

clusters is 3.278 (1) Å [Mo(1)—Mo(3)]. The S atoms bridge either one [S(1), S(3), S(5) and S(6)] or two [S(2) and S(4)] Mo triangular faces of the clusters. Moreover, the S(1) and S(3) atoms are linked to an Mo atom of a neighbouring cluster. The Mo—S bond distances range from 2.403 (3) to 2.624 (2) Å within the Mo<sub>9</sub>S<sub>11</sub> unit and from 2.395 (3) to 2.580 (2) Å within the Mo<sub>12</sub>S<sub>14</sub> unit.

The Cs<sup>+</sup> ions occupy large intersecting channels which run parallel to the axes of the rhombohedral unit cell. Both are located on special 12(c) positions and are each surrounded by ten S atoms. Six of them form a trigonal prism and the remaining four cap the three rectangular and one triangular face. The Cs—S distances range from 3.535 (4) to 3.904 (2) Å (mean value 3.681 Å) for the Cs(1) site and from 3.282 (2) to 3.759 (2) Å (mean value 3.549 Å) for the Cs(2) site.

## References

- B. A. FRENZ & ASSOCIATES, INC. (1985). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- GOUGEON, P. (1984). Thesis. Univ. of Rennes, France.
- GOUGEON, P. (1990). Unpublished results.
- GOUGEON, P., PADIOU, J., POTEL, M., SERGENT M. & COUACH, M. (1984). *Ann. Chim. Fr.* **9**, 1083–1086.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- POTEL, M. (1981). Thesis. Univ. of Rennes, France.
- POTEL, M., CHEVREL, R. & SERGENT, M. (1980). *Acta Cryst.* **B36**, 1319–1322.
- POTEL, M., CHEVREL, R. & SERGENT, M. (1981). *Acta Cryst.* **B37**, 1007–1010.
- STOUT, G. & JENSEN, L. H. (1968). *X-ray Structure Determination*. London: Macmillan.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1993). **C49**, 430–433

## Structure of (NH<sub>4</sub>)<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub> in High-Temperature Phases I and II

BY K. ŁUKASZEWICZ AND A. PIETRASZKO

*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 927,  
50-950 Wrocław, Poland*

AND M. A. AUGUSTYNIAK

*Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17/19,  
60-179 Poznań, Poland*

(Received 31 March 1992; accepted 7 July 1992)

**Abstract.** Triammonium hydrogenbis(tetraoxoselenate), (NH<sub>4</sub>)<sub>3</sub>H(SeO<sub>4</sub>)<sub>2</sub>,  $M_r = 341.04$ ,  $Z = 3$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ ,  $F(000) = 498$ . Phase I: trigonal,  $R\bar{3}m$ ,  $a = 6.090 (1)$ ,  $c = 22.759 (5) \text{ \AA}$ ,  $V = 731.0 (2) \text{ \AA}^3$ ,  $D_x = 2.32 \text{ g cm}^{-3}$ ,  $\mu = 68.7 \text{ cm}^{-1}$ ,  $T = 355 \text{ K}$ ,  $R = 0.0336$  for 241 unique reflections with  $I > 4\sigma(I)$ . Phase II: trigonal,  $R\bar{3}$ ,  $a = 6.064 (1)$ ,  $c = 22.904 (5) \text{ \AA}$ ,  $V = 729.4 (2) \text{ \AA}^3$ ,  $D_x = 2.33 \text{ g cm}^{-3}$ ,  $\mu = 68.8 \text{ cm}^{-1}$ ,  $T = 310 \text{ K}$ ,  $R = 0.0374$  for 397 unique reflections with  $I > 4\sigma(I)$ . In both phases, SeO<sub>4</sub> tetrahedra are linked by a dynamic system of symmetrically disordered hydrogen bonds in planes perpendicular to the trigonal axis. In phase II, SeO<sub>4</sub> tetrahedra deviate from the (210) plane owing to a small rotation of about 4° about the trigonal axis. In phase I, owing to symmetry enhancement, both orientations of SeO<sub>4</sub> tetrahedra are equally probable on both sides of (210), which is therefore a mirror plane.

