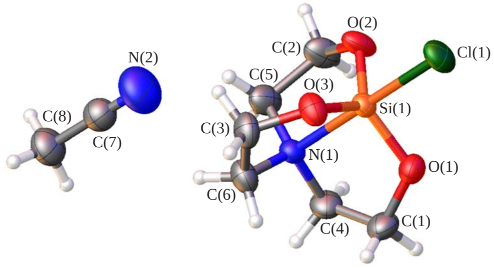


Figure 1 Molecular structure of solvate of 1-chlorosilatrane with MeCN.

The geometry of the coordination unit of 1-chlorosilatrane in the solid phase is close to a trigonal bipyramid. The degree of pentacoordination of silicon atom (η_e) is ~98%, and previous[10] X-ray experiment gave 97% value. The degree of pentacoordination of silicon atoms, η_e, in $XSi(OCH_2CH_2)_3N$ silatranes is calculated using the revised formula Tamao[17] in the crystal characterized by C_3 symmetry of the molecular core. Its framework consists of three five-membered rings connected to each other by bridging Si and N atoms.

The displacement values for the silicon atom from the plane of the three equatorial oxygen atoms (ΔSi) were 0.082 and 0.095 Å in the previous experiment.[10] Both values of ΔSi are greater than those characteristic of the 1-isothiocyanatosilatrane [see structure **A**, R = NCS: ΔSi = 0.070 Å, l_{SiN} = 2.007(3) Å],[18] but less than those determined for 1-fluoro- (R = F: ΔSi = 0.117 Å)[8] and 1-methylsilatrane [R = Me: ΔSi = 0.211 Å, l_{SiN} = 2.175(4) Å],[19] characterized by shorter and longer Si···N distances, respectively. A comparison shows that the Si←N dative bond in solvate of 1-chlorosilatrane is about longer ~0.016 Å than that in the previous experiment.[10] However, this value (2.039 Å) is also less than the length of the Si←N dative bond in 1-fluorosilatrane.[8,9] Our experiment demonstrates longer and more realistic values of the C–C (1.494–1.524 Å) and C–N (1.474–1.477 Å) bond lengths, exceeding the corresponding values of the previous experiment by an average of ~0.07 and ~0.03 Å, respectively. These values are close to those observed in crystals of 1-isothiocyanatosilatrane (R = NCS: l_{CC}^{av} ~ 1.514 Å; l_{NC}^{av} ~ 1.481 Å)[18] and 1-methylsilatrane (R = Me: l_{CC}^{av} ~ 1.524 Å; l_{NC}^{av} ~ 1.474 Å).[19] The other bond lengths in both experiments are in good agreement with each other. The difference between their values averaged over three $–CH_2CH_2O–$ chains does not exceed 0.01 Å (see Table 1). Good agreement is also observed for the bond angles of these compounds, and their differences do not exceed 2°. Only the NCC angle is decreased by ~5.5°, which corresponds to the results given in the previous works.[12,13,20] In the solid phase, the five-membered rings of silatrane molecules take on an envelope or twist conformation.[1–3,18,19] According to X-ray diffraction data,[10] the cycles have an intermediate flattened conformation ($\angle$C–O–Si–N^{av} = –4.0°, $\angle$O–Si–N–C^{av} = –9.2°), and these results have received criticism.[12,13] Our experiment points to the twist conformation of five-membered rings of 1-chlorosilatrane ($\angle$C–O–Si–N^{av} = –9.8°, $\angle$O–Si–N–C^{av} = = –13.5°). The values of the dihedral angles $\angle$C–C–O–Si^{av} in these experiments differ significantly (see Table 1). Their average value increased from 16.7° in old experiment[10] to 30.7° (our results), approaching $\angle$C–C–O–Si^{av} for 1-isothiocyanatosilatrane (–27.4°)[18] and 1-methylsilatrane (30.5°).[19]

The acetonitrile molecule forming a cluster with three molecules of 1-chlorosilatrane due to short CH···O contacts (l = 2.466 Å, Figure 2) is the ‘initiator’ of the formation of the crystal structure of 1-chlorosilatrane. In addition, silatrane molecules are connected to each other by the Cl···CH_2 interaction (l = 2.874–2.919 Å, Figure 3).

