

**STRUCTURE OF SODIUM HYDROGEN SELENITE–SELENIOUS ACID ADDUCT (1 : 3), NaHSeO<sub>3</sub> · 3 H<sub>2</sub>SeO<sub>3</sub>**Josef LOUB<sup>a</sup>, Zdeněk MIČKA<sup>a</sup>, Jana PODLAHOVÁ<sup>a</sup>, Karel MALÝ<sup>b</sup> and Jürgen KOPF<sup>c</sup><sup>a</sup> Department of Inorganic Chemistry,  
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Structure of sodium hydrogen selenite–selenious acid (1 : 3) was solved by heavy-atom method and refined anisotropically to  $R = 0.098$  for 1 223 unique observed reflections. The title compound crystallizes in the  $Pc$  space group with  $a = 5.756(2)$ ,  $b = 4.911(2)$ ,  $c = 20.010(5)$  Å,  $\beta = 100.48(3)^\circ$ ,  $V = 556(1)$  Å<sup>3</sup>,  $T = 293$  K, ( $a = 5.763(2)$ ,  $b = 4.878(1)$ ,  $c = 20.03(1)$  Å,  $\beta = 100.48(3)^\circ$ ,  $V = 554(1)$  Å<sup>3</sup>,  $T = 173$  K),  $Z = 2$ . The structure consist of HSeO<sub>3</sub><sup>-</sup> anions, molecules of selenious acid and Na<sup>+</sup> cations which are octahedrally coordinated with oxygen atoms. The structure is stabilized by a system of hydrogen bonds.

This paper is a continuation of the systematic study of the crystalline products with the general formulae MHSeO<sub>3</sub> ·  $n$  H<sub>2</sub>SeO<sub>3</sub> or MH<sub>2 $n$ +1</sub>(SeO<sub>3</sub>) <sub>$n$ +1</sub>, where  $n = 0 - 3$ , formed in the M<sup>+</sup>–H<sub>2</sub>SeO<sub>3</sub>–H<sub>2</sub>O systems (M alkali metal or ammonium: LiHSeO<sub>3</sub> (ref.<sup>1</sup>), NaHSeO<sub>3</sub> (ref.<sup>2</sup>), KHSeO<sub>3</sub> (ref.<sup>3</sup>), RbHSeO<sub>3</sub> (ref.<sup>4</sup>), CsHSeO<sub>3</sub> (ref.<sup>5</sup>), LiH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (ref.<sup>6</sup>), NaH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (ref.<sup>7</sup>), KH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (refs.<sup>8,9</sup>), RbH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (ref.<sup>10</sup>), CsH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (ref.<sup>11</sup>), NH<sub>4</sub>H<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (ref.<sup>12</sup>), CsH<sub>5</sub>(SeO<sub>3</sub>)<sub>3</sub> (ref.<sup>13</sup>)). These compounds constitute a group of materials with ferroelectric and ferroelastic properties. The title compound was already prepared and formulated as Na<sub>2</sub>SeO<sub>3</sub> · 7 H<sub>2</sub>SeO<sub>3</sub> (ref.<sup>14</sup>).

**EXPERIMENTAL**

The material studied was obtained from the mixture of Na<sub>2</sub>SeO<sub>3</sub>, H<sub>2</sub>SeO<sub>3</sub> and H<sub>2</sub>O (ref.<sup>15</sup>) as pale-rosy, slightly hygroscopic crystals stable in air and to X-rays, but very unstable towards chemical reduction. Therefore the measured crystal was sealed in the Lindemann capillary tube. Density was determined pycnometrically under xylene at 293 K.

**Crystal Structure Determination**

Monoclinic, space group  $Pc$ ,  $D_0 = 3.19(1)$ ,  $D_x = 3.211(1)$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 14.29$  mm<sup>-1</sup>,  $F(000) = 500$ ,  $M_r = 537.9$ .

The structure was solved by the heavy-atom method, H atoms were not localized. The values of  $F$  magnitudes were refined in the full-matrix least-squares refinement including positional and anisotropic displacement parameters. Application of an absorption increased the  $R$ -factor final value and therefore was neglected. Atomic scattering factors and corrections for anomalous dispersion were those from ref.<sup>16</sup>. Data collection and structure refinement parameters are summarized in Table I\*.

