

- Strouse, C. E. (1982). *UCLA Crystallographic Package*. Univ. of California, Los Angeles, USA.
- Stucky, G. D., Phillips, M. L. F. & Gier, T. E. (1989). *Chem. Mater.* **1**, 492–509.
- Watkin, D. J., Carruthers J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

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Octahydridosilasesquioxane Determined by Neutron Diffraction

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Abstract

The structure of H₈Si₈O₁₂ has been determined by neutron diffraction at 29 K and compared with X-ray determinations at 9.5 and 100 K. There are only small geometrical differences, but it can be concluded that the deviation from the ideal molecular symmetry, *O_h* (*m $\bar{3}m$*), increases with decreasing temperature and that the large vibration amplitudes for the O atoms observed in the X-ray analyses are also present in the neutron structure. Static disorder of the O atoms is excluded. The molecular deformation is caused by the rigid HSiO₃ tetrahedra performing a cooperative torsional movement inducing vibrational deformations of the flexible Si—O—Si angles.

Comment

This investigation has been carried out in order to locate the atomic positions, particularly those of the H atoms, and to try to establish whether static disorder of the O atoms may be present in the crystal structure of H₈Si₈O₁₂, as shown in Fig. 1. The compound was prepared as described by Agaskar (1991). The X-ray experiments revealed notably large anisotropic mean-square displacements of the O atoms, principally in a direction orthogonal to the Si—O—Si plane, as well as along the bisector of the Si—O—Si angle. The structural information gained from this neutron diffraction experiment, including the anisotropic atomic displacement parameters for the H atoms, is of use in a current study of the electron-density deformation of this compound. For that study, X-ray data have been collected at 100 K (Auf der Heyde, Bürgi, Bürgy & Törnroos, 1991) and at 9.5 K (Törnroos, Schwarzenbach, Delley & Larsen, 1994).

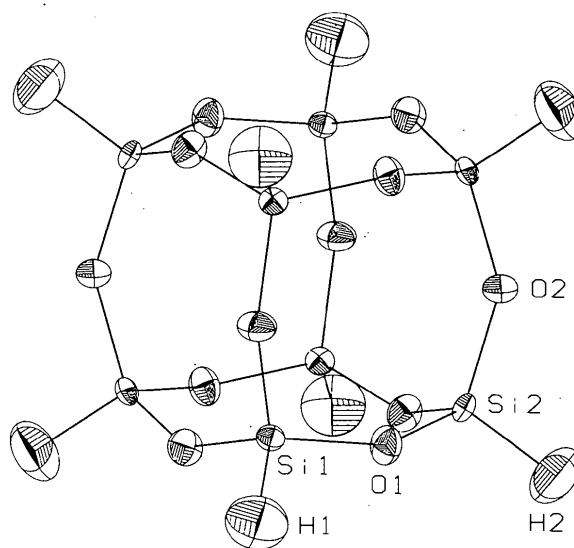


Fig. 1. Structure of the title compound displaying mean-square displacement ellipsoids at 90% probability.

The temperature in the neutron diffraction experiment, 29 K, was the minimum temperature attainable with the cryo-instrument at the site.

The crystallographic symmetry of the H₈Si₈O₁₂ structure is *C_{3i}* ($\bar{3}$), but the molecule has non-crystallographic symmetry of *T_h* (*m $\bar{3}$*). It may, however, ideally be of *O_h* symmetry. The reasons for the departure from the *O_h* symmetry are intriguing, but the soft Si—O—Si angles seem crucial in this context as they provide flexible connections between the relatively rigid HSiO₃ tetrahedra. The geometrical parameters best describing this deviation from the ideal *O_h* symmetry are the O(1,5) non-bonded distances (across faces of the Si₈ cube) and the two Si...Si body diagonals in the Si₈ cube. These are given for all three determinations in Table 4. The largest differences in the three experiments occur at the O(1,5) non-bonded distances. For these ideally equal distances, the difference increases consistently with decreasing temperature. For the Si...Si body diagonals this tendency is insubstantial considering the e.s.d.'s. The distances of the Si...Si cube edge are the same to within experimental error for the X-ray data, but differ significantly towards larger values in the neutron structure determination. We thus note that the Si...Si and also possibly the Si—O