**Introduction.** Triammonium hydrogenbis(tetraoxoselenate) (TAHSe) is a member of the isomorphic series with the general formula  $A_3H(BO_4)_2$ , where  $A = \text{NH}_4, \text{K}, \text{Rb}$  or  $\text{Cs}$  and  $B = \text{S}$  or  $\text{Se}$ . Unlike other isomorphic compounds with a single high-temperature trigonal superionic phase, TAHSe has two trigonal superionic phases. TAHSe undergoes four successive phase transitions at 332, 302–305, 276–279 and 181 K, with phases denoted I, II, III, IV and V in order of descending temperature (Osaka, Makita & Gesi, 1979; Baranov, Tregubtchenko, Shuvalov & Shagina, 1987). Phase V is ferroelectric, phases II and I are superionic conductors. Recently, Merinov, Antipin, Baranov, Tregubtchenko, Shuvalov & Struchkov (1991) obtained crystals of TAHSe with the III–II phase-transition temperature lowered to 291 K and determined the crystal structure of TAHSe at 295 K in phase II. We have performed a detailed study of the crystal structure of

TAHSe at temperatures of 310 and 355 K which is essential for understanding the nature and mechanism of I–II phase transition in TAHSe. Owing to the domination of heavy Se atoms situated in special positions, the proper choice of space group required precise experimental data and special considerations.

**Experimental.** Single crystals of TAHSe were grown by slow evaporation of a stoichiometric aqueous solution at  $T = 280$  K. TAHSe in phase III is triclinic at room temperature (Pietraszko, Łukaszewicz & Augustyniak, 1992) and at 305 K it transforms to the trigonal phase II. The crystals are susceptible to plastic deformation and we were not able to prepare small spheres of good quality for crystal structure analysis. Small single-domain crystals were carefully selected and checked for twinning. A crystal of approximate dimensions  $0.30 \times 0.20 \times 0.25$  mm was mounted with epoxy glue and used for measurements at three consecutive temperatures, 310, 355 and 366 K. Data were collected on a KUMA-Diffraction KM4 four-circle automatic diffractometer with graphite-monochromated Mo  $K\alpha$  radiation, a simple high-temperature attachment with hot-air flow and an estimated uncertainty in crystal temperature of  $\pm 1$  K. Lattice parameters were obtained for each temperature from a least-squares fit of 23 reflections selected in the range  $15.5 < \theta < 31^\circ$ . Intensity data were collected in  $\omega/\theta$  mode. Each reflection was measured in 100 scan steps in  $\Delta\omega = 1.75^\circ + 0.35\tan\theta'$  ( $\sin\theta' = 1.002\sin\theta$ ); 12 steps at each side of the reflection profile were taken as background. At each temperature 2177 reflections were measured with  $-9 \leq h \leq 9$ ,  $-9 \leq k \leq 9$ ,  $0 \leq l \leq 35$  and  $2 < \theta < 35^\circ$ . Standard reflections 201,  $\bar{2}16$  and  $\bar{2}\bar{2}1$  were checked after every 50 reflections, with no significant intensity variation ( $\sigma < 1\%$ ). Absorption correction based on  $\psi$  scans gave  $R_{\text{int}} = 0.0161$ , 0.0188 and 0.0192 for temperatures 310, 355 and 366 K, respectively. Lorentz–polarization corrections were applied in a routine way.

The structures were refined with full-matrix least squares using *SHELXTL* PC programs (Sheldrick, 1986). The weighting scheme was  $w = 1/\sigma^2(F_o)$ , where  $\sigma(F_o)$  is the standard deviation for each reflection as derived from counting statistics. The positions of all H atoms were found from difference maps and they refined surprisingly well, even those with occupancy 1/6. When removed from the refinement procedure they invariably reappeared as small peaks in difference syntheses. The authors are aware that the determination of H-atom positions with 1/6 occupancy in the presence of selenium may be considered questionable, nevertheless, the picture obtained is logical and explains the bonding and properties of TAHSe in phases I and II well.

