The First SiH_2^{2+} Complex, Dihydridotetrakis(3-picoline)silicon Dichloride–Tetrakis(chloroform), $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$: Formation, Chemical Equilibria, and Structural Investigation by NMR Spectroscopy and Single-Crystal X-ray Diffraction

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Bis(dichlorosilyl)amine reacts in chloroform solution with 2-picoline to give H_3SiCl, H_2SiCl_2, and $HSiCl_3$, whereas with 3-picoline the two hypervalent silicon compounds $H_2SiCl_2(3pic)_2$ and $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ containing hexacoordinated Si atoms are formed. These complexes are in a chemical equilibrium with each other in chloroform solution, from which crystals of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ could be isolated. The crystal structure of the latter was determined by single-crystal X-ray diffraction. The complex can be regarded as an "contact ion trio" of $[H_2Si(3pic)_4]^{2-}$ and two Cl^- ions. The N→Si bond lengths, r(Si–N) = 196.9(3) and 197.5(3) pm, are similar to those found in neutral hexacoordinated Si complexes. The data obtained from a $^1H^1H$ ROESY experiment suggest that dissolution has no significant impact on the molecular structure of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$.

Dative interaction of the N→Si type is well-established, the first example, $SiF_4(NH_3)_2$[1], being the first Si–N compound ever described. In recent years, much research has been done to investigate structural[2-5] as well as spectroscopic[6,7] aspects and the reactivity[8] of that bond type. Most of these investigations were concerned with compounds exhibiting intramolecular N→Si interactions, e.g. silatranes[9] and 1-silyl-8-(dimethylamino)naphthalenes[10], but in these cases N→Si distances not only depend on "genuine dative" Si-N interactions but also on conformational and steric conditions and requirements of cage and ring structures. We were interested in compounds with intermolecular N→Si interaction, like the well-known $SiCl_4(py)_2$[4,11] (py = pyridine), where these effects can be largely excluded. This allowed us to study the influence of the properties of different tertiary amines and the substituents bound to silicon on the strength of the N→Si bond.

All compounds of the type $Me_nSiCl_{(4-n)}L_m$ (L = pyridine, picoline, lutidine); $n = 0-3$; $m = 1, 2$) investigated so far could only be shown to exist in the solid state. They are insoluble in most organic solvents and, if soluble, dissociate quantitatively[12,13], the same occuring in the melt[14] and in the gas phase[15,16].

Disilylamines bearing electronegatively substituted silicon atoms and a N–H functional group may act both as Lewis and Bronsted acids[17,18]. We studied the influence of different steric demands of the Lewis base on both types of acidity. With this in mind, we chose 2- and 3-picoline and investigated their reaction with bis(dichlorosilyl)amine, $(HSiCl_2)_2NH$.

Results

Reaction of Bis(dichlorosilyl)amine with 2-Picoline

Several thermotitrations in chloroform show a 1:1 reaction between bis(dichlorosilyl)amine and 2-picoline. A small amount of a white solid precipitates but dissolves again at the point of 1:1 equivalence. Using $CDCl_3$, we investigated this solution by ^1H- and $^1H^{29}Si$-HSQC (Hetero Single-Quantum Coherence) NMR spectroscopy, the latter allowing the study of the Si–H connectivity. Figure 1 shows the ^1H-NMR spectrum and Table 1 compiles ^1H- and ^{29}Si-NMR shifts as well as $^1J(^{29}Si\text{-}^1H)$ coupling constants and gives an assignment of the peaks as far as possible. The hydrogen atoms are numbered according to the carbon atoms to which they are bound. The numbering starts at the N atom and goes along the ring, giving the smallest possible number to the ring C atom which carries the methyl group.

The chemical shift of 2-picoline in this system is not much different from that of a solution of neat 2-picoline in $CDCl_3$[19]. In contrast, the two signals of $(HSiCl_2)_2NH$ [δ = 5.76, H(Si); δ = 2.81, H(N)][18] disappeared and several others emerged instead. The peak at δ = 17.80 indicates a strongly deshielded H atom as it usually occurs in hydrogen bridges. Deprotonation of $(HSiCl_2)_2NH$ and formation of $[2picH]^+$ can be excluded as this would exert a stronger

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Figure 1. ^{1}H-NMR spectrum of a mixture of $(HSiCl_2)_2NH$ and three equivalents of 2-picoline in $CDCl_3$ (δ scale)

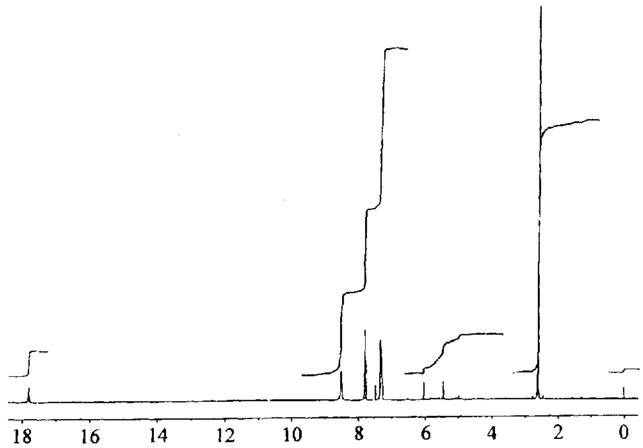


Table 1. δ(^{1}H), δ(^{29}Si), ^1J(^{29}Si-^{1}H) and peak assignment of the ^{1}H-NMR (see Figure 1) and the HSQC spectrum of the mixture of $(HSiCl_2)_2NH$ with three equivalents of 2-picoline in $CDCl_3$. Reference values for a solution of neat 2-picoline in $CDCl_3$ are given in parenthesis[19]. For the numbering scheme see text

