The Crystal and Molecular Structure of the Symmetrical Silasesquioxane H8Si8O12 at 100 K, a Molecular Building Block of Some Zeolites

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Abstract. The crystal and molecular structure of the symmetrical octasilasesquioxane $H_8Si_8O_{12}$ has been redetermined from three dimensional X-ray diffraction data. The $H_8Si_8O_{12}$ molecule shows effective $m\bar{3}$ (T_h) symmetry. The molecular packing indicates intermolecular O···Si distances of ~ 3.6 Å reminiscent of incipient nucleophilic attack of O on Si. The anisotropic displacement parameters indicate non-rigidity of the molecule.

Introduction

The symmetrical, molecular octasilasesquioxanes $X_8Si_8O_{12}$ show an aesthetically appealing polycyclic structure (*Fig. 1*) with 8 Si-atoms arranged at the corners of a cube, 12 O-atoms bridging the edges of the Si_8 cube, and 8 X groups completing tetrahedral coordination of the Si-atoms. Several representatives of this class of molecules have been characterized structurally (X = H [1], CH_3 [2], C_2H_3 [3], C_6H_5 [4][5], OCH_3 [6], $OSi(CH_3)_3$ [7]). The interest in these compounds derives from the fact that their Si_8O_{12} core is analogous to the T_8O_{12} fragment (T_8 usually a mixture of Al, Si, P, Co(II)) found in zeolites such as Linde A and others [8]. However, in the case of octasilasesquioxanes, only one type of tetrahedral atoms (Si) is present; they may thus be considered to be prototypical and to provide a reference for comparison.

The structure of $H_8Si_8O_{12}$, the most simple member in the series, has been determined from two-dimensional diffraction data only [1]. Here, we describe and discuss significantly more accurate results obtained from three-dimensional X-ray diffraction data measured at 100 K.

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Results

Molecular Structure

The crystal symmetry requires the molecule to have $\bar{3}$ (S_6) symmetry. Its actual symmetry is higher, namely $m\bar{3}$ (T_h). *Table 3* shows that chemically equivalent but crystallographically inequivalent structural parameters are generally the same to within two e.s.d.'s. The angles at the Si-atoms correspond almost exactly to regular tetrahedral coordination, and the angles at the O-atoms are in the expected range (130–160°) [9]. The nonbonding Si···Si distances also show that the Si_8 cube is slightly elongated (by ~ 0.009Å) along the crystallographic threefold axis (Si(1)···Si(1), *Fig. 1*). The nonbonded O···O distances across the faces of the Si_8 cube differ substantially, by ~ 0.31 Å. They are the clearest manifestation of the molecular T_h symmetry.