For phase II at 310 K, merging of equivalent reflections in space groups  $R32$ ,  $R3m$  and  $R\bar{3}m$  resulted in  $R_{\text{int}} = 0.0432$ , compared to  $R_{\text{int}} = 0.0161$  for  $R3$  and  $R\bar{3}$ , which unambiguously indicated the latter two space groups. The only possible choice was space group  $R\bar{3}$ ;  $R3$  could be readily discarded on the basis of a much higher number of free parameters with only a slightly better  $R$  index and unrealistic Se–O distances in the  $\text{SeO}_4$  tetrahedra. Atomic parameters of TAHSe in phase II at 310 K are presented in Table 1\* and bond lengths are in Table 2.

In keeping with the space group  $R\bar{3}$  and contrary to the structure described by Merinov, Antipin, Baranov, Tregubtchenko, Shuvalov & Struchkov (1991),  $\text{SeO}_4$  tetrahedra in phase II of TAHSe deviate by  $4^\circ$  from the symmetrical position (Fig. 1a). The crystal structure is disordered because O(2) atoms are displaced out of the threefold axes by 0.405 Å and, consequently, six O(2) atoms occupy 18( $f$ ) equivalent positions randomly. O(2) atoms are linked in pairs by symmetrically disordered hydrogen bonds and constitute a dynamic two-dimensional network. Each O(2) atom may be bonded to another O(2') atom from one of three neighbouring  $\text{SeO}_4$  tetrahedra. The bonding results in a shortening of the O(2)⋯O(2) distance down to 2.7 Å, the value typical for moderately strong hydrogen bonds, and is closely related to the displacement and disorder of O(2) atoms. Hydrogen bonds O(2)—H(1)⋯O(2') and O(2)⋯H(1)—O(2') are in dynamic equilibrium, and three H(1) atoms are located in 18( $f$ ) positions with occupancy 1/6. Considerable mobility of the H(1) atom is an obvious reason for the superionic conductivity of TAHSe in phases I and II. One of the three ammonium groups is disordered owing to the symmetry centre, with the H(2) atom pointing either up or down. Numerous weak hydrogen bonds N—H⋯O connect ammonium ions with the  $\text{SeO}_4$  groups.

For phase I at 355 K, the symmetry of the diffraction pattern corresponds to space groups  $R32$ ,  $R3m$  and  $R\bar{3}m$ . Higher number of free parameters and unrealistic Se–O distances with no significant improvement of  $R$  indices allowed us to discard groups  $R32$  and  $R3m$ . The choice of  $R\bar{3}m$  is in good agreement with the observation that the phase transition I–II is second order (Osaka, Toshiaki & Makita, 1984) because  $R\bar{3}$  is a subgroup of  $R\bar{3}m$ .

Two structure models of phase I are to be considered with ordered and disordered  $\text{SeO}_4$  tetrahedra,

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths including H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55595 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA0025]

Table 1. Atomic parameters and thermal parameters ( $\text{\AA}^2 \times 10^3$ ) of TAHSe with *e.s.d.*'s in parentheses