δ(^{1}H)	δ(^{29}Si)	^1J(^{29}Si-^{1}H) [Hz]	assignment
17.80	-	-	[2pic···$\underline{H}$-N=]
8.50 (8.47)	-	-	H^6 (2pic)
7.77 (7.54)	-	-	H^4 (2pic)
7.36 (7.13)	-	-	H^3 (2pic)
7.30 (7.05)	-	-	H^5 (2pic)
6.10	-9.5	368	$HSiCl_3$
5.45	-10.8	292	-
5.45	-6.0	292	-
5.40	-11.5	288	H_2SiCl_2
5.15	-23.8	270	-
4.55	-37.5	238	H_3SiCl
2.61 (2.55)	-	-	H_3C (2pic)

influence on the shift of the 2-picoline signals, as a comparison with the ^{1}H-NMR shifts of pyridine and some [pyH]X compounds shows[19]. The sharpness of the peak at δ = 17.80 and the existence of only one set of signals for 2-picoline show that a very fast exchange reaction according to equation (1) occurs:

$$[2pic^{*}\cdots H{-}N{=}] + 2pic \rightleftharpoons 2pic^{*} + [2pic\cdots H{-}N{=}] \qquad (1)$$

Most of the intensity in the H(Si) region (δ = 4.0–6.5) is not due to sharp but very broad signals, thus indicating cleavage and reformation of Si–H bonds. This result is in accordance with the appearance of peaks for H_3SiCl, H_2SiCl_2, and $HSiCl_3$. Some ^{29}Si peaks of the HSQC spectrum could not be assigned but must for stoichiometric reasons be due to oligo- or cyclosilazanes. No ^{29}Si signals shifted to higher field than δ = -37 were found, showing that no penta- or hexacoordinated Si atoms are present[2,20].

Reaction of Bis(dichlorosilyl)amine with 3-Picoline

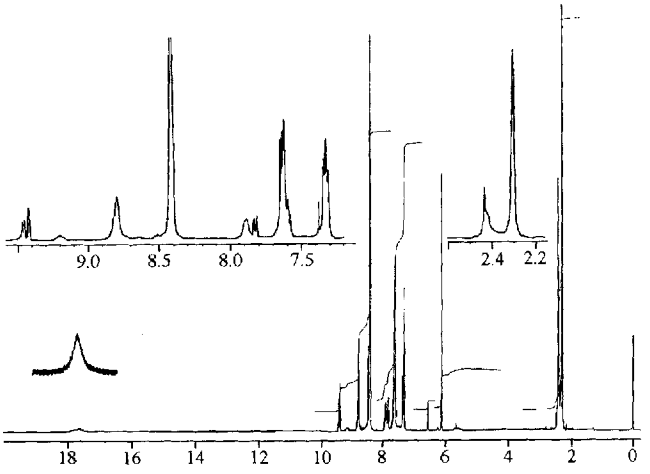
Thermotitrations of this system in chloroform did not reveal a certain point of stoichiometric equivalence, but it became clear that more than one equivalent of 3-picoline does react with $(HSiCl_2)_2NH$. A solid product forms in the course of the reaction but it dissolves again if more than three equivalents of 3-picoline are added. This fact allowed us to investigate the present system by high-resolution NMR spectroscopy.

The ^{1}H-NMR spectrum of the system is shown in Figure 2. Together with a ^{29}Si-NMR and a ^{1}H^{1}H ROESY spectrum (Figure 4) of this sample, the ^{1}H-NMR spectrum of 3-picoline in $CDCl_3$[19], and the ^{1}H-NMR spectra of the system H_2SiCl_2/3-picoline in $CDCl_3$ (Figure 3), an assignment of the peaks was possible (see Table 2). The ROESY experiment (**R**otating Frame **O**verhauser **E**ffect **S**pectroscopy)[21,22] measures the transient Nuclear Overhauser Effect during irradiation of a radiofield B_1 (then called **Ro**tating Frame **O**verhauser **E**ffect = ROE) and always guarantees the extreme limiting conditions. Thus, in contrast to a NOESY experiment, the ROE does not disappear for medium-sized molecules, and cross peaks due to chemical exchange can be distinguished by their sign from genuine ROE cross peaks. The build-up rate of intensity (I) of ROE cross peaks, ($\mathrm{d}I/\mathrm{d}t$), is inversely proportional to the sixth power to the internuclear distance according to eq. (2).

$$(r_{AB})^6 = \left(\frac{\mathrm{d}I/\mathrm{d}t_{CD}}{\mathrm{d}I/\mathrm{d}t_{AB}}\right)(r_{CD})^6 \qquad (2)$$

The rate of ROE build-up is determined by varying the mixing time and determining the resulting change in volume of the two-dimensional cross peak. ROE cross peaks are normally not observed for internuclear distances beyond 400 pm because of the r^{-6} dependence[23].

