

Preparation and Constitution of the Crystalline Silicic Acid Trimethylsilyl Ester $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$

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Abstract. A new crystalline compound has been synthesized by trimethylsilylation of tetraethylammonium silicate which was identified by means of gas chromatography, mass spectrometry, ²⁹Si NMR and X-ray analysis to be a cage-like double three-ring silicic acid trimethylsilyl ester containing six inequivalent SiO₄ tetrahedra and trimethylsilyl groups.

Herstellung und Konstitution des kristallinen Kieselsäuretrimethylsilylesters $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$

Inhaltsübersicht. Durch Trimethylsilylierung des Tetraethylammoniumsilicats wurde ein neuer kristalliner Kieselsäuretrimethylsilylester hergestellt. Konstitutionsuntersuchungen mit Hilfe der Gaschromatographie, Massenspektrometrie, ²⁹Si NMR- und Röntgenanalyse zeigen, daß der Kieselsäuretrimethylsilylester aus käfigartigen Doppeldreiringen aufgebaut ist, die jeweils sechs nichtäquivalente SiO₄ Tetraeder und Trimethylsilylgruppen enthalten.

1. Introduction

The double three-ring silicate anion Si₆O₁₅⁶⁻ is known as building unit of the crystalline silicate $[\text{Ni}(\text{en})_3]_3\text{Si}_6\text{O}_{15} \cdot 26 \text{H}_2\text{O}$ [1] and $[\text{N}(\text{C}_2\text{H}_5)_4]_6\text{Si}_6\text{O}_{15} \cdot 57 \text{H}_2\text{O}$ [2], and has also been proved to be present in tetraethylammonium silicate solutions [3, 4]. The trimethylsilyl ester of the double three-ring silicate $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$ (Q₆M₆)¹⁾ has been synthesized so far only in diluted solutions of organic solvents by trimethylsilylation of the above silicates or silicates solutions [3, 4]. However, difficulties arose in the preparation of the crystalline ester due to the high instability of the strained SiOSi bonds of the double three-ring structure against proton

¹⁾ In this article the following abbreviations are used: Q: Si(O_{0,5})₄; M: (CH₃)₃SiO_{0,5}

attack [5]. We describe here for the first time the preparation of the pure crystalline Q_6M_6 compound and its structural characterization by gas chromatography, mass spectrometry, X-ray analysis, and solution and solid state ^{29}Si NMR.

2. Preparation

Q_6M_6 was synthesized by trimethylsilylation of tetraethylammonium silicate $[N(\text{C}_2\text{H}_5)_4]_6\text{Si}_6\text{O}_{15} \cdot 57 \text{H}_2\text{O}$ according to the slightly modified method of TAMÁS *et al.* [6] but without treating the reaction product with cation exchanger.

A solution of 30 ml trimethylchlorosilane, 30 ml hexamethyldisiloxane, and 60 ml dimethylformamide was vigorously stirred for 15 min, and 1.4 g of the powdered silicate were added in small portions at 15°C. The mixture was stirred for another 15 min and 100 ml of water cooled to 2°C were added. Subsequently, the organic phase was separated and washed with water until neutral reaction was achieved. After partial removal of hexamethyldisiloxane under vacuum at 35°C a portion of 0.58 g (yield: 61%) colorless crystals were obtained from the residual liquid phase.

Elemental analysis of the crystals gave carbon and hydrogen contents of 25.6% and 6.5%, respectively (calculated for Q_6M_6 25.5% C and 6.4% H). The capillary gas chromatogram of the crystals solved in heptane shows a single peak in the retention region typical for compounds of six M groups [3].