In summary, we demonstrated that the solvate of 1-chlorosilatrane with acetonitrile (3 : 1) was isolated after crystallization of 1-chlorosilatrane from MeCN. Its X-ray investigation made it possible to refine the conformation of five-membered heterocycles and the numerical values of geometrical parameters of molecule of 1-chlorosilatrane. These results confirm the existence of shorter dative bond Si←N in molecule of 1-chlorosilatrane compared 1-fluorosilatrane. Apparently, the length of dative bond Si←N in silatranes depends not only on the electronegativity of the axial substituent R. We are continuing this research and the results will be published elsewhere.

Table 1 Geometric parameters of the 1-chlorosilatrane molecule in this research and reference 10.

Bond length (l)/Å			Bond angle (°)			Torsion angle (°)		
Atoms	Ref. 10	This work	Atoms	Ref. 10	This work	Atoms	Ref. 10	This work
Si←N	2.023	2.039(5)	Si–N–C	106.0	105.6(2)	C–O–Si–N	–3.9	–11.0(2)
Si–Cl	2.153	2.160(4)		106.0	105.8(2)		–3.7	–9.6(2)
Si–O	1.644	1.646(4)		105.7	105.7(2)		–4.4	–8.8(2)
Si–O	1.651	1.646(3)	N–C–C	110.9	106.0(3)	O–Si–N–C	–9.1	–13.2(2)
Si–O	1.652	1.650(2)		111.2	105.5(2)		–9.7	–14.0(2)
O–C	1.421	1.426(5)		112.5	106.5(3)		–8.7	–13.4(2)
O–C	1.408	1.435(5)	C–C–O	111.6	108.2(2)	C–C–O–Si	16.5	32.1(3)
O–C	1.419	1.425(4)		111.4	109.4(2)		16.8	31.0(3)
C–C	1.443	1.523(5)		110.3	109.7(3)		16.7	29.1(3)
C–C	1.428	1.509(6)	C–O–Si	120.4	119.2(2)			
C–C	1.433	1.494(5)		119.8	118.3(2)			
N–C	1.451	1.475(7)		120.4	119.0(2)			
N–C	1.454	1.477(5)	O–Si–N	86.4	87.1(1)			
N–C	1.441	1.473(4)		87.1	87.4(1)			
				86.6	86.9(1)			
			O–Si–Cl	93.4	93.00(8)			
				93.0	93.17(8)			
				93.5	92.41(8)			
			O–Si–O	120.0	119.8(1)			
				119.7	119.1(1)			
				119.4	120.4(1)			
			N–Si–Cl	179.8	179.33(9)			

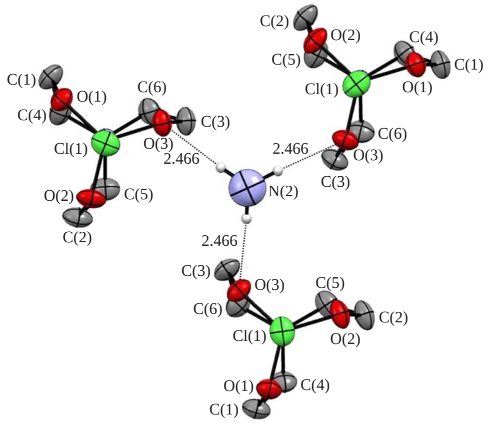


Figure 2 Short contacts between MeCN and 1-chlorosilatrane (CH···O).

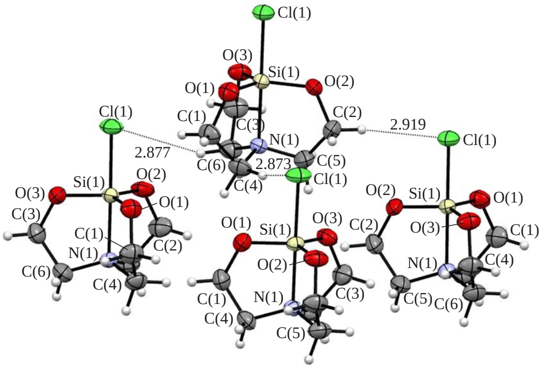


Figure 3 Intermolecular halogen bond (CH···Cl).

NMR and SCD experiments were carried out using the material and technical base of the Baikal Analytical Center for Collective Use of the SB RAS (http://ckp-rf.ru/ckp/3050). This work was carried out within the framework of the research project of Russian Academy of Sciences no. 121021000264-1.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.039.

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