TABLE I  
Data collection and structure refinement parameters

Parameter	Data
Crystal dimensions	0.1 × 0.2 × 0.2 mm
Diffractometer and radiation used	automatic Hilger -Watts four-circle diffractometer, MoK $\alpha$ radiation ( $\lambda = 0.7173 \text{ \AA}$ )
Scan technique	$\omega - 2\theta$
No. and $2\theta$ range of reflections for lattice parameter refinement	14, 16 $\rightarrow$ 38°
Range of $h, k$ and $l$	0 $\rightarrow$ 6, 0 $\rightarrow$ 6, -24 $\rightarrow$ 24
Standard reflections and their intensity fluctuation	3 after every 30 reflections, no intensity variation
Total number of reflections measured; $2\theta$ range	1 223, 0 $\rightarrow$ 128°
No. of observed reflections	1 119
Criterion for observed reflections	$I > 1.96 \sigma(I)$
Function minimized	$\Sigma w( F_o  -  F_d )^2$
Weighting scheme	$w = [\sigma^2(F_o) + 0.0009F_o^2]^{-1}$
Parameters refined	153
Values of $R, wR$ and $S$	0.098, 0.108, 2.5
Ratio of maximal and average $LS$ shift to e.s.d. ( $\Delta / \sigma$ )	0.18 for $\beta(3,3)$ of O(12) and 0.04
Maximal and minimal heights in final $\Delta\rho$ map	3.8 and $-5.6 \text{ e \AA}^{-3}$ (0.81 and 0.84 $\text{\AA}$ away from the Se1 and Se3 atom)
Program used	SDS System (ref. <sup>17</sup> )
Computer used	Siemens 7536

\* Tables of structure factors and anisotropic thermal parameters of non-H atoms are available from the authors on request.

## DISCUSSION

The final atomic coordinates and equivalent isotropic displacement factors of non-H atoms are given in Table II. Selected interatomic distances and angles are listed in Table III. The structure is shown in Fig. 1.

Initial attempt to solve the structure was unsuccessful<sup>15</sup>, even one using the low-temperature data ( $T = 173$  K), which had yielded only unit-cell dimensions. Although the crystals appeared in the polarization microscope as good single crystals with pretty developed faces the analysis of the previous investigations revealed additional maxima in the scan profiles for certain set of reflections and thus suggested possibility of the twinning. This was confirmed during preliminary preparation of the measurement on the Hilger–Watts diffractometer and twin matrix was determined as

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1.26 & 0 & -1 \end{bmatrix}.$$

TABLE II  
Atomic coordinates ( $\cdot 10^3$ ) and equivalent isotropic displacement factors of non-H atoms, with e.s.d.'s in parentheses

$$B_{\text{eq}} = [B_{22} + (B_{11} + B_{33} + 2B_{13} \cos \beta) / \sin^2 \beta] / 3$$

Atom	$x$	$y$	$z$	$B_{\text{eq}}, \text{\AA}^2$
Se1	521.4	445.8(6)	445.9	0.8(1)
Se2	57.9(6)	940.8(7)	525.1(2)	1.0(1)
Se3	397.6(7)	179.4(7)	266.2(2)	1.1(1)
Se4	813.9(7)	633.8(7)	174.0(2)	1.1(1)
Na	934(2)	795(3)	350(1)	1.6(3)
O11	347(4)	608(6)	376(1)	1.8(6)
O12	790(4)	521(5)	430(1)	1.2(5)
O13	488(4)	656(5)	507(1)	1.1(5)
O21	-212(4)	1059(5)	541(1)	1.3(5)
O22	56(4)	1104(5)	448(1)	1.1(5)
O23	223(4)	1138(5)	577(1)	1.6(6)
O31	119(4)	91(5)	280(1)	2.0(6)
O32	420(5)	-72(7)	208(1)	2.7(8)
O33	559(4)	35(5)	332(1)	1.5(6)
O41	1034(4)	460(6)	142(1)	1.8(6)
O42	584(4)	417(5)	139(1)	1.9(6)
O43	848(4)	515(6)	251(1)	1.6(5)

TABLE III  
 Interatomic distances (Å) and angles (°); d and a denote donor and acceptor atoms. Symmetry code: (i)  $1 + x, 1 + y, z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $1 + x, y, z$ ; (iv)  $x - 1, y, z$ ; (v)  $x - 1, y + 1, z$ ; (vi)  $x, 1 - y, z - 0.5$ ; (vii)  $1 + x, 2 - y, z - 0.5$

