

Not Unhydrolyzed at pH 8**

Xaver Kästele, Peter Klüfers,* and Reinhold Tacke

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The search for silicon complexes that exhibit hydrolytic stability in neutral aqueous solution is a major challenge in contemporary silicon chemistry and has both technical and biochemical relevance. The recently published claim by one of us^[1] that a zwitterionic bis-(diolato)silicate, derived from anhydroerythritol (*meso*-oxolane-3,4-diol; AnEryt) is hydrolytically stable at pH 7–8, thus appeared to be a milestone. The compound in question is bis[*meso*-oxolane-3,4-diolato(2–)](morpholinomethyl)silicate (**1** (originally labeled **10** in Ref. [1]); see Figure 1). It was report-

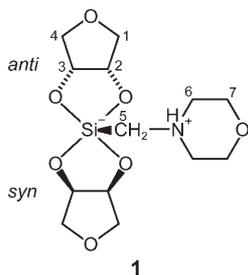


Figure 1. The zwitterionic (oxalenediolato)silicate **1**. The orientation of an oxalane ring with respect to the monovalent substituent at the silicon center defines *syn* or *anti* bonding. The numbering of the oxalane carbon atoms corresponds to that for a furanose.

ed that no tetracoordinate silicon species could be detected upon dissolution of **1** in water; that is, no hydrolytic decomposition occurred.

The hydrolytic stability that was claimed would have meant that **1** is drastically different from pentacoordinate bis[*meso*-oxolane-3,4-diolato(2–)]silicates, which do not have the morpholinomethyl group as their fifth substituent. An example is the analogous pentacoordinate anionic species, bis[*meso*-oxolane-3,4-diolato(2–)]hydroxosilicate. On the one hand, its alkali salts share with **1** a convenient synthetic accessibility from aqueous solution by simple evaporation of the solvent.^[2] On the other hand, these hydroxosilicates and the related phenylsilicates show partial hydrolysis in aqueous solution at high pH values, typically at about pH 12, and complete hydrolysis in neutral aqueous environment, as observed by NMR spectroscopy.

Though it appears to be a reasonable hypothesis that the introduction of a positive charge close to the silicon center may suppress hydrolytic decomposition, the first step of which may be the protonation of a silicon-bonded alkoxide O atom, the claimed extent of stabilization of **1** seemed highly unlikely in light of a report by Kästele et al. on anionic pentacoordinate oxalenediolatosilicates.^[3] It thus appeared sensible to connect the areas of anionic and zwitterionic silicates in a step-by-step procedure in order to identify the origin of the apparent inconsistencies.

The experimental procedure chosen is summarized in Figure 2. Starting from the well-known area of pentacoordinate oxalenediolatosilicate anions under non-hydrolyzing conditions,^[3] the experiments eventually approach the conditions reported in Ref. [1]. The NMR

spectra of the anionic morpholinomethyl homologue of a bis(oxalenediolato)phenylsilicate or -hydroxosilicate in methanolic solution are shown in Figure 2a. Under these basic, non-hydrolyzing conditions, the conjugate base of **1**, the anion [(AnErytH₂)₂-SiCH₂NC₄H₈O][–], was expected to be the only reaction product. In fact, the signal patterns in both the ²⁹Si and ¹³C NMR spectra (Figure 2a) consistently resembled the spectra of the analogous phenyl- or hydroxosilicates. The spectra in Figure 2a thus show all the typical features related to the characteristic *syn/anti* isomerism.^[3] First, the ²⁹Si NMR spectrum consists of three signals that span a typical chemical shift range of some 3–8 ppm. The signal of the minor component, tentatively the *syn/syn* isomer, appeared, as expected, most upfield. The *syn/anti* and *anti/anti* isomers were the main species. Crystals of K[(AnErytH₂)₂-SiCH₂NC₄H₈O]·MeOH grown from such solutions accordingly contained one of the two main isomers, namely the *anti/anti*-configured anion.^[4]

Second, the ¹³C NMR spectrum (Figure 2a) revealed a spectral feature corresponding to the phenylsilicate analogue: The ¹³C NMR signals of the monovalent substituent at the silicon center mirrored the pattern of the ²⁹Si NMR signals. The signals assigned to C6 and C7 showed the *syn/syn* minor component clearly separated and shifted upfield by about 1 ppm from a pair of signals corresponding to the main isomers. The signal for C5, corresponding to one carbon atom only, appears to be a less suitable probe owing to its lower intensity, a situation that parallels the difference in usefulness of the C_{ipso} and C_{ortho} signals of phenylsilicates.^[3]

[*] X. Kästele, Prof. Dr. P. Klüfers
Department Chemie und Biochemie
Ludwig-Maximilians-Universität
Butenandtstrasse 5–13, 81377 München
(Germany)
Fax: (+49) 89-2180-77407
E-mail: kluef@cup.uni-muenchen.de

Prof. Dr. R. Tacke
Institut für Anorganische Chemie
Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)

[**] A correction to "A Zwitterionic Spirocyclic Pentacoordinate Silicon Compound Synthesized in Water by Si–O and Si–C Bond Cleavage".^[1]