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Si(1)	0	0	0.32152 (18)	0.0049 (5)
Si(2)	0.31958 (19)	0.20905 (19)	0.44037 (10)	0.0048 (3)
O(1)	0.19471 (14)	0.11230 (15)	0.35740 (8)	0.0083 (3)
O(2)	0.31997 (15)	0.06903 (14)	0.50720 (8)	0.0080 (3)
H(1)	0	0	0.22521 (25)	0.0222 (8)
H(2)	0.49339 (26)	0.32175 (27)	0.40885 (16)	0.0218 (5)

Table 2. Anisotropic displacement parameters (\AA^2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hkab^*U_{12}]$.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Si(1)	0.00565 (78)	0.00565	0.00329 (121)	0	0	0.00282
Si(2)	0.00290 (67)	0.00460 (67)	0.00569 (71)	0.00021 (54)	0.00065 (58)	0.00094 (57)
O(1)	0.00623 (53)	0.00909 (55)	0.00809 (54)	-0.00148 (46)	-0.00128 (46)	0.00266 (47)
O(2)	0.00812 (55)	0.00687 (53)	0.00855 (51)	0.00243 (43)	0.00065 (45)	0.00339 (46)
H(1)	0.02728 (123)	0.02728	0.01216 (166)	0	0	0.01364
H(2)	0.01378 (103)	0.02100 (105)	0.02451 (108)	0.00374 (99)	0.00525 (91)	0.00417 (89)

Table 3. Geometric parameters (\AA , $^\circ$)

Si(1)—O(1)	1.626 (1)	Si(2)—O(2 ¹)	1.628 (2)
Si(2)—O(1)	1.623 (2)	Si(1)—H(1)	1.459 (5)
Si(2)—O(2)	1.624 (2)	Si(2)—H(2)	1.463 (3)
Si(1)—O(1)—Si(2)	147.25 (13)	O(2)—Si(2)—O(2 ¹)	109.14 (10)
Si(2)—O(2)—Si(2 ¹)	147.45 (13)	H(1)—Si(1)—O(1)	109.53 (10)
O(1)—Si(1)—O(1)	109.41 (10)	H(2)—Si(2)—O(1)	109.86 (14)
O(1)—Si(2)—O(2)	109.53 (10)	H(2)—Si(2)—O(2)	109.07 (14)
O(1)—Si(2)—O(2 ¹)	109.45 (10)	H(2)—Si(2)—O(2)	109.77 (14)

Symmetry codes: (i) $x - y, x, 1 - z$; (ii) $y, y - x, 1 - z$.

Table 4. Non-bonding distances (\AA)

	Neutron 29 K	X-ray 9.5 K	X-ray 100 K
Si(1)···Si(1 ^{III}) (body diagonal of Si ₈ cube)	5.408 (5)	5.396 (1)	5.390 (2)
Si(2)···Si(2 ^{III}) (body diagonal of Si ₈ cube)	5.401 (3)	5.383 (1)	5.381 (1)
O(1)···O(2 ^{II}) (across face of Si ₈ cube)	3.546 (2)	3.531 (1)	3.575 (1)
O(2)···O(1 ^{IV}) (across face of Si ₈ cube)	3.927 (2)	3.923 (1)	3.883 (1)
Si(1)···Si(2) (Si ₈ cube edge)	3.117 (2)	3.110 (1)	3.109 (1)
Si(2)···Si(2 ¹) (Si ₈ cube edge)	3.121 (2)	3.109 (1)	3.108 (1)

Symmetry codes: (i) $x - y, x, 1 - z$; (ii) $y, y - x, 1 - z$; (iii) $-x, -y, 1 - z$; (iv) $y - x, -x, z$.

distances (see above) are systematically larger in the neutron structure. Nevertheless, we eschew an attempt to explain the reasons for this observation. In all, the geometric data indicate that the deviation from the ideal molecular symmetry increases with decreasing temperature and that the nature of the deformation may be explained by a cooperative torsional displacement of the rigid HSiO₃ tetrahedra about the body diagonals of the Si₈ cube, preserving the positions of the Si atoms but displacing the three corners of the base of the tetrahedra. Although inferior in resolution to the X-ray experiments, it is concluded from the neutron experiment that no evidence of a static disorder of the O atoms, *i.e.* no split positions, can be detected.