Figure 2. ^{1}H-NMR spectrum of a mixture of $(HSiCl_2)_2NH$ and six equivalents of 3-picoline in $CDCl_3$. The enlarged sections in the upper part show the peaks of the aromatic protons and the methyl group of 3-picoline (δ scale)



In contrast to the system $(HSiCl_2)_2NH$/2-picoline, the ^{1}H-NMR spectrum of the system $(HSiCl_2)_2NH$/3-picoline (see Figure 2) exhibits a simple pattern in the H(Si) region, but the aromatic region shows chemically different types of 3-picoline. A broad hump at δ = 17.7 indicates the formation of a hydrogen bond, [3pic···H–N=]. No ROE cross

Figure 3. ^{1}H-NMR spectra of a mixture of H_2SiCl_2 and three equivalents of 3-picoline in $CDCl_3$ at (a) 300 K, (b) 280 K (δ scale)

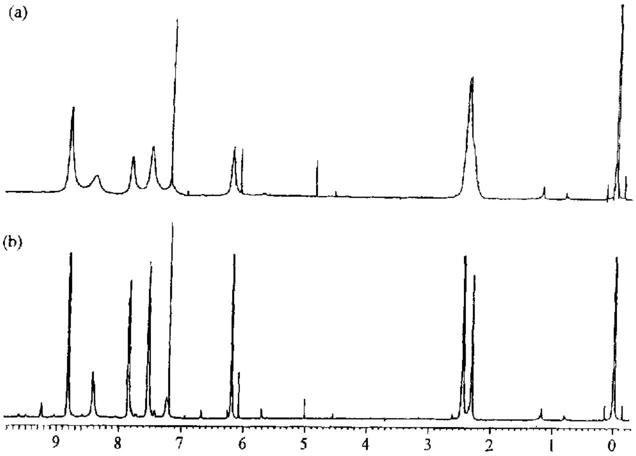


Figure 4. Section of the ^{1}H^{1}H ROESY spectrum of a mixture of $(HSiCl_2)_2NH$ and six equivalents of 3-picoline in $CDCl_3$. Spin locking time 230.9 ms. ROE cross peaks are enclosed in circles (δ scale)

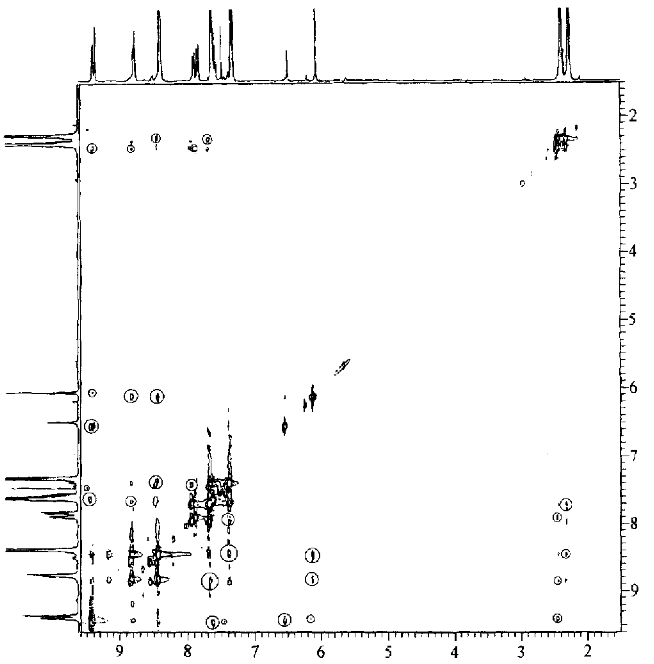


Table 2. Peak assignment of the ^{1}H-NMR spectrum in Figure 2. Reference values for a solution of neat 3-picoline in $CDCl_3$ are given in parenthesis[19]. For the numbering scheme see text (sh = shoulder)

	3-picoline	$H_2SiCl_2(3pic)_2$	[$H_2Si(3pic)_4$]Cl_2
CH_3	2.31 (2.30)	2.44	2.44(sh)
H^2	8.40 (8.45)	8.80	9.42
H^4	7.63 (7.45)	7.89	7.83
H^5	7.33 (7.15)	7.60	7.59
H^6	8.40 (8.40)	8.80	9.47
H(Si)	-	6.12	6.57

peak between this signal and any other signal could be observed (the corresponding region is not shown in Figure 4). The broadness of this peak indicates an exchange reaction according to equation (3).

$$[3pic^{*}\cdots H{-}N{=}] + 3pic \rightleftharpoons 3pic^{*} + [3pic\cdots H{-}N{=}] \qquad (3)$$

It is therefore assumed that the coalescence conditions for H^2, H^4, H^5, H^6, and CH_3 of 3-picoline in [3pic···H−N=] with the corresponding signals of free 3-picoline are fulfilled, and so no individual peaks for these protons can be observed. This also explains the slight shift of the signals of free 3-picoline compared to the reference data (see Table 2).

