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Phase Transition in the Crystal of Tetramethoxysilane Studied by In Situ X-Ray Diffraction Analysis

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Abstract—Single crystals of tetramethoxysilane (**I**), which is liquid at room temperature, are grown using an original setup for in situ crystallization. The X-ray diffraction analysis of compound **I** at two temperatures (CIF files CCDC nos. 2006156 and 2006157 for 150 and 200 K, respectively) shows the phase transition accompanied by the disordering of the methoxy groups. The setup developed that is different from commercial analogs by an unusually low cost and a possibility of modifying all components provides wide opportunities for crystal growth directly on a diffractometer for structure determination of various organoelement compounds and, possibly, metal complexes in the liquid or even gaseous state.

Keywords: viscous liquids, zone smelting, organosilanes, X-ray diffraction analysis, crystal growth, phase transition, organoelement compounds, in situ crystallization

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INTRODUCTION

X-ray diffraction analysis (XRD) is the main method for the determination of structures of new chemical compounds if their single crystals of appropriate quality can be grown [1]. Unfortunately, this requirement usually cannot be fulfilled for compounds being liquid at room temperature. Since their molecular mobility is high and predetermines low barriers for rotation arout the bonds and deformation of the bond angles [2] and no strong intermolecular interactions are observed in these compounds, they crystallize at low temperatures to form crystal packings with the partial disordering of individual molecular fragments [3–5]. As a result, the XRD data obtained for these compounds suffer from experimental errors, primarily because of a low completeness of the datasets and a low accuracy of the geometric parameters [3, 4].

The published examples for the XRD studies of the substances, which are liquids at room temperature [5–8], are devoted, as a rule, to organic compounds. This can be due to difficulties [9] associated with the decontamination of organoelement compounds and metal complexes from impurities, their sensitivity to air moisture and oxygen, and a higher viscosity noticeably impeding crystallization. Simple organosilanes and siloxanes form one of classes of such compounds [10]. They are widely used in industry and medicine as inert thickeners, water-repellents, and lubricants [10]. Unfortunately, they are viscous liquids at room temperature [10], which prevents solving their structures by XRD and, therefore, determining a wide range of physicochemical properties [11].

This problem can be solved by growing crystals of such compounds directly on an X-ray diffractometer [4], which assumes cooling–heating using special setups for zone smelting [5, 12]. Starting from the pioneer studies of the in situ crystallization of benzene and cyclohexane [13, 14], a similar approach made it possible to determine the crystal structures of the liquids [4], monitor the reaction course [5], and study the intrinsic crystallization process [12]. For this purpose, the liquid compound under study was placed in a glass capillary, which was mounted on a special goniometric head equipped with a guide stage and placed directly on an X-ray diffractometer [4].

We have previously carried out successfully the in situ crystallization of liquid dimethyldimethoxysilane [15] using the developed by us original setup for in situ crystal growth, which differs from its commercial analog OHCD (Optical Heating and Crystallization Device) [16] by a significantly lower cost and a possibility of the operative modification of all components.

The single crystals of tetramethoxysilane (**I**) were obtained similarly in this work. The structure of compound **I** [17] was determined by XRD at two different temperatures (150 and 200 K), which allowed us to observe the phase transition accompanied by the disordering of the methoxy groups in the crystal.

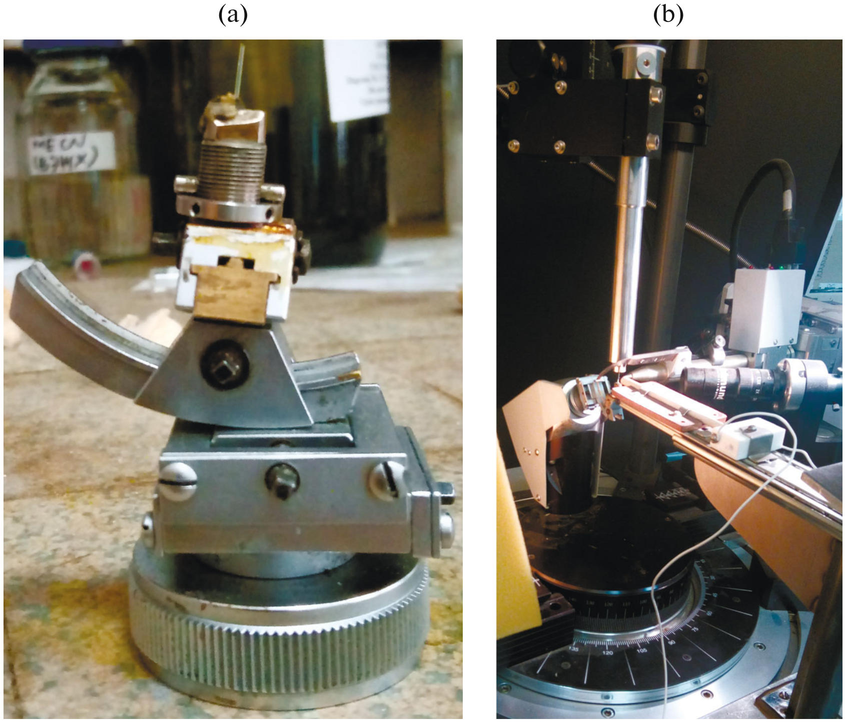
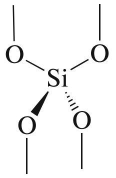