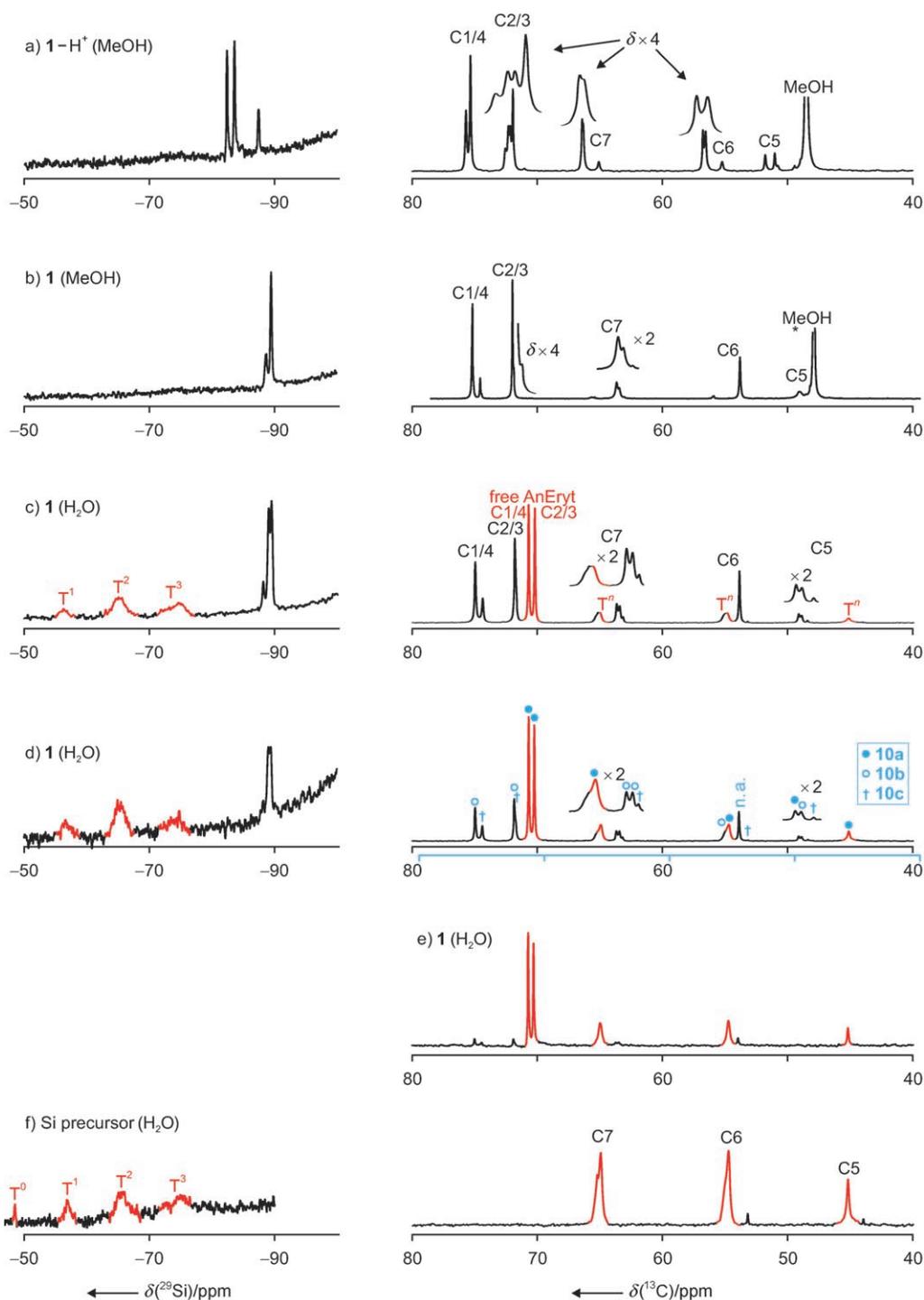


Figure 2. ^{29}Si (left) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (right) for **1** (a–e) under various conditions. a) 1:2:1 molar ratio of $(\text{MeO})_3\text{SiCH}_2\text{NC}_4\text{H}_8\text{O}/\text{AnEryt}/\text{KOMe}$ in methanol; $[\text{Si}] = 0.48 \text{ mol kg}^{-1}$. b) As for Figure 2a but without KOMe. The ^{13}C NMR spectrum was recorded at -30°C and is shifted such that the signal for C6 is aligned with that in Figure 2c for comparison (the original position of the signal is marked by an asterisk). c) Aqueous solution of **1** (1.04 mol kg^{-1}) at pH 8.2. Signals corresponding to hydrolysis products of **1** are shown in red, and those assigned to free AnEryt resemble those for a sample of pure AnEryt in water. d) Aqueous solution of **1** (0.45 mol kg^{-1} ; 0.47 mol L^{-1}) at pH 8.0. The assignment of signals, the scale, and compounds labels **10a–c**, according to Ref. [1] are shown in blue (n.a. = not assigned in Ref. [1]). e) Aqueous solution of **1** (0.1 mol kg^{-1}) at pH 7.8. The ^{29}Si NMR spectrum was not recorded as a result of the low total concentration. f) Aqueous solution of trimethoxy(morpholinomethyl)silane (0.58 mol kg^{-1}). A stock solution (1.5 mol kg^{-1}) in water was left for 3 days and diluted prior to the measurement. Inserts labeled “ $\delta \times 4$ ” show the respective signals with fourfold magnification along the δ axis, while those labeled “ $\times 2$ ” show the respective signals with double magnification along both axes. The numbering scheme for carbon atoms corresponds to that shown in Figure 1. See text for details.

