

The Crystal Structure of [Tris(trimethylsilyl)methyl]silanetriol. A Novel and Remarkably Stable Hydrogen-bonded Cage Structure

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The compound $(\text{Me}_3\text{Si})_3\text{CSi}(\text{OH})_3$ crystallizes as discrete hexameric hydrogen-bonded cage units of remarkable stability.

The observation¹ that the silanediol $\text{TsiSiPh}(\text{OH})_2$, [$\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$] has a crystal structure consisting of discrete dimers of the form (1) (which bears some analogy to the dimers formed by carboxylic acids) suggested the possibility that a silanetriol might be able to crystallize as discrete polyhedral cages. The only previously known structure of an organo-silanetriol, that of cyclohexylsilanetriol, determined at -60°C , does not have this form, but instead consists of molecules linked together by hydrogen bonds into infinite sheets.² We have now found, however, that the triol $\text{TsiSi}(\text{OH})_3$ does have the type of structure we were seeking. The triol was prepared by hydrolysis of $\text{TsiSiH}(\text{OH})\text{I}$ as described elsewhere,³ and recrystallized from heptane.

Crystal data: $\text{C}_{10}\text{H}_{30}\text{O}_3\text{Si}_4$, $M = 310.7$, rhombohedral, $a = 15.154(1)$, $c = 42.079(2)$ Å, $U = 8368.1$ Å³, $Z = 18$, $D_c = 1.12$ g cm⁻³, Cu-K α radiation (Ni filter), $\lambda = 1.5418$ Å, $\mu = 30.0$ cm⁻¹. Space group $R\bar{3}$ from successful structure refinement. $R = 0.13$, $R' = 0.16$, for 1594 unique reflections with $|F^2| > \sigma(F^2)$ measured on an Enraf-Nonius CAD-4 diffractometer in the range $2 < \theta < 55^\circ$. There was some disorder involving alternative sites for O and for Si generated by rotation of the $\text{Si}(\text{OH})_3$ and $(\text{Me}_3\text{Si})_3\text{C}$ groups about the $\text{Si}(1)\text{--C}(1)$ bond, and in the refinement the O sites were given fixed occupancies of 80 and 20% and the Si sites fixed occupancies of 66 and 33%. Hydrogen atoms could not be located.†

Two views of the structure (showing the main occupancies only) are given in Figures 1 and 2, the Me_3Si groups being omitted from the latter so that the cage can be seen more clearly. It is evident that if the hydrogen atoms of the hydrogen bonds are not considered, the structure consists of discrete trigonal cages formed from six triol molecules maximally hydrogen bonded. The cage can be regarded as made up of two regular triangles, six 5-membered rings in an envelope conformation (giving 12 faces), and six 6-membered rings in a boat conformation (giving 18 faces), making up a

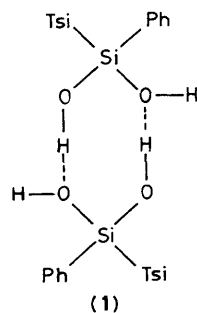


Figure 1. Structure of the hydrogen-bonded hexamer formed from $(\text{Me}_3\text{Si})_3\text{CSi}(\text{OH})_3$, with atom numbering scheme. The open lines indicate hydrogen bonds.

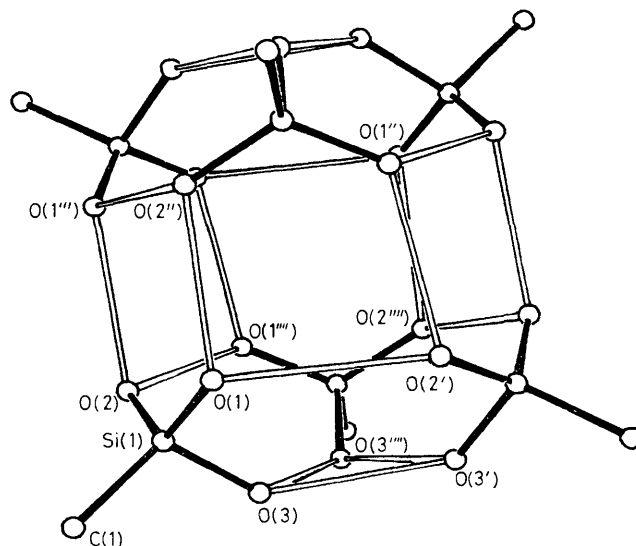


Figure 2. Another view of the cage formed by $(\text{Me}_3\text{Si})_3\text{CSi}(\text{OH})_3$, with Me_3Si groups omitted. Selected angles and distances: $\text{O}(2')\text{---O}(1)\text{---O}(2'')$, 91° ; $\text{O}(1'')\text{---O}(2)\text{---O}(1''')$, 83° ; $\text{O}(3')\text{---O}(3)\text{---O}(3''')$, 60° ; $\text{O}(1)\text{---O}(2')$, 3.12 ; $\text{O}(1)\text{---O}(2'')$, 2.93 ; $\text{O}(3)\text{---O}(3')$, 2.82 Å; symmetry elements: $\bar{y}, x - y, z$; $'' x - y, x, 1 - z$; $''' y, y - x, 1 - z$; $'''' y - x, \bar{x}, z$.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

total of 32 faces. There is a sizeable cavity; the distance across the cage between the two triangular faces is 6.7 Å, the internuclear distance between O(1) and O(1^{'''}) is 5.1, and that between O(1) and O(2^{'''}) is 5.9 Å. In order that this closed cage can be formed the O–Si–O angles have to be significantly and differently distorted from tetrahedral; the O(1)Si(1)O(2) angle is 116.8(6), the O(1)Si(1)O(3) angle 98.8(7), and the O(2)Si(1)O(3) angle 102.5(5)°.

The crystal has remarkable thermal stability, melting (with decomposition) only at 285–290 °C.

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