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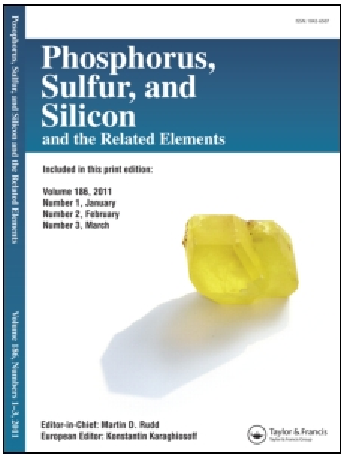

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# Organic Silicate Ring Systems

Heinrich C. Marsmann[a]; Edith Bertling[a]; Meinolf Seifert[a]
[a] Fachbereich Chemie der Universität, Paderborn

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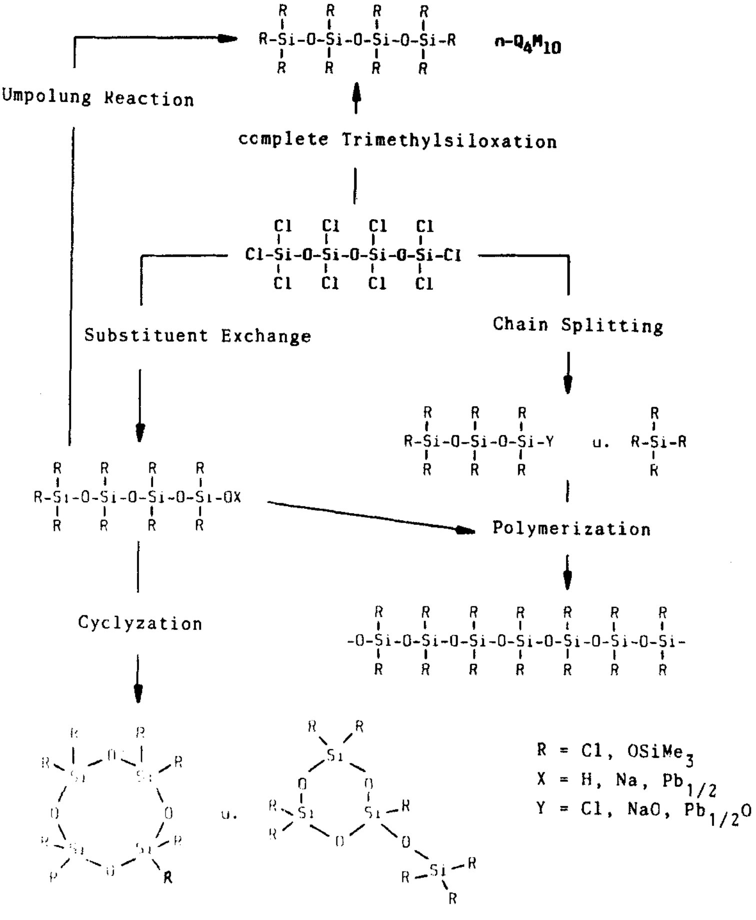
# Organic Silicate Ring Systems.

Heinrich C. Marsmann, Edith Bertling and Meinolf Seifert
Fachbereich Chemie der Universität -GH- Paderborn
D-4790 Paderborn, Warburgerstraße 100

Abstract Cyclic silicic acid esters were characterized by silicon NMR spectroscopy and tested as complexing agents.

Silicates occur in a great variety of structures. Most of them are known from their crystalline state and are in a highly polymeric form. But some silicates never crystallize and are therefore much more difficult to characterize. This is especially true for the oligomeric cyclic and polycyclic silicate ions, which can be thought of as a part of a zeolithe structure.

Silicic acid esters are much better to handle because they are - except the polymers - volatile and soluble in organic solvents and therefore purification by the usual methods of organic chemistry is possible. Silicic acid esters can be obtained from chloro siloxanes. The formation of Si-O-Si bridges is done either by hydrolysis of Si-Cl bonds or by reaction with oxygen at high temperatures. The hydrolysis yields with few exceptions linear and branched siloxanes but by the high temperature oxidation of chloro siloxanes the cyclic and polycyclic chloro siloxanes are accessible. Methyl and trimethylsilyl esters are then prepared by reaction with methyl ortho formiate or trimethylsilanol. The preparation of trimethyl silyl silicates has to follow a number of steps because the reaction of a Si-Cl with a Si-OH group is not unambiguous. The procedure to maximize the yield of the reaction is shown using n-$[(CH_3)_3SiO]_{10}Si_4O_3$ as an example.