An analysis of the optimal superposition by non-iterative least-squares minimization (Diamond, 1988) of the 9.5 K X-ray structure and the 29 K neutron structure, omitting the H atoms, gives an r.m.s. deviation of 0.008 \AA . The average Si—O distance reflects the only significant difference between the average bonding distances and angles for the neutron structure and the 9.5 K X-ray data. The average angles are essentially the same to within experimental error. [Average Si—O distance:

1.626 (2) (neutron, 29 K), 1.621 (1) \AA (X-ray, 9.5 K). Average O—Si—O angle: 109.39 (9) (neutron, 29 K), 109.43 (2)° (X-ray, 9.5 K). Average Si—O—Si angle: 147.35 (12) (neutron, 29 K), 147.18 (2)° (X-ray, 9.5 K).] The mean Si—H distance is 1.461 (5) \AA and is, as expected, significantly longer than the mean distance determined from, *e.g.* the 9.5 K X-ray data [1.36 (2) \AA].

The anisotropic atomic displacement parameters for Si and O atoms are in fair agreement with those of the 9.5 K X-ray experiment. For this reason it seemed meaningful to analyse these parameters, as determined from the neutron data, by means of rigid-body methods (Trueblood, 1985). Based on the translation, libration and screw coupling tensors, **T**, **L** and **S**, derived from $U(\text{Si})$, the $U(\text{O})$ values were calculated. The result is displayed in Fig. 2 and verifies that: (a) the motion of the Si atoms may be described well by a rigid body model, (b) the O atoms, with large residual atomic motion, $U(\text{O}_{\text{obs}}) - U(\text{O}_{\text{model}})$, deviate substantially from such a model, and (c) that this motion is probably the result of intramolecular vibrations. The large residual intramolecular vibrations of the O atoms out of the Si—O—Si plane and along the bisector of this angle are in agreement with those determined from the X-ray data.

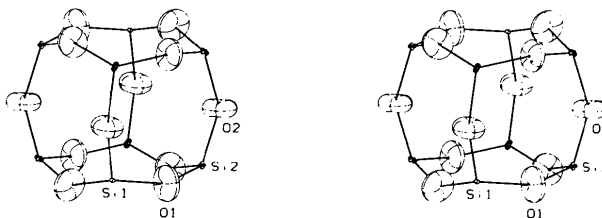


Fig. 2. Stereoscopic view of difference r.m.s. deviation surfaces for the title compound at 29 K. Solid outlines: positive differences; dotted outlines: imaginary differences. The probability level of the deviation surfaces is 50% multiplied by a magnification factor of 4.0 for increased clarity.

Experimental

Crystal data

H₈O₁₂Si₈
 $M_r = 424.74$
 Trigonal
 $R\bar{3}$
 $a = 9.053 (1) \text{\AA}$
 $c = 15.149 (1) \text{\AA}$

Neutron radiation
 $\lambda = 1.215 \text{\AA}$
 Cell parameters from 12 reflections
 $\theta = 20.13\text{--}33.25^\circ$
 $\mu = 0.088 \text{ mm}^{-1}$

$V = 1075.2 (2) \text{ \AA}^3$
 $Z = 3$
 $D_x = 1.968 \text{ Mg m}^{-3}$

$T = 29 \pm 0.5 \text{ K}$
 Rhombic
 $1.68 \times 1.53 \times 1.23 \text{ mm}$
 Colourless

Data collection

Huber four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical
 $T_{\min} = 0.862$, $T_{\max} = 0.903$
 790 measured reflections
 569 independent reflections

364 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.0552$
 $\theta_{\max} = 53.38^\circ$
 $h = -10 \rightarrow 9$
 $k = -10 \rightarrow 5$
 $l = -19 \rightarrow 19$
 Intensity variation of standard reflections: $< \pm 1$

Refinement

Refinement on F^2
 $R(F) = 0.0310$
 $wR(F^2) = 0.0526$
 $S = 1.122$
 364 reflections
 44 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 0.01P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 Extinction correction: SHELXL92 (Sheldrick, 1992)
 Extinction coefficient: 1.31 (6)
 Nuclear coherent scattering lengths from Koester, Rauch, Herkens & Schröder (1981)