Atoms		Distance	Atoms		Angle	
Se1-O11		1.76(2)	O11-Se1-O12		99(1)	
Se1-O12		1.67(2)	O11-Se1-O13		100(1)	
Se1-O13		1.64(2)	O12-Se1-O13		104(1)	
Se2-O21		1.74(2)	O21-Se2-O22		98(1)	
Se2-O22		1.74(2)	O21-Se2-O23		97(1)	
Se2-O23		1.60(2)	O22-Se2-O23		102(1)	
Se3-O31		1.73(2)	O31-Se3-O32		97(1)	
Se3-O32		1.72(2)	O31-Se3-O33		100(1)	
Se3-O33		1.63(2)	O32-Se3-O33		98(1)	
Se4-O41		1.74(2)	O41-Se4-O42		96(1)	
Se4-O42		1.74(2)	O41-Se4-O43		102(1)	
Se4-O43		1.63(2)	O42-Se4-O43		97(1)	
Na...O12		2.35(3)	O12-Na-O31 <sup>i</sup>		173(1)	
Na...O43		2.39(3)	O22 <sup>iii</sup> -Na-O43		174(1)	
Na...O31 <sup>i</sup>		2.40(3)	O11 <sup>iii</sup> -Na-O33 <sup>ii</sup>		172(1)	
Na...O33 <sup>ii</sup>		2.43(3)	O12-Na-O22 <sup>iii</sup>		84(1)	
Na...O22 <sup>iii</sup>		2.48(3)	O43-Na-O33 <sup>ii</sup>		96(1)	
Na...O11 <sup>iii</sup>		2.51(3)	O31 <sup>i</sup> -Na-O11 <sup>iii</sup>		81(1)	
Se <sup>d</sup>	O <sup>d</sup>	O <sup>a</sup>	Se <sup>a</sup>	O <sup>d</sup> ...O <sup>a</sup>	Se <sup>d</sup> -O <sup>d</sup> -O <sup>a</sup>	O <sup>d</sup> -O <sup>a</sup> -Se <sup>a</sup>
Se1	O11	O33 <sup>ii</sup>	Se3 <sup>ii</sup>	2.66(3)	113(3)	112(3)
Se2	O21	O13 <sup>iv</sup>	Se1 <sup>iv</sup>	2.63(3)	105(3)	120(3)
Se2	O22	O12 <sup>v</sup>	Se1 <sup>v</sup>	2.54(3)	114(3)	110(3)
Se3	O31	O43 <sup>iv</sup>	Se4 <sup>iv</sup>	2.60(3)	107(3)	118(3)
Se3	O32	O23 <sup>vi</sup>	Se2 <sup>vi</sup>	2.68(3)	133(3)	131(3)
Se4	O41	O23 <sup>vii</sup>	Se2 <sup>vii</sup>	2.70(3)	102(3)	121(3)
Se4	O42	O13 <sup>vi</sup>	Se1 <sup>vi</sup>	2.62(3)	120(3)	129(3)

The twinning ratio differed for different specimens. For intensity data collection the crystal was chosen which did not show splitting in the reflection profiles. However the quality of the measured crystal was not fully satisfying as it is proved by the results of the structure refinement (higher reliability factors and high residuals in the difference electron density map), nevertheless the structure was determined with accuracy which made possible to discuss the crystal geometry.

Because the H-atom positions were not localized in the structure, the  $\text{HSeO}_3^-$  and  $\text{H}_2\text{SeO}_3$  formations were distinguished on the basis of the  $\text{SeO}_3$  geometry. The most profound differentiating criterion between Se–O(H) and Se–O bonding consist in the Se–O distance which averages to 1.74(1) Å ( $n = 7$ ) for Se–O(H) and 1.63(2) Å ( $n = 5$ ) for Se–O (with e.s.d.'s of arithmetic means in parentheses). These values are similar to those reported in refs<sup>1–13,18–20</sup>. The oxygen atoms arrangement around Se1 atom differs from that around Se2, 3 and 4, see Table III. Also the distance Se1 from the O11, O12, O13 oxygen atoms plane differs significantly from the distances Se2,3,4 to the O2,3,4 atoms planes (1: 0.761(3), 2: 0.805(3), 3: 0.829(3), 4: 0.833(3) Å). The Na atoms are octahedrally coordinated by O and O(H) atoms of all selenites with the average Na–O distance of 2.43(5) Å and the average O–Na–O *cis*-angle of 90(6)°. The next Na–O distances are greater then 3.5 Å. All H atoms are involved in hydrogen bonding characterized by the average distance and angles  $\text{O}^{\text{d}}\cdots\text{O}^{\text{a}}$ ,  $\text{Se}^{\text{d}}\text{--}\text{O}^{\text{d}}\text{--}\text{O}^{\text{a}}$  and  $\text{O}^{\text{d}}\text{--}\text{O}^{\text{a}}\text{--}\text{Se}^{\text{a}}$  of 2.63(5) Å, 113(10) and 120(7)° ( $n = 7$ ).

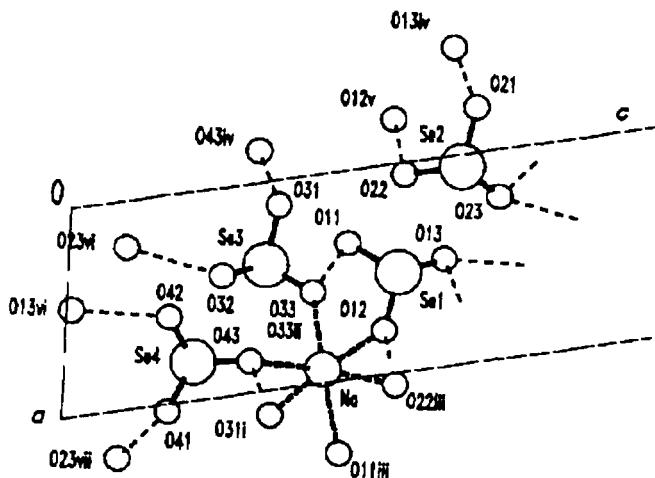


FIG. 1

A view of the part of the structure along *b* axis with atom numbering. The coordination bonds are indicated by thick dashed lines, the hydrogen bonds by thin dashed lines

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