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	$U_{eq}/U_{iso}$
Phase II (310 K), $R\bar{3}m$					
Se	0	0	0.40906 (3)	1	39
O(1)	0.2918 (6)	0.1634 (8)	0.4301 (2)	1	79
O(2)	0.0408 (23)	0.0773 (16)	0.3376 (3)	$\frac{1}{3}$	61
N(1)	0	0	0	1	46
N(2)	0	0	0.1974 (3)	1	53
H(1)	0.123 (3)	0.226 (7)	0.326 (3)	$\frac{1}{6}$	19
H(2)	0	0	0.037 (3)	$\frac{1}{2}$	66
H(3)	0.062 (6)	0.112 (3)	0.018 (2)	$\frac{1}{2}$	71
H(4)	0	0	0.149 (5)	1	131
H(5)	0.062 (3)	0.141 (3)	0.223 (2)	1	135
Phase I (355 K), $R\bar{3}m$					
Se	0	0	0.40876 (3)	1	46
O(1)	0.2893 (7)	0.1748 (16)	0.4301 (2)	$\frac{1}{2}$	74
O(2)	0.0639 (22)	0.0817 (15)	0.3365 (3)	$\frac{1}{2}$	65
N(1)	0	0	0	1	56
N(2)	0	0	0.1981 (6)	1	65
H(1)	0.103 (3)	0.205 (6)	0.323 (3)	$\frac{1}{6}$	48
H(2)	0	0	0.043 (3)	$\frac{1}{2}$	57
H(3)	0.080 (3)	0.160 (5)	0.006 (2)	$\frac{1}{2}$	72
H(4)	0	0	0.171 (2)	1	86
H(5)	0.081 (2)	0.162 (5)	0.219 (2)	1	137

Table 2. Selected bond lengths ( $\text{\AA}$ ) and O(2)—H(1)···O(2') hydrogen-bond geometry ( $\text{\AA},^\circ$ ) for phases I and II of the title compound

	Phase II	Phase I
Se—O(1)	1.610 (3)	1.611 (3)
Se—O(2)	1.687 (8)	1.705 (6)
O(1)—O(1')	2.660 (6)	2.661 (8)
O(2)—O(1)	2.507 (10)	2.441 (9)
O(2)—O(1')	2.550 (10)	2.641 (10)
O(2)—O(1 <sup>ii</sup> )	2.873 (8)	2.892 (8)
N(1)—H(2)	0.84 (6)	0.99 (3)
N(1)—H(3)	0.71 (3)	0.85 (3)
N(2)—H(4)	1.10 (6)	0.62 (5)
N(2)—H(5)	0.94 (3)	0.98 (3)
O(2)···O(2 <sup>iii</sup> )	2.696 (16)	2.674 (17)
O(2)—H(1)	0.82 (3)	0.73 (4)
H(1)···O(2 <sup>iii</sup> )	1.91 (2)	2.01 (3)
O(1)—H(1)···O(2')	159 (6)	150 (6)

Symmetry code: (i)  $-y, x-y, z$ ; (ii)  $y-x, -x, z$ ; (iii)  $\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$ .

respectively. In the first case, O(1) atoms occupy special positions  $18(h)$  on the mirror plane. In the disordered model,  $\text{SeO}_4$  tetrahedra are deflected from the mirror planes and O(1) atoms occupy general positions  $36(i)$  randomly (Fig. 1*b*). Both models were refined with almost equal discrepancy indices. Additional information comes from the EPR measurements of TAHSe crystals doped with  $(\text{NH}_4)_2\text{CrO}_4$  (Augustyniak, 1992). EPR showed that  $\text{CrO}_4^{3-}$  produced by X-ray irradiation is sensitive to II–I phase transition. The changes of anisotropy of the resonance lines indicate a disordered model for the crystal structure of phase I.

Atomic parameters of TAHSe in phase I at temperature 355 K are presented in Table 1 and selected bond lengths are collected in Table 2. O–O bond lengths have been calculated on the assumption of rigid highly deformed  $\text{SeO}_4$  tetrahedra. The dynamic system of hydrogen bonds in phase I remains similar to that in phase II, which confirms the observation by Osaka, Toshiaki & Makita (1984) that hydrogen bonds play no significant role in phase transition I–II, because substitution of H atoms by deuterium does not influence the transition. The order parameter is therefore closely related to the deflection and ordering of the  $\text{SeO}_4$  tetrahedra.