Scheme 1 Trimethylsilylation of Chloro siloxanes.

The cyclic trimethyl silyl silicates so prepared are depicted in Fig. 1.The $^{29}Si$ chemical shift data are collected in tab. 1.[1] The values show that an unequivocal assignment of the structures by chemical shift arguments alone is not possible. The spin couplings between the silicon atom $^2J_{Si-O-Si}$ of the siloxane skeleton were used as additional information. Signal enhancement was obtained from the coupling of the protons of the trimethyl silyl groups with the silicon atoms of the siloxane skeleton despite of the fact, that the values of these couplings are too small to be measured.

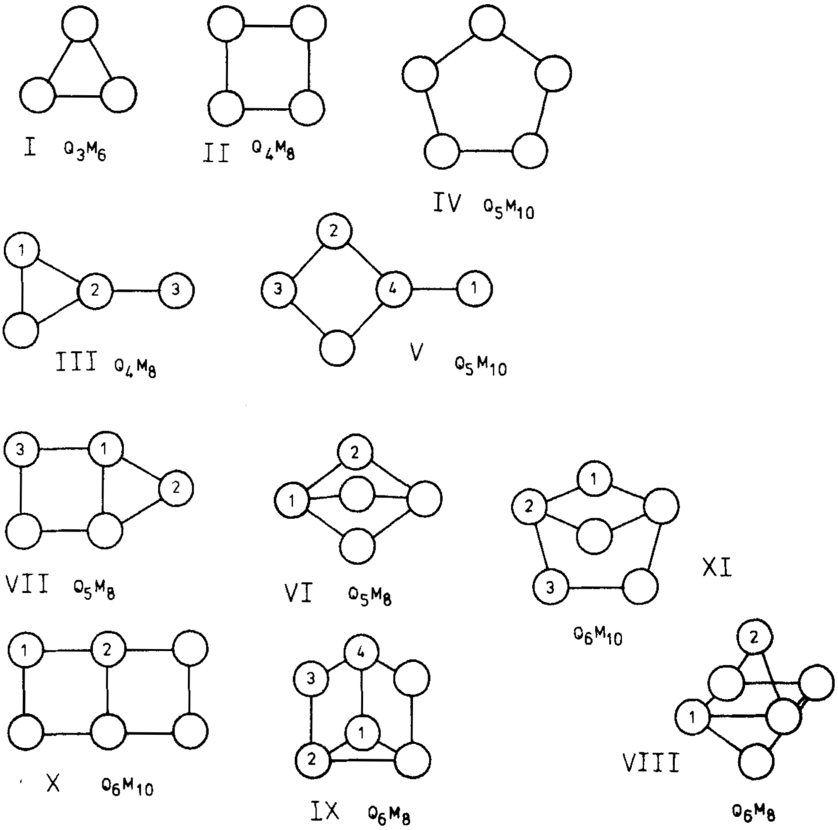


Fig. 1 Structural diagrams for some cyclic trimethyl silyl silicates. Circles represent silicon atoms, the connecting lines oxygen, and $(CH_3)_3SiO$-groups (not shown) complete the coordination number of silicon to four.