Fig. 1. (a) Goniometric head and (b) its installation on an X-ray diffractometer.



(I)

EXPERIMENTAL

Liquid tetramethoxysilane (Sigma-Aldrich) was used as received. The corresponding single crystals, whose quality was suitable for subsequent XRD, were grown by zone smelting using the setup developed by us for in situ crystallization (Fig. 1). The setup consists of a goniometric head for an X-ray diffractometer constructed of available components and a removable guide stage. This construction feature of the goniometric setup (Fig. 1) makes it possible to orient the capillary filled with the studied sample at various angles toward the stage and nitrogen flow coming from a nozzle of a low-temperature device. This allows one to achieve a substantial increase in the scanning angle range during the XRD experiment, which is necessary for the collection of the corresponding data with high redundancy.

After the single crystal of the studied substance was grown by zone smelting in a capillary placed on the goniometric head, the operator on a personal computer inputs all necessary parameters into a specially developed program that processes the data obtained and sends them to the Arduino microcontroller according to the Bluetooth protocol of wireless personal networks. The Arduino microcontroller generates control pulses reporting the driver of the step engine of the setup at what angle, with what velocity, and in what direction the motor should be rotated. The driver controls the motor following the obtained instructions. This sequence of data transmission and the absence of dependences between the components make it possible to distantly control the developed setup for in situ crystal growth and also to replace its components "on-the-fly" without risks for troubles to appear.

The XRD of the single crystal of compound **I** was carried out at 150 and 200 K on a Bruker APEX2 CCD diffractometer (MoK_α radiation, graphite monochromator, ω scan). The structure of compound **I** was solved using the ShelXT program [18] and refined by full-matrix least squares using the Olex2 program [19] in the anisotropic approximation against F^2_{hkl}. The positions of the hydrogen atoms were calculated geometrically and refined in the isotropic approximation by the riding model. Selected crystallographic data and structure refinement parameters for compound **I** are presented in Table 1.

The structural parameters for compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2006156 and 2006157 at

Table 1. Selected crystallographic data and structure refinement parameters for compound **I** at 150 and 200 K

Parameter	Value	
Temperature	150 K	200 K
Empirical formula	$C_4H_{12}O_4Si$	$C_4H_{12}O_4Si$
FW	152.23	152.23
T, K	150	200
Crystal system	Monoclinic	Monoclinic
Space group	$P2/n$	$C2/c$
Z	4	4
a, Å	11.4881(12)	13.039(3)
b, Å	5.8655(6)	5.9999(18)
c, Å	12.7824(12)	11.852(3)
α, deg	90	90
β, deg	116.249(3)	116.476(9)
γ, deg	90	90
V, Å^3	772.50(14)	830.0(4)
ρ_{calc}, g cm^{-3}	1.309	1.218
μ, cm^{-1}	2.56	2.38
F(000)	328	328
$2\theta_{max}$, deg	52	52
Number of measured reflections	4662	2358
Number of independent reflections (R_{int})	1613	787
Number of reflections with $I > 2\sigma(I)$	1438	673
Number of refined parameters	88	44
R_1, wR_2 ($I > 2\sigma(I)$)	0.0333, 0.0885	0.1700, 0.5017
R_1, wR_2 (all data)	0.0371, 0.0912	0.1766, 0.5147
GOOF	1.072	2.511
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.276/–0.262	0.788/–0.781

150 and 200 K, respectively; http:// www.ccdc.cam. ac.uk/).