The peak at δ = 6.12 is due to an H atom bound to a Si atom as the ^{29}Si satellites [$^1J(^{29}Si{-}^1H)$ = 369 Hz] show. It corresponds to the triplet in the ^{29}Si-NMR spectrum [δ = −134, $^1J(^{29}Si{-}^1H)$ = 370 Hz] whose strong shift to a high field indicates the presence of a hexacoordinated Si atom[20]. The composition $H_2SiCl_2(3pic)_2$ is confirmed by the ROE cross peak at 6.12/8.80 and the corresponding peak intensity ratio in the ^{1}H-NMR spectrum. By the reaction of H_2SiCl_2 with 3-picoline and a comparison of the ^{1}H-NMR spectra of the reaction product (Figure 3) with those of $(HSiCl_2)_2NH$ and 3-picoline (Figure 2), we could confirm the existence of $H_2SiCl_2(3pic)_2$ in the latter system. H_2SiCl_2 and 3-picoline form $H_2SiCl_2(3pic)_2$ as a white precipitate from *n*-hexane. It dissolves in $CDCl_3$ on addition of one equivalent of 3-picoline, so that high-resolution NMR experiments could be carried out (see Figure 3). An exchange reaction clearly occurs at 300 K, resulting in broader unresolved peaks. In contrast, at 280 K the peaks are sharper, and a comparison of this spectrum with that in Figure 2 shows corresponding chemical shifts for $H_2SiCl_2(3pic)_2$ (see Table 2).

Additionally, the ^{1}H-NMR spectrum of $(HSiCl_2)_2NH$/3-picoline exhibits a peak at δ = 6.57, $^1J(^{29}Si{-}^1H)$ = 346 Hz. It corresponds to a second type of silicon complex in this system, and a weak exchange cross peak to $H_2SiCl_2(3pic)_2$ (see Figure 4) indicates that it must also contain a H_2Si unit. Otherwise, cleavage and formation of Si−H bonds would be involved in the exchange process, and the signal intensity within the H(Si) region of the ^{1}H-NMR spectrum could not be concentrated mainly in two peaks but would be smeared over a wider range, like in the system $(HSiCl_2)_2NH$/2-picoline (see above). The intensity ratio of δ = 6.57 to δ = 9.42 and 9.47 shows that this second complex has the composition $H_2SiCl_2(3pic)_4$. The fact that no ^{29}Si signal belonging to this complex is observed can be explained by its low abundancy compared to that of $H_2SiCl_2(3pic)_2$.

The intensities of the exchange cross peaks between free 3-picoline, $H_2SiCl_2(3pic)_2$, and $H_2SiCl_2(3pic)_4$ show that $H_2SiCl_2(3pic)_2$ has a shorter lifetime than $H_2SiCl_2(3pic)_4$, thus being kinetically less stable. The exchange reactions occurring in this solution can thus be formulated as in equations (4) and (5).

$$H_2SiCl_2(3pic)_2 \rightleftharpoons H_2SiCl_2 + 2\ 3pic \qquad (4)$$

$$H_2SiCl_2(3pic)_4 \rightleftharpoons H_2SiCl_2(3pic)_2 + 2\ 3pic \qquad (5)$$

Reaction (4) is much faster than (5). Neither the ^{1}H-NMR spectrum in Figure 2 nor the spectrum in Figure 3 exhibit signals attributed to H_2SiCl_2. This means, that equilibrium (4) is shifted fairly completely to the left side.

The intensities of all 3-picoline species allow their abundancies to be calculated relative to a total of six equivalents of the amine, i.e. 4.2 equivalents of 3-picoline, 1.2 equivalents of 3-picoline in $H_2SiCl_2(3pic)_2$, and 0.5 equivalents of 3-picoline in $H_2SiCl_2(3pic)_4$. The relative intensities of unassigned peaks are about 0.2 equivalent. The latter could comprise signals of $H_2SiCl_2(3pic)$, $H_2SiCl_2(3pic)_3$ and other possible intermediates of equilibria (4) and (5). The concentrations of $H_2SiCl_2(3pic)_2$, $H_2SiCl_2(3pic)_4$, and free 3-picoline allow the calculation of the equilibrium constant K_c and of ΔG^0 at 298 K for reaction (5):

$$K = 13.2 \text{ mol}^2 \text{ l}^{-2} \quad \Delta G^0 = -6.4 \text{ kJ mol}^{-1}$$

This means that $H_2SiCl_2(3pic)_4$, in spite of its kinetic stability, is thermodynamically unstable towards decomposition into $H_2SiCl_2(3pic)_2$ and two molecules of 3-picoline.

An octacoordinated Si atom in $H_2SiCl_2(3pic)_4$ can be excluded. Eightfold coordination at silicon has recently been mentioned[24], but the N→Si bond lengths within that compound [r(N→Si) = 289.5 and 311.7 pm] are far too large to account for the observed ROE cross peak intensity in the present case. On the other hand, any closer N→Si contacts in an octacoordinated complex would cause too much mutual steric hindrance between the ligands. A hexacoordinated dicationic complex $[H_2Si(3pic)_4]Cl_2$ is much more reasonable, as it also explains the kinetic stability relative to $H_2SiCl_2(3pic)_2$. The existence of a $[H_2Si(3pic)_4]Cl_2$ species could be confirmed by crystal structure analyses (see below).

The ^{29}Si-NMR spectrum of the system $(HSiCl_2)_2NH$/3-picoline exhibits besides the triplet at $\delta = -134$ two singlets at $\delta = -33$ and -40, which have together the same intensity as the triplet. These two signals could not be assigned to any known chlorosilane or chlorosilazane and must correspond to two Si atoms not bearing an H atom. These side products were not investigated any further.

Structural Investigations on $[H_2Si(3pic)_4]Cl_2$

a) Study of the Structure in Solution

Of the two complexes $H_2SiCl_2(3pic)_2$ and $[H_2Si(3pic)_4]Cl_2$ only the latter could be structurally investigated by using the ROESY data. It is not reasonable to calculate $r[H(Si)\cdots H^6]$ for $H_2SiCl_2(3pic)_2$ on the basis of the ROE cross peak intensities. Due to the chemical exchange with free 3-picoline, these intensities do not reflect the genuine distance in the complex, but an average of the distances of the coordinating and free states.

