X-RAY STRUCTURAL STUDY OF SILASESQUIOXANES. THE CRYSTAL STRUCTURE OF OCTA(ALLYLSILASESQUIOXANE)

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In the series of organosilasesquioxanes $[RSiO_{1.5}]_8$, the crystal structure of the compound with R = allyl has been determined. It has been shown that increase in the length of the hydrocarbon group has no influence on the structure of the silicon–oxygen core: The average value of the length of the Si–O bond, 1.63 Å, is the same as that with the substituent R = CH_3, C_6H_5, and vinyl.

X-ray structural studies of octamethylsilasesquioxane $[CH_3SiO_{1.5}]_8$, octasilasesquioxane $[HSiO_{1.5}]_8$, octaphenylsilasesquioxane $[C_6H_5SiO_{1.5}]_8$, and octavinylsilasesquioxane $[C_2H_3SiO_{1.5}]_8$ [1-4] did not reveal any differences in the structures of the silicon–oxygen cores (frameworks) of the molecules, greater than the uncertainty of the determination. It has been shown, however, that with increase in the length of the hydrocarbon group there is a change in various physicochemical properties of the compounds (an increase in solubility, a decrease in the melting point, a decrease in density, etc.), which in turn must be due to structural characteristics; in fact, disorder of alkyl groups [1, 4], an increase in the thermal vibrations of the atoms towards the end of the hydrocarbon chain of the substituent, and a decrease in the interactions between the molecules in the crystal have been observed.

The crystal structure of octa(allylsilasesquioxane) $[C_3H_5SiO_{1.5}]_8$ was determined in order to investigate the influence of a new type of substituent on the structure of the silicon-oxygen core in the molecules of organosilasesquioxanes $[RSiO_{1.5}]_8$ and also on the packing of the molecules in the crystals.

EXPERIMENTAL

The transparent colorless crystals are triclinic: $a = 8.95(3)$, $b = 10.36(4)$, $c = 10.50(3)$ Å, $\alpha = 93.6(2)$, $\beta = 91.3(2)$, $\gamma = 94.7(2)°$, $V = 962(6)$ Å^3, $d_{calc} = 1.28$ g/cm^3, $\mu MoK_\alpha = 3.3$ cm^{-1}, Z = 1 $C_{24}H_{40}Si_8O_{12}$, space group $P\bar{1}$.

Single crystals were obtained by recrystallizing from a mixture of acetone and chloroform the crystalline product obtained by the hydrolysis of allyltrichlorosilane, previously purified by sublimation.

The large errors obtained in the refinement of the cell parameters on a "Syntex $P2_1$" automatic diffractometer are apparently due to the dimensions of the crystal (0.15 × 0.35 × 1.25 mm), which lie beyond the optimum range; it was not possible to decrease the length of the crystal, because of its high sensitivity to the slightest strain and because of the restriction in the selection of a specimen for the structural study. The change in the quality of the crystal during the recording also influenced the final result – the high values of the standard deviations of the interatomic distances and valence angles, and the fairly high final R-factor (0.14).

The intensities of 2615 reflections were measured by the standard method (MoK_α radiation, graphite monochromator, $\theta/2\theta$ scanning at a variable rate with $V_{min} = 5$ deg/min, $2\theta_{max} = 45°$). The rejection of the weak reflections ($< 2\sigma$) and averaging of the equivalent reflections left 1934 reflections, which were used to construct the three-dimensional Patterson function; analysis of the positions of the peaks of this function using crystal-chemical data on the structure of the framework located the silicon and oxygen atoms of the molecule. The substituent carbon atoms joined to the silicon atoms were also found (R = 0.274).

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TABLE 1. Coordinates ($\times 10^3$) and Isotropic Thermal Parameters of the Atoms Other than Hydrogen

Atom	*x*	*y*	*z*	B_{iso}, Å^2	Atom	*x*	*y*	*z*	B_{iso}, Å^2
Si(1)	—232	152	—008	4,84	C(2)	191	412	—101	5,95
Si(2)	101	242	—055	4,43	C(3)	342	158	294	6,67
Si(3)	208	107	180	5,46	C(4)	—206	017	388	6,52
Si(4)	—133	016	228	5,16	C(5)	—393	293	—122	12,27
O(1)	181	210	066	5,48	C(6)	131	447	—234	10,98
O(2)	264	—034	107	7,71	C(7)	257	285	358	13,83
O(3)	218	—096	—139	5,36	C(8)	—228	157	450	10,98
O(4)	141	136	—160	5,98	C(9)	—481	288	—195	15,0
O(5)	042	069	235	6,17	C(10)	016	521	—286	17,9
O(6)	081	—234	045	4,61	C(11)	376	344	416	19,4
C(1)	—401	238	—020	4,90	C(12)	—151	199	550	15,6