RESULTS AND DISCUSSION

We succeeded to grow a single crystal of an appropriate quality for commercially available (Sigma-Aldrich) tetramethoxysilane **I**, which is a viscous liquid at room temperature, only after several attempts of in situ crystallization in a glassy capillary by zone melting in a range of 150–200 K. The key parameter was the cooling–heating rate of the capillary, which was 60 K/h in the optimum case. The subsequent XRD of this single crystal unambiguously confirmed the structure of tetramethoxysilane **I** (Fig. 2), while the earlier attempts of structure determination were unsuccessful [17]. Moreover, the quality of the single crystal grown on our setup for in situ crystallization made it possible to obtain the XRD data at two different temperatures: 150 and 200 K. The observed difference in the unit cell parameters at 150 and 200 K (Table 1) indicates the phase transition occurring in the corresponding temperature range. Although tetramethoxysilane **I** forms single crystals in all cases, at 150 K the single crystals belong to the space group $P2/n$, whereas at 200 K they belong to the space group $C2/c$.

According to the obtained XRD data, at 150 K the unit cell contains two symmetrically independent molecules of tetramethoxysilane **I** (Fig. 2) occupying the special position in the crystal: the 2-fold symmetry axis passing through the silicon atoms and the middle of the O(1)...O(1) and O(2)...O(2) lines. Note that dimethyldimethoxysilane studied by us earlier [15], which is also liquid at room temperature, crystallizes in the space group $C2/c$ with the molecule on the crystallographic 2-fold symmetry axis. In both cases, the silicon atom exists in the tetrahedral environment (Table 2), which undergoes an insignificant distortion on going from compound **I** to dimethyldimethoxy-

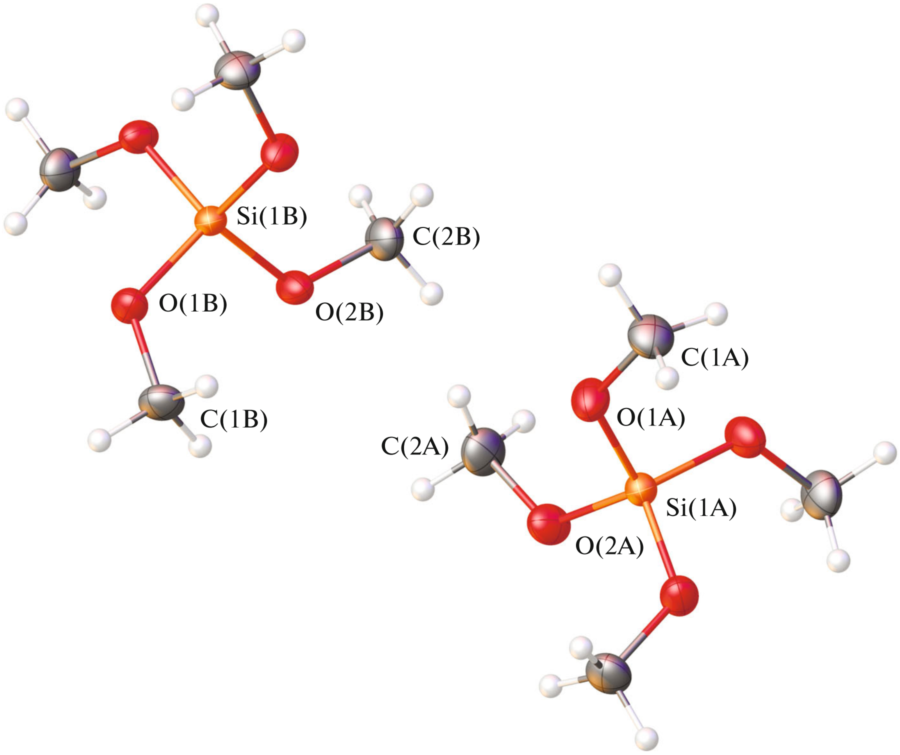


Fig. 2. General view of two symmetry independent molecules of compound **I** in the representation of atoms by thermal ellipsoids ($p = 50\%$) at 150 K.

dilane [15] because of the replacement of two methoxy groups by methyl groups. This can graphically be presented in the form of the so-called "symmetry measures" [20], which describe the deviations of the shapes of the SiO_4 polyhedron in compound **I** and SiO_2C_2 in dimethyldimethoxysilane [15] from an ideal tetrahedron (S(T-4)) and an ideal planar square (S(SP-4)). The lower the corresponding values, the better the description of the polyhedron shape by the corresponding polyhedron. In compound **I**, the tetrahedral S(T-4) and planar square S(SP-4) "symmetry measures" estimated from the XRD data at 150 K using the Shape 2.1 program [20] are 0.178, 29.418 and 0.190, 29.297 for two independent molecules of tetramethoxysilane **I** (Table 2). For comparison, similar values for dimethyldimethoxysilane [15] reach 0.544 and 31.204, respectively.