Two questions arise: why do the angles
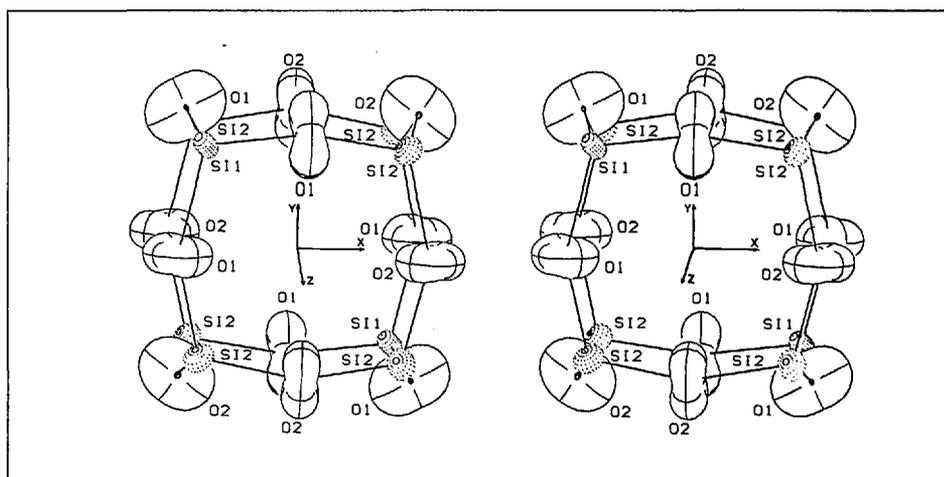
Fig. 1. *PEANUT stereo plot* [21] *of Si_8O_{12} showing atomic numbering, r.m.s. atomic displacements not explained by a rigid body model* ($\Delta U_{ij} = U_{ij}(obs) - U_{ij}(L,T)$, solid lines: $\Delta U_{ij} > 0$, dotted lines: $\Delta U_{ij} < 0$, r.m.s. scale 6.15) *and molecular coordinate system*
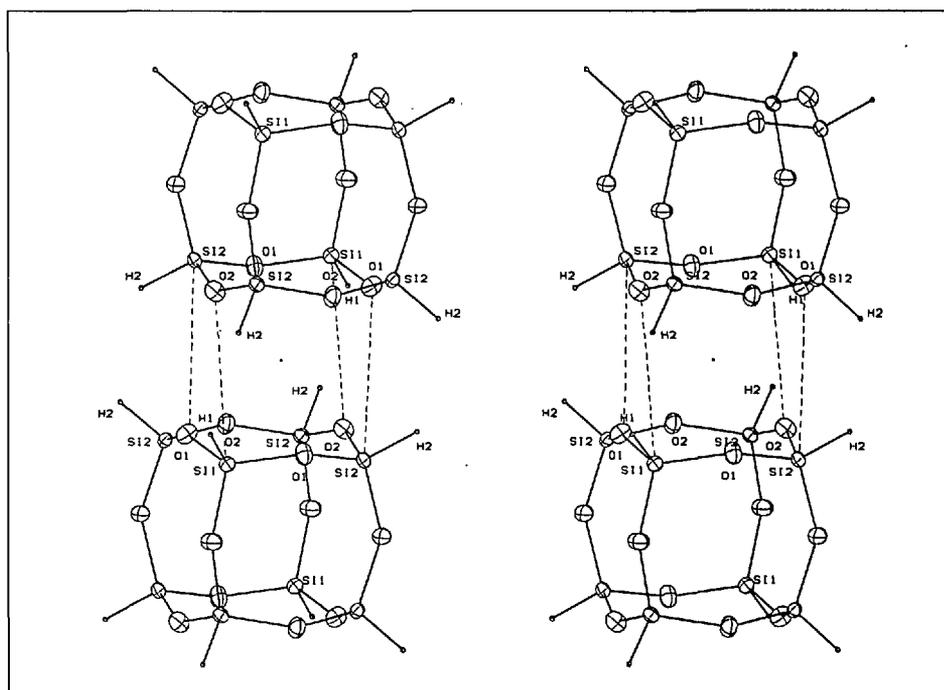
Fig. 2. *PEANUT stereo plot* [21] *of two molecules related by a center of inversion.* The nonbonded distances are 3.64 (Si(1)···O(2)) and 3.62 Å (Si(2)···O(1)). The two Si(1)-atoms in each molecule define crystallographic threefold axes.

assume their observed values and why does the molecule not show $m\bar{3}m$ (O_h) symmetry?

Geometrical Considerations

Let us first consider a Si_8O_{12} fragment of symmetry O_h. The positions of Si and O are then completely determined by only two parameters (a,b). Given cartesian coordinate axes passing through the centers of the faces of the Si_8 cube (Fig. 1) the Si's may be placed at $(x,y,z)_{Si} = (a,a,a)$, $(a,\bar{a},a)$, $(a,\bar{a},\bar{a})$, $(\bar{a},\bar{a},\bar{a})$, etc., the O's at $(x,y,z)_O = (b,b,O)$, etc. One pair of O-atoms thus sits on each of the six diagonal mirror planes of the Si_8 cube. It may be shown that $d(Si-O) = (2(a-b)^2 + a^2)^{1/2}$, $\cos\alpha(SiOSi) = (1-2a^2/d^2)$, $\cos\beta(OSiO) = (1-b^2/d^2)$ and $4\cos\beta = 3\cos(\alpha + \arccos(-1/3)) + 1$, i.e. for O_h symmetry α and β depend on each other. If we assume, $\beta = 109.5°$, it follows that $\alpha = 148.4°$, i.e. for a relatively strain-free value of the angle at Si, the angle at O is automatically in the expected range [9]. The lowering of molecular symmetry from O_h to T_h increases the number of independent structural parameters from 2 to 3. The atomic positions are (a,a,a), etc. for Si and $(b+\Delta, b-\Delta, O)$, etc. for O. The O-atoms are now displaced from the diagonal mirror planes of the Si_8 cube by an amount $\Delta(2)^{1/2}$ (towards $\pm y$ for the atoms in the molecular x,y plane, towards $\pm z$ for the atoms in the y,z plane and towards $\pm x$ for the atoms in the z,x plane, see Fig. 1). The internal coordinates are $d = (2(a-b)^2 + a^2 + 2\Delta^2)^{1/2}$, $\cos\alpha = (1-2a^2/d^2)$, $\cos\beta = (1-b^2/d^2 - 3\Delta^2/d^2)$, all independent. Except for the correction terms in Δ^2, the equations look the same as those above. For a given α, β depends on Δ; specifically for $\cos\beta = -1/3$ ($\beta = 109.5°$), we get $\sin(\alpha/2) = (1 + 2(4-9 \Delta^2/d^2)^{1/2})/3$. The angle α is maximal, if Δ is zero; thus lowering the symmetry from O_h to T_h decreases α as observed (147.5 vs. 148.4°).

