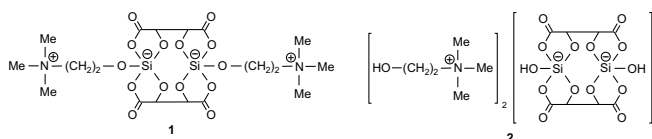


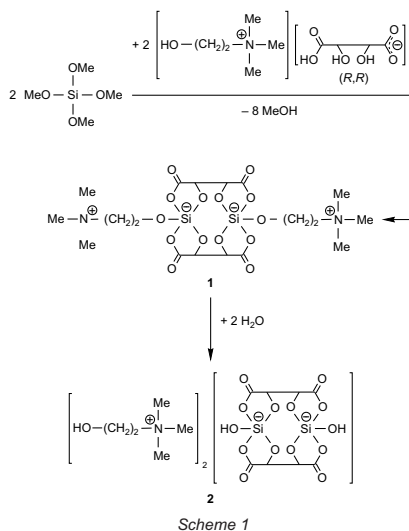
Introduction

In continuation of our ongoing systematic studies on higher-coordinate silicon compounds that exist in aqueous solution (in this context, see ref. [1] and references cited therein), the dinuclear pentacoordinate silicon(IV) complexes **1** (zwitterionic) and **2** (anionic) were synthesized and characterized by solution and solid-state NMR spectroscopy. In addition, compound **1** was structurally characterized by single-crystal X-ray diffraction. The stability of **1** and **2** towards hydrolysis in aqueous solution was studied by NMR spectroscopy.



Syntheses

Compound **1** was synthesized according to Scheme 1 by treatment of tetramethoxysilane with choline (*R,R*)-trihydrogentartrate (molar ratio 1:1) in boiling *N,N*-dimethylformamide. Dissolution of **1** in water at ambient temperature and immediate freeze drying of the resulting aqueous solution afforded compound **2**.



Scheme 1

Crystal Structure Analysis

Compound **1** was structurally characterized as the solvate 1·3DMSO by single-crystal X-ray diffraction (Figure 1).

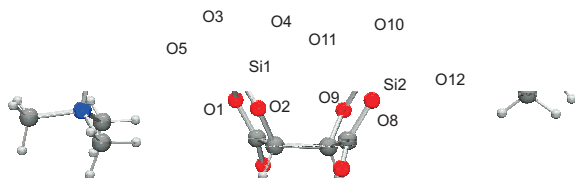


Figure 1. Molecular structure of **1** in the crystal of 1·3DMSO

Selected bond lengths [pm]:		Axial bond angles [°]:			
Si1–O1	1.789(2)	Si2–O8	1.801(2)	O1–Si1–O3	177.36(12)
Si1–O2	1.666(2)	Si2–O9	1.658(2)	O8–Si2–O10	176.59(12)
Si1–O3	1.813(2)	Si2–O10	1.807(2)		
Si1–O4	1.660(2)	Si2–O11	1.666(2)		
Si1–O5	1.636(2)	Si2–O12	1.647(3)		

Berry distortions (TBP→SP): 6.6% (Si1, pivot atom O5), 8.2% (Si2, pivot atom O12).

Reference

[1] B. Theis, C. Burschka, R. Tacke, *Chem. Eur. J.* **2008**, *14*, 4618–4630.

Stability in Aqueous Solution

The kinetic stability of **2** in aqueous solution was studied by ¹H NMR spectroscopy using the CH resonance signals of the bound (*R,R*)-tartrato(4-) ligands of **2** and those of the free tartaric acid formed by hydrolysis. At concentrations of 10 and 100 mM (solvent D₂O), compound **2** was found to undergo a slow hydrolysis over a period of more than 10 days, followed by gel formation. The kinetic stability of **2** in aqueous solution strongly depends on the pH value (Figure 2).

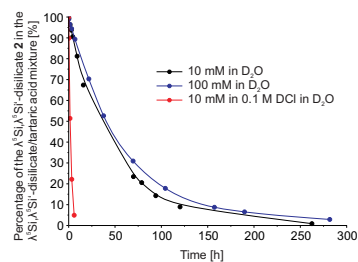


Figure 2

The kinetic stability of the pentacoordinate silicon complex **2** is significantly higher than that of the tetracoordinate silicon compound tetramethoxysilane [Si(OMe)₄]. This has been demonstrated by kinetic studies (¹H NMR spectroscopic analysis; 300.1 MHz; 23 °C) with an equimolar mixture of **2** and Si(OMe)₄ in D₂O/CD₃CN [1:1 (v:v); c = 50 mM] (Figure 3).

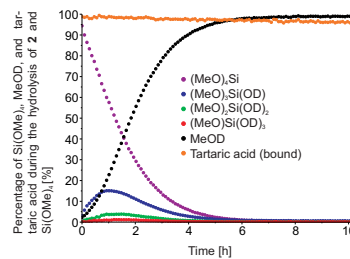
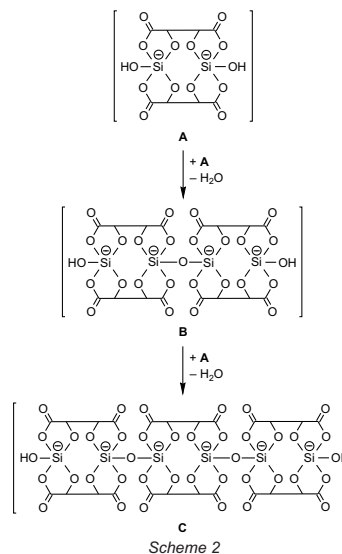


Figure 3

As shown in Scheme 2, the dianion of **2** (**A**) undergoes a condensation reaction in DMSO (20 °C) to give the tetra- and hexanuclear complexes **B** and **C**. The identities of **B** and **C** were established by multinuclear NMR spectroscopy.



Scheme 2

Conclusions

The zwitterionic dinuclear pentacoordinate silicon(IV) complex **1** can be prepared in a one-step synthesis starting from tetramethoxysilane and choline (*R,R*)-trihydrogentartrate. Compound **1** undergoes a rapid hydrolysis in aqueous solution at ambient temperature to form the dianionic λ⁵Si, λ⁵Si'-disilicate **2**, which can be isolated by freeze drying.

In aqueous solution, compound **2** shows a remarkable kinetic inertness against hydrolysis and hydrolyzes very slowly to afford (*R,R*)-tartaric acid, choline, and orthosilicic acid. However, under strongly acidic and basic conditions, rapid hydrolysis is observed.

Future studies of the condensation reaction of the dianion of **2** (**A**) (→ formation of polynuclear silicon(IV) complexes such as **B** and **C**) have to elucidate the potential of this chemistry for material sciences.