3. Structure Characterization

The molecular mass of the silicic acid trimethylsilyl ester was determined by mass spectrometry. In the mass spectrum the $M-\text{CH}_3$ peak, characteristic of methylsiloxanes, was observed at m/z 831. This indicates a molecular mass of 846 for the crystals. Elemental composition of the m/z 831 ion, determined from exact mass measurements is $\text{Si}_{12}\text{O}_{15}\text{C}_{17}\text{H}_{51}$ (831.0441 measured, 831.0459 calculated) in accordance with the expected Q_6M_6 structure. The MS fragmentation pattern of Q_6M_6 shows no significant differences to that of the larger cage-like silicic acid trimethylsilyl esters Q_8M_8 and $Q_{10}M_{10}$.

The ^{29}Si NMR spectrum of Q_6M_6 in heptane solution displays two sharp peaks at +13.5 ppm and -98.8 ppm für the M- and Q-type silicons, respectively (see Fig. 1a). This indicates a highly symmetrical structure of the Q_6M_6 molecule with equivalent silicons in either of the six Q and M sites or a fast dynamic exchange between inequivalent sites. As expected for the trimeric ring, the peak of the Q silicons is strongly shifted to low field in comparison to the double four- and double five-ring compounds Q_8M_8 (-108.3 ppm) and $Q_{10}M_{10}$ (-109.7 ppm) [7]. Corresponding low-field shifts of the double three-ring silicate anions have been observed in tetraethylammonium silicate solutions [3].

In contrast to the solution spectrum of Q_6M_6 , the high-resolution ^{29}Si NMR spectrum of solid Q_6M_6 shows splittings into several lines both for the M and Q peaks. The solid-state ^{29}Si NMR spectrum is shown in Fig. 1b and the splitting of the M peak into six lines and the Q peak into five lines with one having double intensity is clearly visible. The solid-state spectrum reveals that the six silicons in either of the Q and M sites of the Q_6M_6 structures are no longer equivalent in the crystalline solid but characterized by slightly different bonding geometry. From

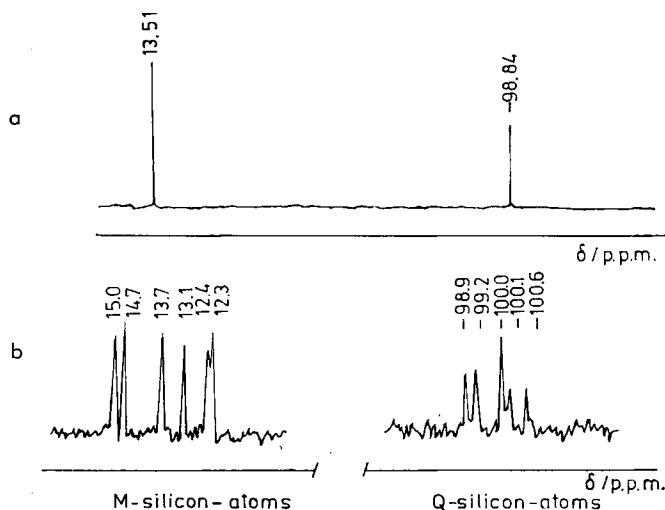


Fig. 1 ^{29}Si NMR spectra of Q_6M_6 in heptane solution (a) and in crystalline state (b).

X-ray diffraction of Q_6M_6 follows the space group $\text{P}2_1/\text{c}$ with four equivalent molecules in the unit cell. The parameters of the unit cell are $a = 2.1386(3)$, $b = 2.3510(3)$, $c = 1.0959(2)$ nm and $\beta = 119.75(5)^\circ$. The structure analysis (1700 reflections, final $R = 0.07$) shows that in the crystalline state the Q_6M_6 molecule is asymmetrically distorted which confirms the conclusions derived from the solid-state ^{29}Si NMR spectrum. In Fig. 2 the structure of the $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$ molecule is given. The atoms are depicted as 50% probability thermal ellipsoids, the hydrogens have been omitted. From Fig. 2 follows that the central part of the molecule is built up of a cage-like double ring of six SiO_4 tetrahedra, each of them connected to three neighbouring SiO_4 tetrahedra by sharing oxygen atoms. The fourth oxygen atom of the SiO_4 tetrahedra is linked to the $(\text{CH}_3)_3\text{Si}$ group. All bond lengths within the molecule are different. The Si—O bond lengths are 0.156(1)—0.163(1) nm and the Si—C distances, under consideration of the thermal motion, are 0.170(4)—0.189(3) nm. A detailed description of the Q_6M_6 structure will be published elsewhere [8].