For $[H_2Si(3pic)_4]Cl_2$, a *trans* configuration of the dication with a symmetry close to C_4 or S_4 must be assumed, due to the sharp peaks originating from the corresponding 3-picoline, which indicate a similar chemical environment for all four amine molecules in this complex. For steric reasons, the four planes of the 3-picoline molecules cannot be perpendicular to the Si–H bonds but must be close to a parallel arrangement. As $[H_2Si(3pic)_4]Cl_2$ shows only weak exchange peaks to $H_2SiCl_2(3pic)_2$ and free 3-picoline, $r[H(Si)\cdots H^6]$ in this complex can be estimated according to equation (2). As $r[H^5\cdots H^6)$ in $[H_2Si(3pic)_4]Cl_2$ is unknown and no structural data of free 3-picoline seems to be available, the appropriate distance in gaseous pyridine [$r(H^5\cdots H^6)$ = 246(1) pm[25]] was taken as a reference. All crystal structure data for this reference distance are not reliable, as bond lengths to hydrogen atoms are always estimated to be shorter according to this method than obtained by gas-phase electron diffraction, microwave or NOE/ROE measurements. The heavy atom distances and angles in gaseous pyridine and in 3-picoline in crystalline $[H_2Si(3pic)_4]Cl_2$ (see Table 3) do not differ considerably. Thus, $r(H^5\cdots H^6)$ in $[H_2Si(3pic)_4]Cl_2$ should also be very similar to $r(H^5\cdots H^6)$ in gaseous pyridine. Considering the relative abundancies of $r[H(Si)\cdots H^6]$ and $r(H^5\cdots H^6)$, it seems that eight distances would contribute to the former and four to the latter. But as four of the eight $H(Si)\cdots H^6$ distances are much longer than the other four, and $dI/dr[H^6\cdots H(Si)] \sim [r(H^6\cdots H(Si))]^{-6}$ (see eq. 2), they do effectively not contribute to the intensity. Thus, we obtained $r[H(Si)\cdots H^6]$ = 234 pm.

Table 3. Selected bond lengths, bond angles, and torsional angles of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$. E.s.d.s are given in parentheses

Bond lengths [pm]		Bond and Torsion angles [°]	
Si(1)-N(1)	196.9(3)	N(1)-Si(1)-N(1')	89.1(2)
Si(1)-N(1')	197.5(3)	C(6)-N(1)-C(2)	119.0(4)
N(1)-C(2)	135.2(5)	N(1)-C(2)-C(3)	122.4(4)
N(1)-C(6)	133.7(5)	C(2)-C(3)-C(4)	117.4(4)
C(2)-C(3)	138.7(6)	C(3)-C(4)-C(5)	120.5(4)
C(3)-C(4)	138.6(7)	C(4)-C(5)-C(6)]	118.7(4)
C(4)-C(5)	138.0(7)	C(2)-C(3)-C(7)	119.9(4)
C(5)-C(6)	137.9(6)	C(6')-N(1')-C(2')	119.4(4)
C(3)-C(7)	150.9(7)	N(1')-C(2')-C(3')	122.3(4)
N(1')-C(2')	134.1(5)	C(2')-C(3')-C(4')	117.7(4)
N(1')-C(6')	134.4(5)	C(3')-C(4')-C(5')	120.2(4)
C(2')-C(3')	138.1(6)	C(4')-C(5')-C(6')	118.8(4)
C(3')-C(4')	138.2(6)	C(2')-C(3')-C(7')	120.2(4)
C(4')-C(5')	138.1(7)	N(1')-Si(1)-N(1)-C(2)	-96.0(4)
C(5')-C(6')	137.4(6)	N(1)-Si(1)-N(1')-C(2')	110.2(4)
C(3')-C(7')	149.9(7)	Cl(1)···H(11)-C(11)	167
Cl(1)···H(11)	244	Cl(1)···H(21)-C(21)	171
Cl(1)···H(21)	240	Cl(1)···H(2')-C(2')	166
Cl(1)···H(2')	272	Cl(1)···H(2A)-C(2A)	160
Cl(1)···H(2A)	280		

Finally, a weak ROE cross peak from $\delta = 7.23$ ($CHCl_3$) to $\delta = 9.42$ (H^2 in $[H_2Si(3pic)_4]Cl_2$) indicates a close steric relationship between these spins. As only one very sharp $CHCl_3$ peak appears in the ^{1}H-NMR spectrum (see Figure 2), these facts reflect a fast exchange between free $CHCl_3$ and a chemically different species, bound to $[H_2Si(3pic)_4]Cl_2$.

b) Study of the Crystal Structure

From a solution of H_2SiCl_2/3-picoline in $CHCl_3$ a single crystal of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ was grown and examined by X-ray diffraction. Its molecular structure (C_i symmetry) is shown in Figure 5 to consist of a hexacoordinated Si dication with slightly distorted C_{2h} symmetry (Figure 6), two Cl^- ions and four molecules of chloroform. Each Cl^-

ion is coordinated by four H atoms in a way that the H atoms donated by the two CHCl$_3$ molecules occupy the apical and the H(2) atoms of two crystallographically independent 3-picoline molecules two of the three equatorial sites of a sightly distorted trigonal bipyramid. The difference in lengths between the two independent N→Si bonds [r(Si−N(1)) = 196.9(3), r(Si−N(1')) = 197.5(3) pm] is insignificant, as are the differences in bond lengths and angles between the two crystallographically independent 3-picoline molecules.