**Discussion.** The crystal structures of TAHSe in phases I and II are similar to the structures of high-temperature phases of  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  (Baranov, Makarova, Muralyan, Tregubtchenko, Shuvalov & Simonov, 1987) and  $\text{Cs}_3\text{H}(\text{SeO}_4)_2$  (Merinov, Baranov & Shuvalov, 1990). In the case of  $\text{Rb}_3\text{H}(\text{SeO}_4)_2$  and  $\text{Cs}_3\text{H}(\text{SeO}_4)_2$  there is only one high-temperature phase with space group  $R\bar{3}m$ . Our study presents the symmetry and structure changes accompanying the I–II phase transitions in TAHSe. Knowledge of the

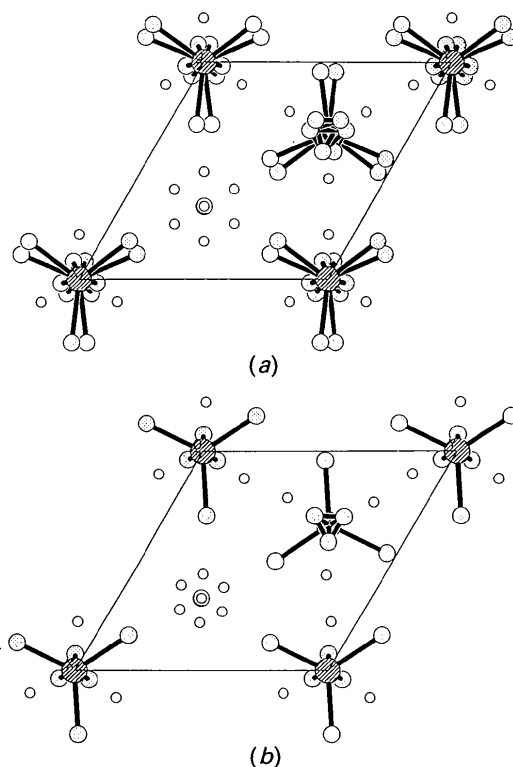


Fig. 1. Crystal structure of  $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$  showing partial projection of the lattice cell along the *z* axis with  $0.230 < z < 0.435$  for (a) phase II at 310 K and (b) phase I at 355 K. Se atoms are denoted by large hatched circles, O atoms by stippled circles, N atoms by circles hatched at one side, and H atoms by small circles.

symmetry and structure of TAHSe in both phases I and II allows us to discuss the mechanism of the I–II phase transition.  $\text{SeO}_4$  tetrahedra in phase II are deflected from the symmetrical position required by space group  $R\bar{3}m$ . The potential barrier preventing  $\text{SeO}_4$  tetrahedra from switching to the other side of the (210) planes decreases with increasing temperature and both orientations of  $\text{SeO}_4$  tetrahedra become equally probable. The problems of anharmonic potentials and pseudo-potential have been discussed by Bachmann & Schulz (1984). They have demonstrated that one cannot distinguish between ordered and disordered structures with just one data set measured at one temperature. The temperature range of phase I of TAHSe is rather small nevertheless, we have also determined the crystal structure of phase I at 366 K. Although atomic parameters did not change significantly, the distance between two angular positions of disordered  $\text{SeO}_4$  tetrahedra became smaller with increasing temperature. We attribute this to the dependence of pseudo-potential on temperature and a decrease of the potential barrier in a double energy well.

We are indebted to Professor Z. Gałdecki for performing the refinement in his laboratory. This work was supported by a grant from the Committee of Scientific Research.

