**STRUCTURE OF ORGANIC COMPOUNDS**

Crystal Structures of [N(CH$_3$)$_4$](HSeO$_4$) at 298, 363, and 380 K

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Received October 4, 2000

Abstract—Three crystalline [N(CH$_3$)$_4$](HSeO$_4$) modifications are studied by X-ray diffraction method at 298, 363, and 380 K. The high-temperature phases are characterized by disordering of HSeO$_4$-tetrahedra. The systems of hydrogen bonds and the mechanism of the phase transitions are considered. © 2001 MAIK “Nauka/Interperiodica”.

**INTRODUCTION**

The compounds described by the general formula M HXO$_4$, where $M = \text{Rb, Cs, NH}_4$, N(CH$_3$)$_4$ and $X = \text{S, Se}$, have intensely been studied since the discovery of the reverse phase transition at 98°C [1]. High protonic conductivity in the tetramethylammonium hydrogen sulfate (TMSO) above 175°C [2] indicates a possible existence of the superionic phase also in tetramethylammonium hydrogen selenate (TMSeO) [3]. The pronounced endothermic effect at 98°C (Fig. 1) correspond to the unidentified phase transition. The latter peak corresponds to the unidentified phase transition in the temperature range 25–200°C revealed three peaks of endothermic effects at 81, 98, and 124°C (Fig. 1). The latter peak corresponds to the unidentified phase transition. The pronounced endothermic effect at 98 ± 1°C was shown to be reversible and is characterized by a small hysteresis of the reverse phase transition at 94 ± 1°C (Fig. 1a). A very weak endothermic effect observed during heating at 81 ± 1°C showed no corresponding exothermic effect during cooling. Thus, the sequence of phase transitions can be represented by the following scheme: III $\xrightarrow{81^\circ}$ II $\xrightarrow{98^\circ}$ I $\xrightarrow{124^\circ}$ unidentified phase (phases), where III is the TMSeO phase at room temperature.

The X-ray diffraction experiment on TMSeO crystals (phase III) was performed on an Enraf-Nonius CAD-4 diffractometer at room temperature and on crystals of phases II and I on a Stoe IPDS diffractometer at temperatures of 90 ± 3 and 107 ± 3°C, respectively. In the latter case, the specimens were heated by an Enraf-Nonius FR-559 high-temperature attachment. The absorption correction for phase III was introduced using the results of the $\psi$-scanning of five reflections. The diffraction data for phases II and I were corrected by the numerical absorption method based on real crystal shape.

All the structures were solved by direct methods using the SHELXL97 program [4]. The positions of non-hydrogen atoms were refined in the anisotropic approximation by the SHELXS97 program [5]. All the hydrogen atoms in phase III and only the hydrogen atoms in the HSeO$_4$ group in phase II were refined in the isotropic approximation. Hydrogen atoms of the methyl groups in phases I and II were considered with due regard for the geometry of the CH$_3$ groups. It was found that hydrogen atoms in one of the tetramethylammonium groups in phase I are disordered over two positions.

The choice of the space group from two possible—C2 and C2/m—is rather difficult. In particular, the statistical criterion based on $|E^2-1|$ indicated the absence of the center of inversion. The sp. gr. C2/m was chosen for phase II for following reasons: the R-factor was lower despite the fact that the number of the parameters to be refined was twice as low; the geometry of disordered HSeO$_4$ groups was closer to tetrahedral; the anisotropy of thermal vibrations of oxygen atoms seemed to be more reasonable (in the sp. gr. C2, some oxygen atoms showed pronounced anisotropy of ther-
mal vibrations); and HSeO$_4$-tetrahedra in the calculations within the sp. gr. C2 statistically occupied two positions with almost equal occupancies.

The crystallographic characteristics of all the three modifications and the corresponding parameters of the X-ray diffraction experiments are listed in table. The atomic positional and thermal parameters for the structures of the three TMSeO modifications are deposited in the Cambridge Structural Database (CCDC 157 404, CCDC 157 405, and CCDC 157 406 for modifications I, II, and III, respectively).

RESULTS AND DISCUSSION

Structure of phase III. Crystal structure of phase III consists of tetrahedral tetramethylammonium cations and HSeO$_4$-tetrahedra (anions). One Se–O distance, is longer by ~0.1 Å (Se–O(4) 1.725(3) Å) than all the other Se–O distances (1.603–1.614 Å), which is explained by the participation of the O(4) atom as a donor in hydrogen bonding. Hydrogen bonds O(4)–H(1)···O(1)' 2.673(5) Å connect HSeO$_4$-tetrahedra into closed centrosymmetric dimers (Fig. 2) similar to those in the NaHSeO$_4$[6] and KHSO$_4$[7] structures. The latter compound, unlike III and NaHSeO$_4$, in addition to closed dimers, also has chains of the HSO$_4$ tetrahedra. The structure of phase III of TMSeO considerably differs from the orthorhombic TMSO (sp. gr. Pna2$_1$) crystallized at room temperature [3] because HSO$_4$-tetrahedra are disordered over two positions and are linked by hydrogen bonds into infinite chains along b-axis. One more characteristic feature of the room temperature TMSeO phase is its stability in air, whereas TMSO phase is highly hygroscopic [3].

Structure of phase II. When studying phase II, we also considered the sp. gr. C2. Similar to phase III, the structure of phase II consists of the [N(CH$_3$)$_4$]$^+$ and HSeO$_4$-tetrahedra. The N-atom occupies the 4h position on the axis 2. The oxygen atoms of the HSeO$_4$-tetrahedra are disordered over two positions with the occupancy 0.5. Two HSeO$_4$ tetrahedra are related by the mirror plane (Fig. 3). It is interesting that the H atom at the selenate ion, localized from difference Fourier maps, lies, in fact, in this plane (i.e., is almost ordered), while the O(4) atom, the hydrogen donor, is located at a very small distance (about 0.1 Å) outside this plane. The Se–O distances in the tetrahedron are different, which is explained by pronounced thermal vibrations of O and Se atoms. Two too short Se–O(1) and Se–O(3) distances (1.523 and 1.557 Å) were corrected for libration by the method described in [8] to yield 1.556 to 1.596 Å, respectively. Of two remaining distances, only the Se–O(4) 1.683 Å distance it approximately corresponds to the distance for an oxygen atom involved in hydrogen bonding as a donor and, thus, requires no considerable correction. The correc-