Figure 5. Plot of [H$_2$Si(3pic)$_4$]Cl$_2$ · 4 CHCl$_3$. The capital "A" denotes atoms generated by the inversion operation, a prime is used to distinguish between crystallographically independent atoms

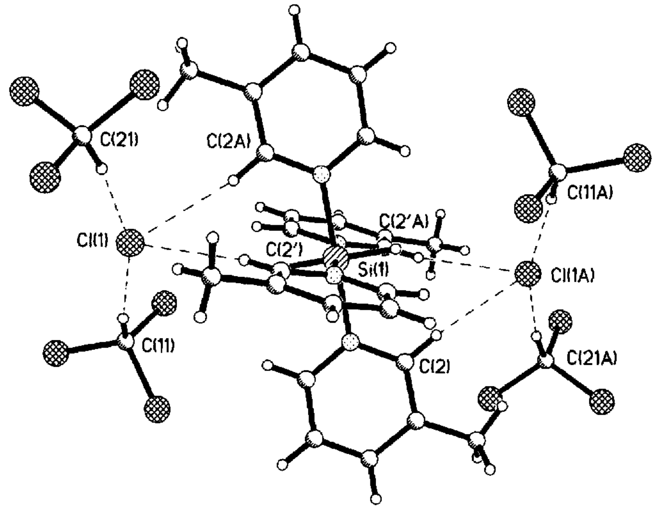
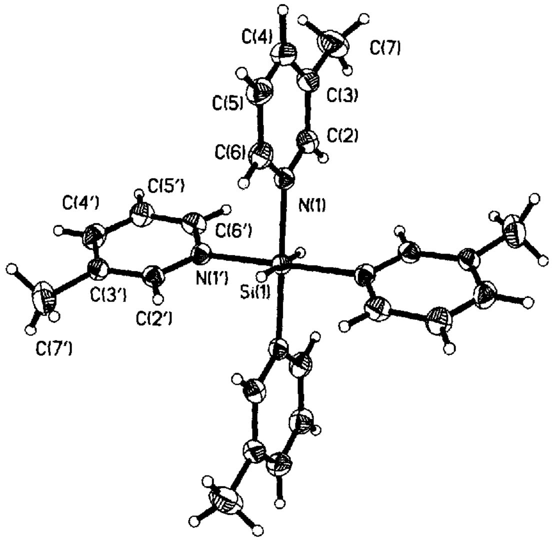


Figure 6. ORTEP plot (50%) of [H$_2$Si(3pic)$_4$]$^{2+}$ (for the numbering scheme see Figure 5)



To compare r[H(Si)···H^6], obtained from the ROESY experiment, with the corresponding distance in the crystal, the X-ray diffraction values for r[C(6)−H(6)] and r(C(6')−H(6')] were set to 108 pm, which is the value in pyridine[25], and r(Si−H) was increased by 10 pm to 148.5 pm. This procedure should roughly account for the differences between the two methods of measuring the positions of the electron density maxima and the locations of the nuclei, respectively. Thus, the results are: r[H(Si)···H(C6)] = 216 and r[H(Si)···H(C6')] = 221 pm.

Discussion

2- and 3-picoline show similar as well as different aspects of reactivity towards (HSiCl$_2$)$_2$NH. With both amines, formation of hydrogen bonds occurs. This is confirmed by the disappearance of the H(N) signal of (HSiCl$_2$)$_2$NH in the ^{1}H-NMR spectra of both systems. The formation of the hydrogen bond can be regarded as an activation towards cleavage of the Si−N bond and dismutation. However, the order of the latter two steps has not yet been clarified. Dismutation of chlorosilanes under the influence of pyridine was already reported by Ebsworth et al.[26].

The steric hindrance of the lone pair of 2-picoline by the methyl group is responsible for its inability to form complexes with expansion of the coordination sphere of Si[27]. In 3-picoline, the methyl group is sufficiently remote from the lone pair to allow this amine to coordinate to H$_2$SiCl$_2$. This complexing ability has consequences for the dismutation reactions. Whereas 2-picoline reacts with (HSiCl$_2$)$_2$NH to give HSiCl$_3$, H$_2$SiCl$_2$, H$_3$SiCl, and oligo-/cyclosilazanes with Si−H bonds, H$_2$SiCl$_2$ is the only silicon compound with Si−H bonds formed in the system (HSiCl$_2$)$_2$NH/3-picoline. It seems that the complex H$_2$SiCl$_2$(3pic)$_2$ is thermodynamically preferred to HSiCl$_3$(3pic)$_2$ and SiCl$_4$(3pic)$_2$, thus driving the dismutation towards H$_2$SiCl$_2$.