On heating the crystal of compound **I** to 200 K (Table 1), the transition is observed from the space group *P*2/*n* to *C*2/*c* in which the single independent tetramethoxysilane molecule lies on the 2-fold symmetry axis also passing through the silicon atom and

Table 2. Selected geometric parameters for the earlier studied dimethyldimethoxysilane [15] and tetramethoxysilane **I** at 150 and 200 K according to the XRD data*

Parameter	Dimethyldimethoxysilane	150 K	200 K
Si–O, Å	1.6391(11)	1.6107(12)–1.6161(11)	1.524(15)–1.649(14)
Si–C, Å	1.8468(19)		
O–C, Å	1.420(2)	1.4258(19)–1.430(2)	1.382(15)–1.522(14)
OSiO, deg	110.92(7)	106.85(6)–114.60(9)	103.4(11)–120.5(11)
OSiC, deg	111.82(8)		
CSiC, deg	113.98(10)		
S(T-4)	0.544	0.178, 0.190	0.101, 0.285
S(SP-4)	31.204	29.418, 29.297	32.875, 29.426

* S(T-4) and S(SP-4) are the deviations of the shape of the SiX_4 polyhedron (X = O, C) from an ideal tetrahedron (T-4) and a planar square (SP-4), respectively.

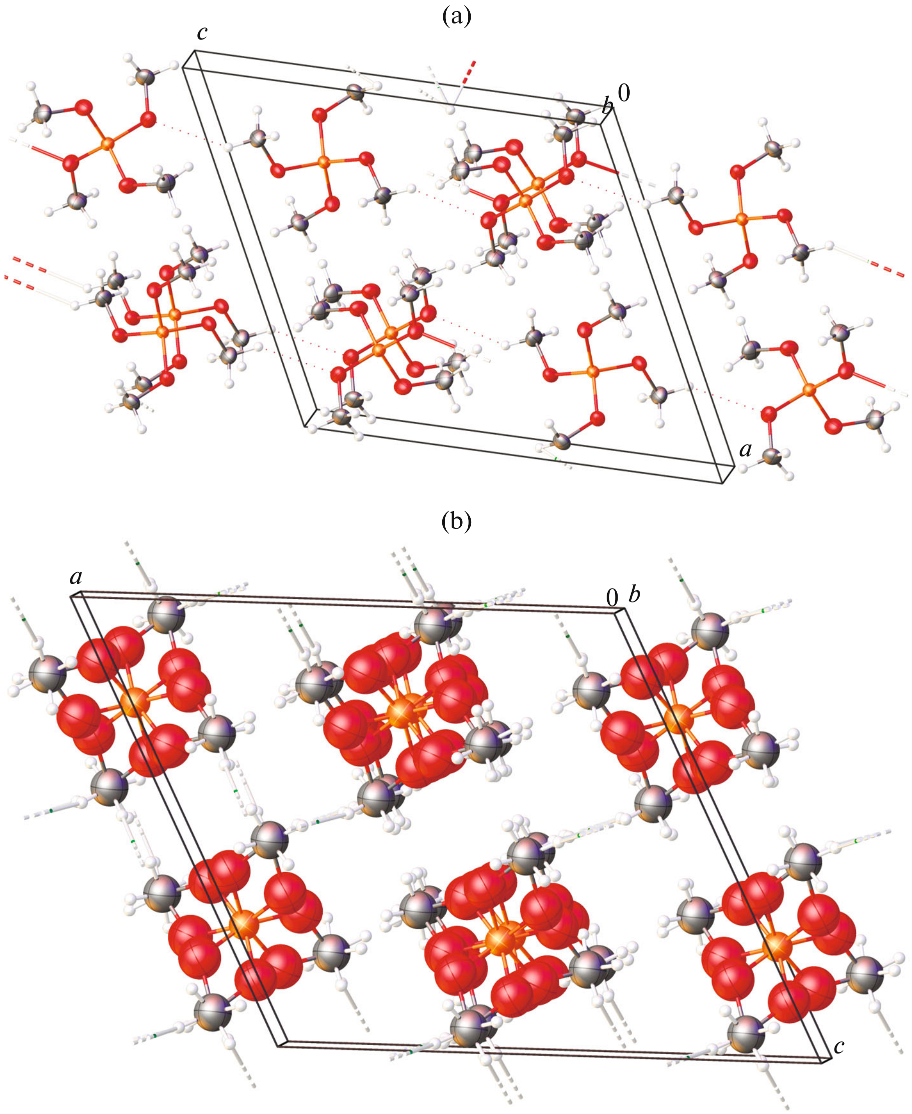


Fig. 3. Fragment of the crystal packing of compound **I** at (a) 150 and (b) 200 K (both components of the disordered methoxy groups are shown).