Data collection was performed at the Studsvik Neutron Research Laboratory in Studsvik, Sweden, using the R2 reactor and a Huber four-circle diffractometer, equipped with a Cryogenics closed-circuit He₂-refrigerator cooling device. Reflections were collected with 40 steps, at an ω -step size of 0.1° , up to $\sin\theta/\lambda = 0.5290 \text{ \AA}^{-1}$ and with 50 steps above that resolution. The effective absorption coefficient, $\mu = 0.088 \text{ mm}^{-1}$, was determined experimentally. SHELXL92 (Sheldrick, 1992) was used to refine the structure. Neutron scattering lengths, b (10^{-12} cm), for the structure-factor calculation were H = -0.3741 , Si = 0.4149 and O = 0.5805 . Molecular graphics were prepared using PEANUT (Hummel, Hauser & Bürgi, 1990).

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A list of structure factors has been deposited with the IUCr (Reference: CR1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Agaskar, P. A. (1991). *Inorg. Chem.* **30**, 2702–2708.
 Auf der Heyde, T. P. E., Bürgi, H.-B., Bürgy, H. & Törnroos, K. W. (1991). *Chimia*, **45**, 38–40.
 Diamond, R. (1988). *Acta Cryst.* **A44**, 211–216.

- Hummel, W., Hauser, J. & Bürgi, H.-B. (1990). *J. Mol. Graph.* **8**, 214–220.
 Koester, L., Rauch, H., Herkens, M. & Schröder, K. (1981). KFA-Report, Jül-1755.
 Sheldrick, G. M. (1992). SHELXL92. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany.
 Törnroos, K. W., Schwarzenbach, D., Delley, B. & Larsen, F. K. (1994). *Acta Cryst.* In preparation.
 Trueblood, K. N. (1985). THMA11. Thermal Motion Analysis. Univ. of California, Los Angeles, USA.

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Cadmium Iron(III) Iron(II) Diphosphate

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Abstract

$\text{Cd}_{2.06}\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_{0.44}(\text{P}_2\text{O}_7)_2$ crystallizes in the orthorhombic space group $C222_1$ with Fe^{III} in a distorted octahedral environment [average Fe—O 2.05 (1) Å] and Fe^{II} sharing sites with Cd atoms in two sites of sixfold coordination [average Cd/Fe—O 2.20 (1) Å]. Two further Cd atoms show sixfold coordination with average Cd—O 2.31 (1) Å.

Comment

Mixed-valence phosphates such as $\text{Fe}_7(\text{PO}_4)_6$ and $\text{Cr}_7(\text{PO}_4)_6$ have been reported in the literature (Gorbunov *et al.*, 1980; Glaum, 1993). Planes of bent ($-\text{M}^{\text{III}}-\text{M}^{\text{III}}-\text{M}^{\text{II}}-$) chains are found in the solid-state structures.

A number of iron diphosphates are known in the solid state. The stoichiometries of the compounds $\text{Fe}_2^{\text{II}}\text{P}_2\text{O}_7$, $\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}_{0.44}\text{Cd}_{2.06}(\text{P}_2\text{O}_7)_2$, $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{II}}(\text{P}_2\text{O}_7)_4$ and $\text{Fe}_2^{\text{II}}\text{Fe}^{\text{II}}(\text{P}_2\text{O}_7)_2$, when expressed as $\text{Fe}_2^{\text{II}}\text{P}_2\text{O}_7$, $\text{Fe}_{0.5}^{\text{III}}(\text{Fe}^{\text{II}}, \text{Cd})_{1.25}\text{P}_2\text{O}_7$ and $\text{Fe}^{\text{III}}\text{Fe}_{0.5}^{\text{II}}\text{P}_2\text{O}_7$, respectively, may be seen to form a series of increasing $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio. The solid-state structures of the series show a progression from planes of metal atoms with hexagonal disposition when the Fe^{II} content is high ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratio low) to isolated and linear metal trimers when the Fe^{III} content is higher. The single-crystal structure of $\text{Fe}_4^{\text{III}}(\text{P}_2\text{O}_7)_3$ is unreported.