A comparison of $^1J(^{29}\text{Si-}^1\text{H})$ for H$_2$SiCl$_2$ and H$_2$SiCl$_2$(3pic)$_2$ shows a larger coupling constant for the hexacoordinated compound. This result is in contrast to a recent statement according to which $^1J(^{29}\text{Si-}^1\text{H})$ should decrease for comparable Si compounds on going from tetrahedral to octahedral coordination[28]. We assume that similar to tetrahedrally coordinated Si compounds, $^1J(^{29}\text{Si-}^1\text{H})$ in hypervalent Si complexes is related to the amount of s-type orbital contributions to the Si−H bond. It thus seems to be a very consequence for $^1J(^{29}\text{Si-}^1\text{H})$ to increase in the sequence tetrahedral < trigonal bipyramidal < octahedral coordination geometry at the Si atom as the type of wavefunction of the Si atom overlapping with the H orbitals is of sp^3, sp^2, and sp type with 25, 33, and 50% s character, respectively. Of course this is only a qualitative argument as the contribution of s-type functions to bonds varies not only with the coordination geometry but also − within one type of geometry − with different ligands and the effective charge of the central atom. $^1J(^{29}\text{Si-}^1\text{H})$ is e.g. bigger in the neutral complex H$_2$SiCl$_2$(3pic)$_2$ than in the complex cation [H$_2$Si(3pic)$_4$]$^{2+}$. This fact might be due to a stronger contraction of the atomic electron wave functions of the formal Si dication, resulting in less efficient transmission of the nuclear spin interaction between Si and H.

The equilibrium between H$_2$SiCl$_2$(3pic)$_2$ and [H$_2$Si(3pic)$_4$]Cl$_2$ [see equation (5)] can be described as an exchange of inner- and outer-sphere ligands. Despite its kinetic stability, [H$_2$Si(3pic)$_4$]Cl$_2$ is thermodynamically instable towards decomposition into $H_2SiCl_2(3pic)_2$ and two molecules of 3-picoline. The exergonicity of reaction (5) is only -6.4 kJ mol^{-1} so that a twofold stoichiometric excess of 3-picoline [according to equation (5)] is sufficient to shift the equilibrium so far to the left side that $[H_2Si(3pic)_4]Cl_2$ can be observed in the ^1H-NMR spectrum (see Figure 2). This is a surprisingly low difference in free enthalpy, taking the cleavage of two Si–Cl bonds, the transfer of electrons from Si to Cl, and the separation of two Cl^- ions from the $[H_2Si(3pic)_4]^{2+}$ cation into account. Several reasons for the balance of the "energy bill" are considered:

a) The formation of two more N→Si bonds.

b) The delocalization of the positive charge over the aromatic systems.

c) The stabilization of the Cl^- ions by hydrogen bonds. Chloroform may coordinate to anions by hydrogen bonds. This is reflected in a high acceptor number on the Gutmann scale[29], but its dielectric constant, $\varepsilon_r = 4.8$, is too small to ensure a complete separation of the present cation from the Cl^- ions. The formation of hydrogen bonds in the crystal is confirmed by the heavy atom distances from which the Cl···H distances are calculated for ideally positioned H atoms. The C–H···Cl angles are close to 180° and thus optimize a σ^*(C–H)-n(Cl) interaction that was shown to be important for hydrogen bond formation[30]. These considerations and the NMR result that chloroform is bound to this complex suggest that the whole structural unit of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ is already present in solution. In this case another stabilization factor arises:

d) Coulomb interaction between Cl^- and $[H_2Si(3pic)_4]^{2+}$. The distance of the Cl^- ions to the complex cation is quite large, e.g. r[Cl(1)–Si(1)] = 477.2 pm, i.e. 100 pm more than the sum of the van der Waals radii. Nevertheless, the coulombic potential decreases only with r^{-1}, so the electrostatic energy is still quite marked in spite of this distance. This rather close distance allows to regard $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ at least in the solid state as a "contact ion trio".

Despite the fact that the four N→Si bonds are formed to a Si dication, their lengths do not differ very much from those in neutral hexacoordinated Si complexes like $SiCl_4(py)_2$ [197.6(9) pm[4]] or $MeSiCl_3(3,5\text{-lut})_2$ [202.3(6) pm[31], lut = lutidine] and are even larger than in $SiF_4(py)_2$ [193(2) pm[32]]. Furthermore – compared to the gas-phase structure of pyridine – the structural changes exerted onto the NC_5 ring of the 3-picoline molecules are much smaller in the present case than in py · HCl[33]. This indicates a weaker interaction between SiH_2^{2+} and 3-picoline than between H^+ and pyridine.

The quite marked difference of r[H(Si)···H^6] between solution (234 pm) and solid state (216/221 pm) calls for an explanation. We are aware of the assumptions we made to make the two different structural methods comparable. Nevertheless, the difference exceeds any amount of uncertainty we might have introduced by those approximations. The main factor for this difference is certainly the different temperatures of the NMR (T = 298 K) and the diffraction experiment (150 K). Higher temperatures cause a lengthening of r(Si–N) due to an increasing population of vibrational states with $v > 0$. Thus, an increase of the average value for r[H(Si)···H^6] has to be expected. On the other hand, the torsional vibration of the 3-picoline plane against the Si–H bond has an influence on r[H(Si)···H^6] as well. As torsional vibrations are known to have mostly low frequencies and large amplitudes, a larger displacement from the equilibrium position is expected at higher temperatures. The equilibrium distance of H(Si) and H^6 is close to its torsional minimum (see Table 3; the shortest distance occurs for $\tau = 0°$) so that torsional vibrations with large amplitudes lead to an increase of r[H(Si)···H^6]. These considerations show that the equilibrium structures of $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ do not necessarily differ appreciably between solution and solid state.