The results of this study reveal unambiguously that the double three-ring structure of the crystalline Q_6M_6 is asymmetrically distorted in a similar way as observed for the solid double four-ring and double five-ring silicic acid trimethylsilyl ester Q_8M_8 [9, 10] and $\text{Q}_{10}\text{M}_{10}$ [9], respectively.

4. Experimental

^{29}Si NMR. The ^{29}Si NMR spectrum of Q_6M_6 in heptane solution was measured with a NMR spectrometer Jeol PS 100 at 19.87 MHz, pulse repetition 60 s, flip angle 60° , number of scans: 36. The solid-state ^{29}Si NMR spectrum were measured on a Bruker CXP 200 instrument at 39.74 MHz

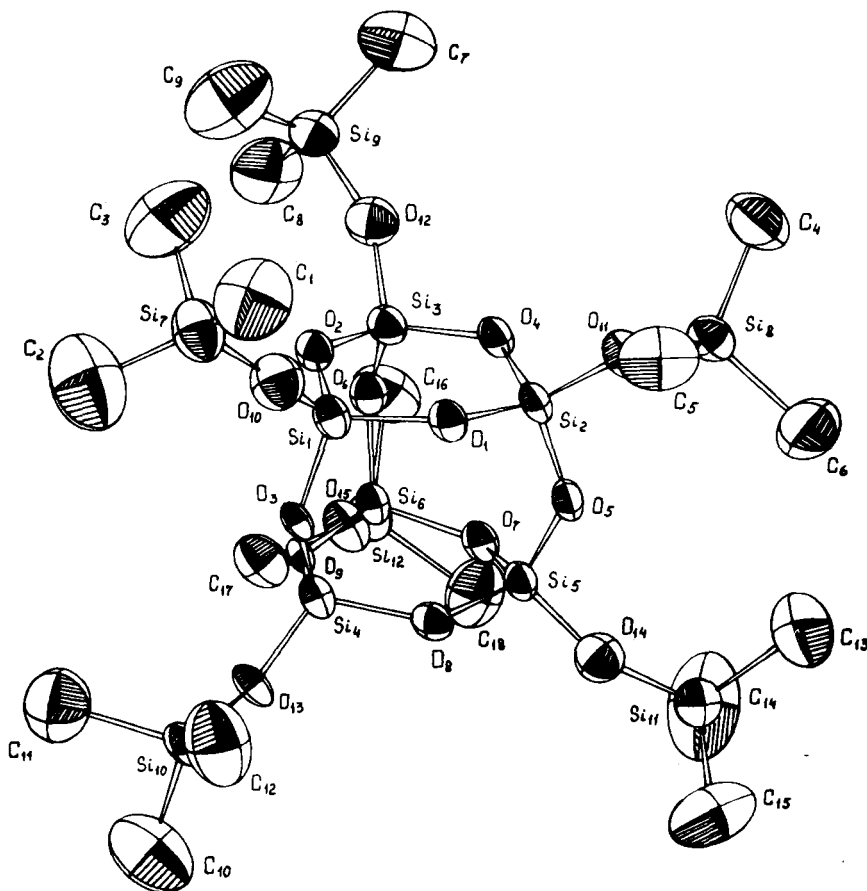


Fig. 2 Structure of the $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_6\text{O}_{15}$ molecule. For details see [8].

using CP-MAS technique with 60 s pulse repetition, 5 ms contact time, and 3 KHz rotation frequency. Number of scans: 27.

Mass spectrometric measurements were performed on a AEI MS 902 instrument at 70 eV ionizing energy. The temperature of the ion source was 180°C. The sample was introduced directly into the ion source from a quartz probe.

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