On the basis of the geometrical arguments given above, the bond angles α and β may now be discussed. Of the two, only the O–Si–O angle β is likely to be very close to its strain-free value. There are two reasons for this: i) A distortion of the β-angles (preserving O_h symmetry) from their strain-free value is much more costly than a distortion of the α-angles, because the force constant is much higher for O–Si–O than for Si–O–Si [10]. ii) Such a distortion affects 24 β-angles, but only 12 α-angles. Thus, given β (109.5°), α has to follow suit ($\leq 148.4°$). The magnitude of the observed distortion is $\Delta2^{1/2} = d(5/6 + \sin(\alpha/2)/3^{1/2} - 3\sin^2((\alpha/2)/2)^{1/2}$, i.e. ~ 0.112 Å. Given the small magnitude of the distortion, the energy difference between T_h and O_h symmetric structures must be small as well and the question arises why the $H_8Si_8O_{12}$ structure is not an average of the observed T_h structure and one in which the O's are sitting on opposite sides of the diagonal mirror planes in the Si_8 cube (displaced towards $\pm x$ for the atoms in the x,y plane, etc., see Fig. 1), i.e. why does Si_8O_{12} not show O_h symmetry, at

least on average? Small distortions like the one observed here are usually attributed to some unspecified influence of molecular packing. We argue in terms of packing as well, but are able to pinpoint the intermolecular interactions which are responsible for the lowering of symmetry.

Molecular Packing

Inspection of the packing reveals 4 relatively short O···Si contacts between each pair of molecules. (Fig. 2, 3.623, 3.644 Å), reminiscent of an incipient nucleophilic attack of O on Si (angles O···Si–O 163.6, 158.7°) [11]. If the Si_8O_{12} fragment was undistorted (O_h) the Si···O distances would be longer by

~ Δ(~ 0.08 Å) and the intermolecular interaction weaker. Analogous interactions have not been described for other $X_8Si_8O_{12}$ molecules [2–7], presumably because the larger size of their X groups prevents a close approach of the molecules.

Molecular Flexibility

One might be tempted to argue that, because of its polycyclic nature, $H_8Si_8O_{12}$ is a rather rigid molecule. We have tested this hypothesis by calculating the rigid body librational and translational amplitudes (L,T) from the observed atomic displacement parameters U_{ij} (obs) of O and Si [12]. The mean square displacements which remain

Table 1. *Experimental Conditions for the Crystal Structure Determination of $H_8Si_8O_{12}$*

Formula	$(HSiO_{1.5})_8$
Formula weight	424.74 amu
Space group	$R\bar{3}$ (No. 148 Hexagonal obverse setting)
Unit cell dimensions	$a = b = 9.0471(13)$, $c = 15.162(4)$ Å
Unit cell volume, V	1074.7(3) Å^3
Formula units per unit cell	3
Calculated density, D_x	1.97 g·cm^{-3}
Radiation, wavelength, λ	AgKα, 0.56083 Å
Temperature, T	100 K
Crystal size	$0.145 \times 0.175 \times 0.178$ mm
Diffractometer	*Enraf-Nonius CAD4*

Determination of unit cell

Number of reflections used	20
θ range (deg.)	15.98–20.20

Intensity data collection

Min. and max. sin $(\theta)/\lambda$	0.725, 1.203
Scan mode	$\omega/2\theta$
Scan angle ω (deg.)	$(0.90+0.45\tan\theta)+0.5(0.90+0.45\tan\theta)$
Scan speed (deg./min)	0.36 –1.17
Aperture horizontal (deg.)	$2.80+0.40\tan\theta$
Range of h, k, and l	$-18-18$, $0-18$, $-36-36$
Standard reflections	3
Standard reflection interval	Every 21600 s
Intensity decay	-12.3%
Internal R	0.0936
Number of collected reflections	6546
Number of unique reflections	2561
Number of observed $(I>3\sigma(I))$ reflections	1150

Absorption correction

Linear absorption coefficient [cm^{-1}]	4.090
Transmission factor range	0.9341–0.9470

Structure refinement

Minimization of	$\Sigma w(\Delta F)^2$
Number of refined parameters	35
Weighting scheme	$1.0513/(\sigma^2(F)+0.0005 |F|^2)$
Final R for observed reflections	0.0314
Final wR for observed reflections	0.0302
Final wR for all 2561 reflections	0.0504
Final $(\Delta/\sigma)_{max}$	0.00068
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$ (eÅ^{-3})	-0.198, 0.203

unexplained by this model, are $\Delta U_{ij} = U_{ij}(obs) - U_{ij}(L,T)$. They are shown graphically in *Fig. 1*. Three things are apparent: *1*) the residuals $\Delta U_{ij}(Si)$ are small compared to $\Delta U_{ij}(O)$. *2*) The residuals $\Delta U_{ij}(O)$ are very large perpendicular to the Si–O–Si plane, large along the bisector of the Si–O–Si angle, and negligible along the Si–O bonds. *3*) The residual displacements for the two crystallographically independent oxygens O(1) and O(2) are very similar and conform very closely to the molecular symmetry T_h. *Fig. 1* must be interpreted to indicate that $H_8Si_8O_{12}$ shows major deviations from rigid body behaviour (*i.e.* from $\Delta U_{ij} \sim O$ for all atoms). The internal motion of the molecule is due primarily to Si–O–Si bending and to cooperative torsion about the body diagonals of the Si_8 cube (which leaves the stiff angles OSiO undistorted). The corresponding vibrations have not been observed, presumably, because they are of very low frequency [13].