the middle of the O(1)...O(1) and O(2)...O(2) lines. A substantial rearrangement of the crystal packing of tetramethoxysilane **I** is observed (Fig. 3). Since efficient proton donors and acceptors are absent, at 150 K the crystal packing of compound **I** is formed by C–H...O contacts (with the minimum C...O distance equal to 3.455(3) Å), whereas at 200 K weaker C–H...H interactions (with the minimum C...H distance equal to 3.123(4) Å) are responsible for structure formation. A rearrangement of the crystal structure on heating is accompanied by an expected increase in the unit cell volume per tetramethoxysilane molecule from 193.12 to 207.5 Å^3 (Table 1).

An additional difference from the low-temperature phase is that the oxygen atoms of the methoxy groups at 200 K are disordered over two positions with the same population 50 : 50 (Fig. 4) due to the high symmetry and weakness of intermolecular interactions leading to the superposition of the indicated groups. It should be mentioned that it is very difficult to refine the coordinates and thermal parameters of the atoms in the disordered substituents at the silicon atom and, therefore, they were refined with many restraints. In the framework of the corresponding experimental inaccuracies and refined model, the silicon atom retains its covalent environment (Table 2), which remains very close to the tetrahedral one. In fact, the values of the tetrahedral S(T-4) and planar square S(SP-4) "symmetry measures" estimated for both components of the disordered molecule at 200 K are 0.101, 32.875 and 0.285, 29.426, respectively (Table 2).

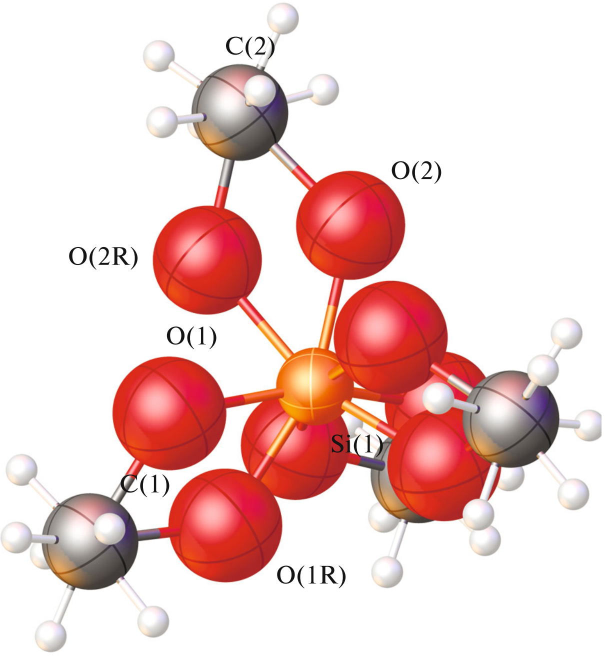


Fig. 4. General view of compound **I** in the representation of atoms by thermal ellipsoids (p = 50%) at 200 K. Both components of the disordered methoxy groups are shown.

Thus, the single crystals of tetramethoxysilane, which is a viscous liquid at room temperature, were grown using the original setup for in situ crystallization (Fig. 1). The XRD study of the single crystals at 150 and 200 K allowed to unambiguous the structure of the compound, and the phase transition accompanied by the disordering of the methoxy groups was also observed in this temperature range. Unfortunately, we failed to repeat the XRD study at 150 K because of technical failures in the operation of the low-temperature device leading to the melting of the corresponding single crystal to form a viscous liquid. Subsequent attempts to grow single crystals of analogous quality suitable for XRD from this liquid were unsuccessful. Nevertheless, the developed setup that differs from its commercial analog OHCD [16] by a significantly lower cost and a possibility of operative modification of various components provides broad opportunities for approaches of the in situ crystallization of organoelement compounds and, perhaps, metal complexes in the liquid or even gaseous state [3] (in the latter case, if they are sealed in quartz capillaries).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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