TABLE 2. Interatomic Distances d, Å*

Bond	*d*	Bond	*d*	Bond	*d*
Si(1)—Si(4)	3,07	Si(1)—O(2′)	1,56	Si(3)—C(3)	1,71
Si(1)—Si(2)	3,11	Si(1)—O(6′)	1,60	Si(1)—C(1)	1,81
Si(1)—Si(3′)	3,18	Si(1)—O(3′)	1,69	Si(4)—C(4)	1,82
Si(2)—Si(3)	3,09	Si(2)—O(1)	1,51	Si(2)—C(2)	1,97
Si(2)—Si(4′)	3,17	Si(2)—O(6′)	1,64	Average	1,83
Si(3)—Si(4)	3,18	Si(2)—O(4)	1,67	C(1)—C(5)	1,24
Average	3,13	Si(3)—O(5)	1,63	C(2)—C(6)	1,57
Si(1)—Si(1′)	4,43	Si(3)—O(1)	1,68	C(4)—C(8)	1,58
Si(1)—Si(3)	4,44	Si(3)—O(2)	1,73	C(3)—C(7)	1,67
Si(1)—Si(4′)	4,45	Si(4)—O(3)	1,52	Average	1,51
Si(2)—Si(4)	4,36	Si(4)—O(5)	1,61	C(5)—C(9)	1,08
Si(2)—Si(1′)	4,43	Si(4)—O(4′)	1,68	C(8)—C(12)	1,27
Si(2)—Si(3′)	4,48	Average	1,63	C(7)—C(11)	1,30
Si(3)—Si(4′)	4,41			C(6)—C(10)	1,44
Average	4,43			Average C=C	1,27

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*The standard deviations in the interatomic distances do not exceed 0.02 for Si–Si and 0.03 for Si–O and Si–C, and vary from 0.03 to 0.06 Å for the C–C bonds. There are two anomalously short distances C(1)–C(5) and C(5)–C(9) and an elongated distance C(6)–C(10), corresponding to a C=C double bond. These distortions are apparently due to the not very high quality of the experimental material. With allowance for the standard deviations, crystal-chemical positioning of these atoms is possible, but we considered it necessary to give the results obtained after the refinement by the method of least squares (the distance C(5)–C(9) between the electron density peaks is 1.15 Å).

The second and third carbon atoms in the allyl groups were found from Fourier and difference Fourier syntheses, constructed from the part of the molecule found. The form of the peaks and the heights of the maxima on the maps of the difference Fourier synthesis confirm that the thermal vibrations of the carbon atoms increase towards the end of the hydrocarbon chain.

The refinement of the structure was carried out by the method of least squares using the program from the set "Syntex-XTL." The coordinates of the atoms do not exceed 0.001 for Si and 0.003 for O, and vary from 0.004 to 0.009 for the C atoms, depending on the distance between the carbon atom of the allyl chain and the silicon-oxygen core of the molecule.

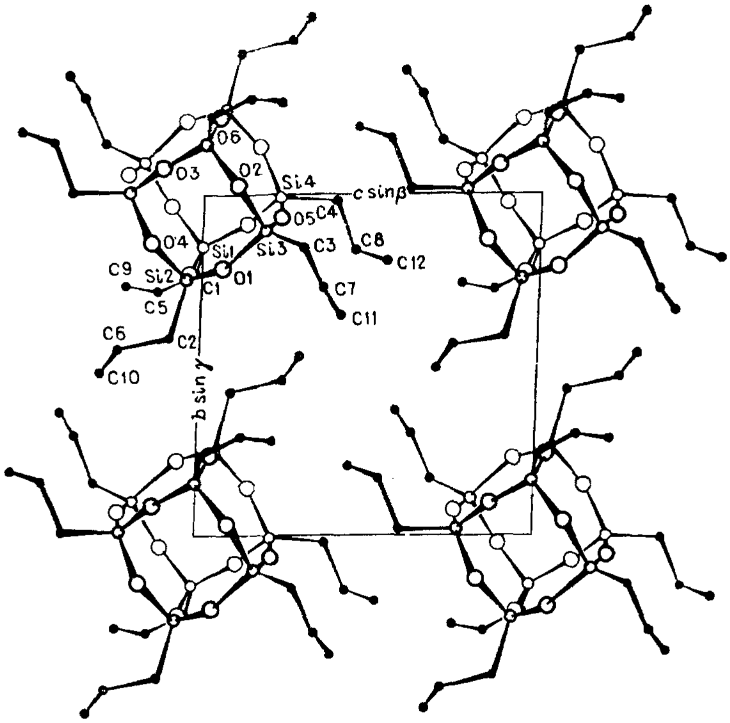

Fig. 1. Packing of the molecules in the crystal.