Outlook

We consider this work as a basis for a more detailed analysis of the (difference) electron density of $H_8Si_8O_{12}$ and a comparison with analogous studies of various modifications of SiO_2 [14][15] and $AlPO_4$ [16]. The highly accurate displacement parameters, resulting as a by-product in electron density work, may be used to complement the infrared and *Raman* data [13] in a normal coordinate analysis.

Experimental

Rhombic colourless crystals have been grown by evaporation from a cyclohexane soln. The crystals are fragile and hygroscopic and deteriorate within min, if left unprotected. A crystal specimen with as isotropic a shape as possible was choosen for the collection of intensities. The crystal was cooled with a commercial N_2 cryosystem [17] with a gas-temp. of 100 K. The intensity decay was monitored with three reflections, and amounted to about 12% at the point when the experiment had to be terminated due to an irrevocable failure of the cryosystem. Intensity data profiles representing half an *Ewald* sphere were collected in four shells of decreasing resolution starting at a θ value of 42.4° and stopping at 24.0. The data set was corrected for intensity decay, *Lorentz*, polarisation, and absorption effects by means of the program package XRAY72 [18]. The subsequent structural refinement was made by use of SHELX76 [19]. Due to the missing low angle part of the data set, the positions of the hydrogens could not be refined in this work. The two hydrogens present in the structure have been put in their calculated positions at a distance of 1.48 Å from their Si-atom according to electron-diffraction literature data. More details of the X-ray experiment as well as on the structure refinement are given in *Table 1*. The atomic scattering factors were taken from *International Tables for X-Ray Crystallography* [20]. The final atomic coordinates and thermal parameters are listed in *Table 2*. Selected distances and angles are given in *Table 3*.

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Table 2. *Fractional Atomic Coordinates and Displacement Parameters for $H_8Si_8O_{12}$*

Atom	x	y	z	B_{eq}
Si(1)	0	0	0.32225(2)	0.81(1)
Si(2)	0.31873(3)	0.20835(3)	0.44079(2)	0.79(1)
O(1)	0.19380(9)	0.11467(11)	0.35784(4)	1.27(1)
O(2)	0.31879(10)	0.06664(10)	0.50599(5)	1.26(1)
H(1)	0	0	0.2246	
H(2)	0.4943	0.3230	0.4086	

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.01153(g)	0.01153(9)	0.00758(10)	0	0	0.00577(9)
Si(2)	0.00796(8)	0.01002(9)	0.01092(8)	0.00073(6)	0.00123(5)	0.00354(6)
O(1)	0.01233(17)	0.01914(25)	0.01342(16)	−0.00253(15)	−0.00169(14)	0.00535(16)
O(2)	0.01465(19)	0.01433(19)	0.01821(20)	0.00525(16)	0.00139(16)	0.00663(16)

Table 3. *Intra molecular distances [Å] and angles [°] in $H_8Si_8O_{12}$*

Bond distances		Angles	
Si(1)–O(1)	1.6195(7)	O(1)–Si(1)–O(1)	109.48(4)
O(1)–Si(2)	1.6185(7)	O(1)–Si(2)–O(2)	109.66(5)
Si(2)–O(2)	1.6191(10)	O(1)–Si(2)–O(2)a)	109.45(5)
Si(2)–O(2)a)	1.6168(11)	O(2)–Si(2)–O(2)a)	109.41(5)
		Si(1)–O(1)–Si(2)	147.49(6)
		Si(2)–O(2)a)–Si(2)a)	147.60(7)

Nonbonding distances

Si(1)···Si(2)	3.1085(5)
Si(2)···Si(2)a)	3.1075(6)
Si(1)···Si(1)b) (body diagonal of Si_8 cube)	5.3901(15)
Si(2)···Si(2)b) (body diagonal of Si_8 cube)	5.3809(7)
O(1)···O(2)c) (across face of Si_8 cube)	3.5752(13)
O(2)···O(1)d) (across face of Si_8 cube)	3.8826(11)

a) $x-y, x, -z+1$

b) $-x, -y, -z+1$

c) $y, -x+y, -z+1$

d) $-x+y, -x, z$

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