Conclusion

2- and 3-picoline are similar in their Bronsted basicities to Bronsted-acidic disilylamines, but their Lewis basicities are different. Whereas 2-picoline does not show any Lewis basicity towards $(HSiCl_2)_2NH$, $HSiCl_3$, H_2SiCl_2, or H_3SiCl, 3-picoline is strong enough a Lewis base to form hypervalent silicon compounds that are stable in solution.

Chloroform proved to be a very suitable solvent for our investigations. It dissolves both systems, thus allowing high-resolution NMR experiments as well as the growth of single crystals from these solutions. Further reactions with other silanes and tertiary amines in chloroform solution are the subject of present investigations.

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Experimental

All procedures were carried out under argon or nitrogen (dried with activated 4-Å molecular sieves and Sicapent®) either in a vacuum line or in a glove box. Solvents were distilled from CaH_2 and stored over activated molecular sieves; the picolines were distilled from CaH_2 and sealed in ampoules. H_2SiCl_2 (Aldrich, 99.99%) was used without further purification. Bis(dichlorosilyl)amine was prepared and purified according to a literature procedure[18]. – C,H,N analyses: CHN-Rapid (Heraeus) combustion analyzer; Cl was determined potentiometrically with $AgNO_3$. – NMR: Bruker AMX 400, B_1 = 400 MHz, Standards: ^1H and ^{29}Si: TMS. Conditions for the sample of $(HSiCl_2)_2NH$ with 2-picoline: 55.9 mg (0.26 mmol) of $(HSiCl_2)_2NH$, 74.8 mg (0.803 mmol) of 2-picoline, 1.0 ml of $CDCl_3$. Conditions for the sample of $(HSiCl_2)_2NH$ with 3-picoline: 82.1 mg (0.38 mmol) of $(HSiCl_2)_2NH$, 208.7 mg (2.24 mmol) of 3-picoline, 1.0 ml of $CDCl_3$. Conditions for the sample of H_2SiCl_2 with 3-picoline: 52.3 mg (0.182 mmol) of $H_2SiCl_2(3pic)_2$, 19.8 mg (0.213 mmol) of 3-picoline, 1.0 ml of $CDCl_3$.

Thermotitrations: About 5 mmol of $(HSiCl_2)_2NH$ was dissolved in 20 ml of chloroform. The solution was stirred and 2- or 3-picoline added in portions of 0.2 ml. The temperature was measured before each addition and afterwards when it peaked. The temperature differences obtained in this way were summed and plotted against the volume of the amine.

Preparation of $H_2SiCl_2(3pic)_2$: 1.0 ml (13.9 mmol) of H_2SiCl_2 (liq.) was condensed into 50 ml of n-hexane, and 6.0 ml (66.4 mmol) of 3-picoline was added within 30 min whilst the solution was stirred and kept at −60 °C. The solution was then allowed to warm up to room temp. and the white precipitate which had formed was washed with *n*-hexane and dried in vacuo. Yield: 100%. − $C_{12}H_{16}Cl_2N_2Si$ (287.3): calcd. C 50.2, H 5.6, Cl 24.7, N 9.8; found C 47.8, H 5.7, Cl 25.1, N 9.2.

X-ray Crystal Structure Determination[34] *of* $[H_2Si(3pic)_4]Cl_2 \cdot 4\ CHCl_3$ *at 150 K:* Single crystals were grown from a solution of about 150 mg (0.52 mmol) of $H_2SiCl_2(3pic)_2$ and 0.2 ml (2.0 mmol) of 3-picoline in 3.0 ml of $CHCl_3$ at 5 °C within 4 d. − $C_{28}H_{34}Cl_{14}N_4Si$ (M = 951.05 g mol^{-1}), colorless crystal, a = 1439.7(1), b = 1008.8(1), c = 1493.0(1) pm, β = 104.25(1)°, V = 2.1017(3) · 10^9 pm^3; Z = 2; $\rho_{calcd.}$ = 1.503 g · cm^{-3}; monoclinic, $P2_1/n$; Siemens P4 four-circle diffractometer, $\mu(Mo\text{-}K_\alpha)$ = 0.97 mm^{-1}, λ = 7.1069 pm; 4355 observed reflections in the range 50° ≥ 2Θ ≥ 3°, of which all 3488 independent reflections were used for refinement ($R_{int.}$ = 0.0359); solution by direct methods and difference Fourier technique (SHELXS-86)[35], structural refinement against F^2 (SHELXL-93)[36], 231 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0692 \cdot P)^2 + 6.56 \cdot P]$, conventional R = 0.0642 for F_o values of 2964 data having $F_o^2 > 2\sigma(F_o^2)$; $wR2$ = 0.1681 for all 3588 data; S = 1.080; residual electron density 1.01/−0.60 e/Å^3, the highest peak having a distance of 90 pm to Cl(1A). The non-hydrogen atoms were refined anisotropically. The H atoms were given geometrically ideal positions and refined with isotropic displacement parameters. Those bound to a C atom were refined with individual isotropic thermal parameters [U_H = 1.2 · $U_{eq}(C_{arom.})$ and 1.5 $U_{eq}(C_{Methyl})$] according to the riding model. The H atom at Si was refined with free coordinates and free isotropic thermal parameters. One of the two crystallographically independent $CHCl_3$ molecules is disordered in two orientations and was refined with a split model (site occupancies of 80:20). The higher occupied site was refined anisotropically, the lower one isotropically. Only the major component is given in the paper.

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