TABLE 3. Valence Angles ω, deg*

Angle	ω	Angle	ω
O(2′)Si(1)O(3′)	108,4	O(2′)Si(1)C(1)	103,1
O(2′)Si(1)O(6′)	108,8	O(3′)Si(1)C(1)	109,6
O(3′)Si(1)O(6′)	111,9	O(6)Si(1)C(1)	114,4
O(1)Si(2)O(4)	105,4	O(1)Si(2)C(2)	106,7
O(1)Si(2)O(6′)	113,4	O(4)Si(2)C(2)	108,3
O(4)Si(2)O(6′)	108,6	O(6′)Si(2)C(2)	114,0
O(1)Si(3)O(2)	107,4	O(1)Si(3)C(3)	116,2
O(1)Si(3)O(5)	105,6	O(2)Si(3)C(3)	106,4
O(2)Si(3)O(5)	105,9	O(5)Si(3)C(3)	114,6
O(5)Si(4)O(3′)	109,6	O(5)Si(4)C(4)	109,2
O(5)Si(4)O(4′)	106,8	O(3′)Si(4)C(4)	113,2
O(3)Si(4)O(4′)	107,1	O(4′)Si(4)C(4)	110,7
Average	108,2	Average	110,5
Si(2)O(1)Si(3)	150,2	Si(1)C(1)C(5)	106,5
Si(3)O(2)Si(1′)	149,5	Si(2)C(2)C(6)	111,4
Si(1′)O(3)Si(4′)	146,8	Si(3)C(3)C(7)	97,4
Si(2)O(4)Si(4′)	153,4	Si(4)C(4)C(8)	113,9
Si(3)O(5)Si(4)	156,3	Average	107,3
Si(1′)O(6)Si(2′)	147,7	C(1)C(5)C(9)	117
Average	150,7	C(2)C(6)C(10)	113
		C(3′)C(7)C(11)	107
		C(4′)C(8)C(12)	111
		Average	113

*The primes denote the atoms related by symmetry to the basis atoms.

STRUCTURE OF THE MOLECULE AND CRYSTAL OF OCTA(ALLYLSILASESQUIOXANE) (ALLYL-T_8)

The molecule of allyl-T_8 $[C_3H_5SiO_{1.5}]_8$ is centrosymmetric. Its structure is shown in Fig. 1, which gives the packing of the molecules in the crystal. The bond lengths and valence angles are given in Tables 2 and 3 respectively.

The three tetrasiloxane rings form three symmetrically independent faces of a "cube" (the deviation from 90° for the angles between the atoms making up the "cube" does not exceed 1.5°). In each ring, the silicon and oxygen atoms are situated in close, almost parallel, planes, the former displaced closer to the center of the "cube" and the latter displaced farther from it. The deviations of the silicon and oxygen atoms from the average plane of the ring in these three rings are ±0.16, ±0.14, and ±0.14 Å, and the oxygen atoms are displaced from the planes drawn through the silicon atoms of "their own" rings by 0.31, −0.28, and −0.27 Å, respectively.

The average value of the valence angle SiOSi is 150.7°. This is greater than in siloxanes with D_4 rings [3], and is due to the increase in the strength of the $p_\pi - d_\pi$ interaction in the molecules of organosilasesquioxanes, compared with siloxanes. The average value of the length of the Si−O bond, 1.63 Å, confirms that the length of this bond is independent of the nature of the organic substituent.

The Si−C distance varies in the range 1.71-1.97 Å, whereas its usual scatter is 1.81-1.85 Å.

The scatter in the Si−Si distances and the agreement between the average value and published data indicate that the parameters of the silasesquioxane framework are independent of the nature of the substituent and of the conditions of packing.

The molecules are joined in the crystal by van der Waals forces.

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CRYSTAL STRUCTURE OF MONOAQUOTRIACETATOSAMARIUM(III) − MONOTHIOUREA

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A complete crystal-structural study of the complex $[Sm(C_2H_3O_2)_3(H_2O)] \cdot SC(NH_2)_2$ has been carried out. The Sm atoms are situated in nine-apex figures formed by the oxygen atoms of the acetate groups and the water molecule (average Sm−O 2.46 Å) and joined to one another by shared O−O edges to form infinite ribbons. The structure as a whole is of the ribbon-isolated unit type and consists of ribbons of Sm polyhedra and thiourea molecules with van der Waals interactions between them. The thiourea molecules and the acetate groups are practically planar; the average distances are O−C 1.27, C−C 1.49, C−N 1.32 and C−S 1.71 Å. A comparison has been carried out with the previously studied structure of a complex compound from the first (La−Pr) isostructural group.

The crystal structure of monoaquotriacetatosamarium(III)−monothiourea $[Sm(C_2H_3O_2)_3(H_2O)] \cdot SC(NH_2)_2$, which is a representative of the second isostructural group (Sm−Lu) of the series of compounds with the general formula $Ln(C_2H_3O_2)_3 \cdot SC(NH_2)_2 \cdot xH_2O$ [1], has been determined in the course of systematic studies of the complex compounds formed by the rare earth element (REE) carboxylates with urea and thiourea. We previously determined the structure of diaquotriacetatolanthanum(III)−monothiourea [2], a compound from the first isostructural group (La−Pr). The aim of the present work was to determine the mode of coordination of the ligands to the metal and the role of the thiourea and water molecules in the structure of the crystal, and also to compare the crystal structures of compounds of this series from different isostructural groups.

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