#### References

- AUGUSTYNIAK, M. A. (1992). In preparation.  
 BACHMANN, R. & SCHULZ, H. (1984). *Acta Cryst.* **A40**, 668–675.  
 BARANOV, A. I., MAKAROVA, I. P., MURALYAN, L. A., TREGUBTCHENKO, A. V., SHUVALOV, L. A. & SIMONOV, V. L. (1987). *Kristallografiya*, **32**, 682–694.  
 BARANOV, A. I., TREGUBTCHENKO, A. V., SHUVALOV, L. A. & SHAGINA, N. M. (1987). *Fiz. Tverd. Tela*, **29**, 2513–2516.  
 MERINOV, B. V., ANTIPIN, M. YU., BARANOV, A. I., TREGUBTCHENKO, A. M., SHUVALOV, L. A. & STRUCHKOV, YU. T. (1991). *Kristallografiya*, **36**, 872–875.  
 MERINOV, B. V., BARANOV, A. I. & SHUVALOV, L. A. (1990). *Kristallografiya*, **35**, 355–360.  
 OSAKA, T., MAKITA, Y. & GESI, K. (1979). *J. Phys. Soc. Jpn*, **46**, 577–580.  
 OSAKA, T., TOSHIKI, S. & MAKITA, Y. (1984). *Ferroelectrics*, **55**, 283–284.  
 PIETRASZKO, A., ŁUKASZEWICZ, K. & AUGUSTYNIAK, M. A. (1992). *Acta Cryst.* **C48**, 2069–2071.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

*Acta Cryst.* (1993). **C49**, 433–434

## Redetermination of the Structure of Barium Peroxide by Single-Crystal X-ray Diffraction\*

BY PAUL D. VERNOOY

*Du Pont Central Research and Development, Experimental Station, Wilmington, DE 19880-0356, USA*

(Received 14 May 1992; accepted 11 August 1992)

**Abstract.**  $\text{BaO}_2$ ,  $M_r = 169.3$ , tetragonal,  $I4/mmm$ ,  $a = 3.8016(4)$ ,  $c = 6.7786(8)$  Å,  $V = 97.97(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 5.74$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 198.5$  cm<sup>-1</sup>,  $F(000) = 144$ ,  $T = 293$  K, final  $R = 0.0092$  for 58 unique reflections.  $\text{BaO}_2$  adopts the  $\text{CaC}_2$  structure; Ba is bound to ten O atoms, eight at 2.788 (1) Å and two at 2.648 (5) Å. The O—O bond length in the peroxide ion is 1.482 (10) Å.

**Introduction.** The structure of  $\text{BaO}_2$  has been studied several times in the past (Abrahams & Kalnajs, 1954, and references therein) owing to interest in the nature of the peroxide bond, but never by single-crystal methods. More recently, Roth, Rawn & Hill (1991) examined the reactivity, non-stoichiometry and decomposition of  $\text{BaO}_2$ . They also grew crystals of  $\text{BaO}_2$  from a  $\text{Ba}(\text{NO}_3)_2$  melt under pure  $\text{O}_2$  and

found the crystals were typically twinned. Although they reported precession photographs on the crystals, no single-crystal structure determination was carried out. In this paper, the structure of  $\text{BaO}_2$  based on a crystal grown from a  $\text{Ba}(\text{OH})_2$ – $\text{BaCl}_2$  flux in air is reported.

**Experimental.** The crystal of  $\text{BaO}_2$  used in this study was obtained during the synthesis of a new barium molybdate aluminate, whose structure will be published shortly. However, crystals of  $\text{BaO}_2$  occasionally appeared in other preparations with the  $\text{Ba}(\text{OH})_2$ – $\text{BaCl}_2$  flux. 0.33 g  $\text{Al}_2\text{O}_3$  and 2.0 g  $\text{MoO}_3$  were mixed with 14 g  $\text{Ba}(\text{OH})_2$  and 2.5 g  $\text{BaCl}_2$  and placed in an alumina crucible with a tightly fitting lid. The crucible was heated in air at 300 K h<sup>-1</sup> to 1073 K, held for 5 h at 1073 K and slowly cooled to 923 K at 4.2 K h<sup>-1</sup>. Colorless rectangular plate, 0.16 × 0.10 × 0.01 mm, sealed in a capillary to prevent

\* Contribution No. 6245.