Table 1 $^{29}$Si-NMR Data$^{a}$ of cyclic Trimethylsilyl silicic acid esters

| Constitution | Skeleton | | Chemical Shifts M | Chemical Shifts Q | $^{2}J_{Si-O-Si}$ |
|---|---|---|---|---|---|
| $Q_3M_6$ | I | | 10.9 | -99.8 | |
| $Q_4M_8$ | II | | 10.1 | -107.8 | |
| $Q_4M_8$ | III | 1 | 11.1/10.8 | -99.7 | |
| | | 2 | 11.3 | -101.9 | |
| | | 3 | 9.3 | -106.5 | |
| $Q_5M_{10}$ | IV | | 9.6 | -109.5 | |
| $Q_5M_{10}$ | V | 1 | 9.0 | -106.7 | $J_{1,4}$=13.5 |
| | | 2 | 10.3/10 | -108.0 | $J_{2,4}$=13.0 |
| | | 3 | 10.1/10.0 | -108.1 | |
| | | 4 | 10.7 | -110.2 | |
| $Q_5M_8$ | VI | 1 | 12.0 | -103.1 | $J_{1,2}$= 9.8 |
| | | 2 | 10.6 | -103.4 | |
| $Q_5M_8$ | VII | 1 | 12.6 | -98.8 | $J_{1,2}$= 7.6 |
| | | 2 | 12.0/11.0 | -99.1 | $J_{1,3}$=10.3 |
| | | 3 | 10.8 | -107.4 | |
| $Q_5M_8$ | VIII | 1 | 10.9 | -103.1 | $J_{1,2}$=10.2 |
| | | 2 | 13.0 | -104.6 | |
| $Q_6M_8$ | IX | 1 | 13.6 | -97.7 | $J_{1,2}$= 6.7 |
| | | 2 | 13.0 | -98.8 | $J_{1,4}$=10.0 |
| | | 3 | 11.1/10.3 | -106.1 | $J_{2,3}$= 9.5 |
| | | 4 | 11.9 | -107.9 | $J_{3,4}$=12.6 |
| $Q_6M_{10}$ | X | 1 | 10.5/10.3 | -107.7 | |
| | | 2 | 11.4 | -108.1 | |
| $Q_6M_{10}$ | XI | 1 | 10.3/10.1 | -105.5 | $J_{1,2}$=10.9 |
| | | 2 | 10.7 | -107.5 | $J_{2,3}$=12.3 |
| | | 3 | 9.7 | -109.2 | |

[a] Constitution: M = $(CH_3)_3SiO_{1/2}$; Q = $SiO_{4/4}$
Skeleton: Roman numerals: Type from fig. 1
Arabic numerals: Position within
Chemical shifts in ppm relative to $(CH_3)_4Si$

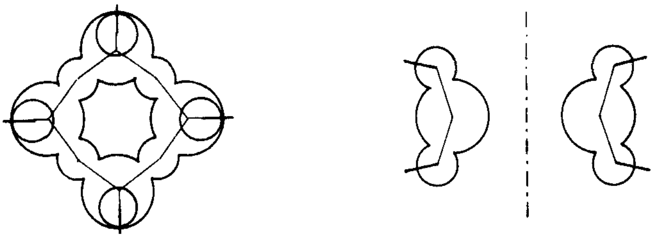


Fig. 2 Look at the channel formed by the $(Si_4O_4)R_8$ (R= $OCH_3$, $OSi(CH_3)_3$ moiety.

The simple ring silicate esters can be considered as oxygen containing channels as depicted in fig. 2 for the $[(CH_3)_3SiO]_8(Si_4O_4)$. Metal cations of the right size can enter these channels. This can be proved by transfer experiments between an alkali picrates in aqueous and the silicate ester in organic ($CH_2Cl_2$) solution.[2] Lithium ions show the best fit in the trimeric ring, but the slightly larger tetrameric ring accommodates the larger potassium ions. This is demonstrated by the extraction constant $K_E$

$$K_E = x \;/\; ((2-x)*(1-x)^2)$$

where x is the concentration of alkali ions in the $CH_2Cl_2$ phase. The data are found in tab. 2.

Table 2 Extraction constant $K_E$ $[*10^6 l^2/mol^2]$ for alkali ions with some cyclic silicic acid esters.

| Transfer reagent | $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ |
|---|---|---|---|---|
| $[((CH_3)_3SiO)_2SiO]_3$ | 0.587 | 0.083 | 0.099 | 0.012 |
| $[(CH_3O)_2SiO]_3$ | 0.655 | 0.072 | 0.071 | 0.006 |
| $[((CH_3)_3SiO)_2SiO]_4$ | | | 0.048 | |
| $[(CH_3O)_2SiO]_4$ | | | 0.099 | |

Ion - silicate interaction is also found in alkali silicate melts.[3] Thus lithium and sodium silicate melts with a high alkali to silicon ratio yield mostly linear silicate anions. But potassium silicates melts contain a considerable amount of the cyclic trisilicate anion $Si_3O_9^{6-}$ with a maximum at 1000°C. The ring expansion at higher temperature allows the binding of the larger cation.

## References

1. E.Bertling, H.C.Marsmann, Z.anorg.allg.Chem. **578**, 166, 1989
2. H.C.Marsmann, M.Seifert, Z.Naturforsch. **46b**, 693, 1991
3. E.Bertlin-Kampf, M.Heimann, R.Kleibrink, H.C.Marsmann in preparation