Third, *syn/anti* isomerism was clearly recognizable in the signal pattern in the ^{13}C NMR region corresponding to AnEryt. As a result of symmetry considerations, one strong signal (the *anti/anti* isomer), two signals of equal intensity (the *syn/anti* isomer), and a weak signal (the *syn/syn* isomer) were expected and indeed observed for the pair of chemically equivalent diol carbon atoms (C2/3). Because of accidental signal overlap, less than four separate signals were observed, as usual, for the carbon atoms adjacent to the diol moiety (C1/4). Quite reliably, the signals for AnEryt are characteristically shifted with respect to free AnEryt by about 1 ppm for the diol carbon atoms (C2/3) and by about 4 ppm for those lying adjacent (C1/4). These shifts are close to the respective mean values of 2 and 5 ppm observed for a series of furanoidic ligands with the AnEryt partial structure.^[3]

In the next step (Figure 2b), one equivalent of protons was added to obtain the zwitterionic species while maintaining the non-hydrolyzing solvent methanol (in practice, the addition of methoxide was omitted). At room temperature, the NMR spectra shown in Figure 2b displayed unexpectedly few signals; for instance, in the ^{13}C NMR spectrum only one signal was observed for each type of carbon atom. However, upon cooling to -30°C , some signals split and adopted the same shape as observed in aqueous media (see below). Note that some spectral features that indicate *syn/anti* isomerism are missing. First, the range of the splitting of the ^{29}Si NMR signal is unusually narrow. Second, the splitting of the mirror signals (C5, C6, C7) is small or absent. Third, the typical pattern for atoms C2/3 is missing. Nevertheless, a thorough

analysis of the peculiarities of zwitterion isomerization is outside the scope of the present contribution. Though questions regarding isomerism remain open, AnEryt is clearly bonded to silicon, as indicated by the typical differences in chemical shift values. The spectra in Figure 2b thus correspond to pure, non-hydrolyzed **1**.

Next, the solvent was changed from methanol to water. Figure 2c shows the distribution of species in an aqueous solution (1M) of the zwitterionic **1**. Additional signals of hydrolytic species appeared (drawn in red) which could be observed separately in blank experiments using solutions of pure AnEryt and pure trimethoxy(morpholinomethyl)silane in water. Typical spectra for the latter are shown in Figure 2f: at $\text{pH} \approx 8.5$, hydrolysis of the pure silicon precursor yielded four groups of signals in the ^{29}Si NMR spectrum which were tentatively assigned to T^0 to T^3 groups of silsesquioxane species (see Ref. [5] for details of the T^n nomenclature and typical ranges of ^{29}Si NMR chemical shifts). As is clear from Figure 2f, the relatively broad ^{13}C NMR signals of C5, C6, and C7 are no longer usable mirrors of the ^{29}Si NMR signals. In the second blank experiment, AnEryt gave rise to two signals, as expected.

The influence of the concentration of silicate is illustrated in Figure 2d and e. The lower the concentration, the more pronounced the hydrolysis. The conditions used in Figure 2d most closely resemble those given in Ref. [1], and thus the spectral assignment used therein is applied here. A comparison of the ^{13}C NMR spectrum (Figure 2d) with the revised assignment given in Figure 2c shows that the hydrolysis products are assigned to the main pentacoordinate species (labeled as **10a** in Ref. [1]). At

the same time, the related ^{29}Si NMR signals of the silsesquioxane part had been overlooked. The pronounced hydrolytic instability of **1** at a pH value close to neutrality is made particularly clear by further dilution. Figure 2e shows the ^{13}C NMR spectrum recorded at a concentration of silicon of 0.1 mol kg^{-1} ; the small amount of residual **1** is clear.

As a result, the statement made in Ref. [1] that **1** (**10**) experiences no hydrolytic decomposition upon dissolution in water is not supported by the correctly assigned NMR spectra shown herein. Contrary to the conclusions made previously,^[1] hydrolysis products dominate the spectra of aqueous solutions, particularly at higher dilution. Despite this troublesome result, it should be noted that, in fact, the hydrolytic stability of a pentacoordinate silicate increases if the silicon center is part of a zwitterion instead of an anion. Moreover, hydrolysis may be increasingly suppressed, as observed by ^{29}Si NMR spectroscopy, when increasing amounts of excess oxolanediol are present in the solution equilibrium.

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