CRYSTAL CHEMISTRY OF THE HYDROGEN SELENITES $MH_{2n+1}(SeO_3)_{n+1}$

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Thirty six SeO_3 formations in 17 crystal structures of selenites with formula $MH_{2n+1}(SeO_3)_{n+1}$, where M = H, Li, Na, K, Rb, Cs, NH_4, Tl and $n = 0$–3 were analysed in this paper. There are found five types of selenites: $SeO(OH)_2$ ($n = 14$), $SeO_2(OH)^-$ ($n = 17$), $SeO(OH_{0.5})_2^-$ ($n = 1$), $Se(OH_{0.5})_3^{0.5-}$ ($n = 3$) and $SeO(OH)(OH_{0.5})^{0.5-}$ ($n = 1$). All formations SeO_3 have the point symmetry *1*. The overall mean value of 108 individual Se–O distances is 1.70(5) Å, of 108 O–Se–O angles is 101(3)° and of 57 O...O distances in hydrogen bonds is 2.60(6) Å. A very significant correlation was found between the ionic radius r (Å) of the element M and the value V/Z (Å^3).

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1. INTRODUCTION

This paper presents a critical review of the crystal chemistry of alkali selenites with the general formula $MH_{2n+1}(SeO_3)_{n+1}$ or $MHSeO_3 \,.\, n\, H_2SeO_3$, where M = H, Li, Na, K, Rb, Cs, NH_4, Tl and $n = 0$–3. These compounds constitute a group of materials with interesting physical properties. The emphasis is intent on the geometry and the connecting of SeO_3 formations and on phase transitions.

2. SeO_3 FORMATIONS

Chemical formulae, symbols, types and references of the studied compounds are given in Table I. The primary data for the calculations of distances and angles were the

TABLE I
Chemical formulae, symbols, types and references of the studied selenites[a]

Compound	Symbol	Type	*S*	References
H_2SeO_3	HH	*A*	N	1
$LiHSeO_3$	LiH	*B*	X	2
$NaHSeO_3$	NaH	*B,C*	N	3
$KHSeO_3$	KH	*B*	N	4
$RbHSeO_3$	RbH	*B*	X	5
$CsHSeO_3$	CsH	*B*	X	6
$CsLi(HSeO_3)_2$	CsLiH2	*B1,B2*	X	7
$LiH_3(SeO_3)_2$	LiH3	*A,B*	N	8
$NaH_3(SeO_3)_2$	NaH3	*D*	N	9
$KH_3(SeO_3)_2$	KH3	*E*	N	10
$RbH_3(SeO_3)_2$ht	RbH3ht	*A,B*	N	11
$RbH_3(SeO_3)_2$lt	RbH3lt	*A1–A4,B1–B4*	N	12
$CsH_3(SeO_3)_2$	CsH3	*D1,D2*	N	13
$NH_4H_3(SeO_3)_2$	NH4H3	*A,B*	N	14
$TlH_3(SeO_3)_2$	TlH3	*A,B*	X	15
$CsH_5(SeO_3)_3$	CsH5	*A1,A2,B*	X	16
$NaH_7(SeO_3)_4$	NaH7	*A1–A3,B*	X	17

[a] For the significance of symbols *A*...*E* see the text. *S* denotes the X-ray (X) or neutron (N) diffraction.

TABLE II
Average Se–O distances (Å) and O–Se–O angles (°) in selenites[a]

Type	*n*	*a*	*b*	*c*	*a–b*	*a–c*	*b–c*
A	14	1.64(1)	1.74(1)	1.75(1)	101(3)	100(3)	98(1)
B	17	1.66(1)	1.69(2)	1.76(2)	104(1)	102(2)	100(1)
C	1	1.647(2)	1.716(2)	1.726(2)	102.6(1)	102.1(1)	100.8(1)
D	3	1.69(1)	1.703(1)	1.72(1)	102.5(6)	101(2)	100(1)
E	1	1.662(1)	1.713(1)	1.731(1)	100.81(6)	102.63(6)	99.47(6)
	36	1.65(2)	1.71(3)	1.75(2)	103(2)	101(2)	99(2)
	108	–	1.70(5)	–	–	101(3)	–

[a] For the significance of symbols *a*...*b* and *a–b*...*b–c* see the text. The values in parentheses are e.s.d.'s of arithmetic means, *n* is the number of values used in calculation.

published lattice parameters and the atomic coordinates. All the distances and angles were recalculated and the most important data are given in Table II*. The SeO_3 formations are pyramidal with three different Se–O bonds. Distances Se–O (*a*, *b*, *c*) are denoted as *a*, *b*, *c*, angles O(*a*)–Se–O(*b*) as *a*–*b* etc. The criteria for labelling are: $a < b, c$, $b < c$, see Fig. 1. All SeO_3 formations have symmetry 1. The average values of SeO_3 formation ($n = 36$) are depicted in Fig. 1. Only one value of distances and angles is greater than the value $\overline{x} \pm 3\,\sigma$, namely the angle *a*–*b* of the compound HH.

Five types of selenites were found in the studied structures: $SeO(OH)_2$ – type *A* ($n = 14$), $SeO_2(OH)^-$ – type *B* ($n = 17$), $SeO(OH_{0.5})_2^-$ – type *C* ($n = 1$), $Se(OH_{0.5})_3^{0.5-}$ – type *D* ($n = 3$) and $SeO(OH)(OH_{0.5})^{0.5-}$ – type *E* ($n = 1$), see Table I.

3. HYDROGEN BONDS

Hydrogen bonding occurs whenever possible. The average values of distances and angles of the hydrogen bonds are given in Table III. $O^d...O^a$ lengths of H-bonds vary between 2.503 Å and 2.80 Å, giving average value 2.59(5) Å. This value correponds to a middle H-bond with the bond valence $s(O^d...H^a) = 0.25$ (Brown and Altermatt[18]). Five values of $O^d...O^a$ lengths are outside the interval $\overline{x} \pm 3\sigma$ (3 in HH, 1 in KH and LiH3, see Full Data Table III).

4. DISTORTION INDICES

The DISQ distortion indices according to Baur[19] are used for quantitative evaluation of deviation of SeO_3 formations from the average geometry. The DISQ index is defined by

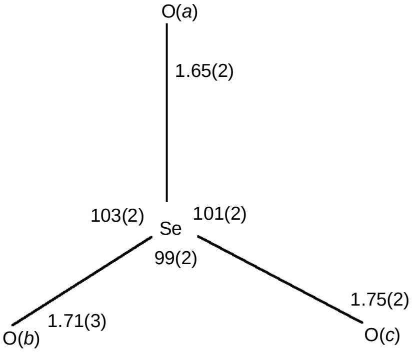

FIG. 1
Labelling scheme for the atoms in SeO_3 and average values of distances Se–O (Å) and angles O–Se–O (°)

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* Full Data Tables II and III can be obtained from the author.

TABLE III
Average distances (Å) and angles (°) of hydrogen bonds in selenites[a]

S	n	$Se^d–O^d$	$O^d–H^d$	$O^d...O^a$	$H^d...O^a$	$O^a–Se^a$	$Se^d–O^d–H^d$	$O^d–H^d...O^a$	$H^d...O^a–Se^a$	$Se^d–O^d–O^a$	$O^d–O^a–Se^a$
N	38	1.74(2)	1.03(3)	2.59(5)	1.57(5)	1.68(3)	112(2)	173(4)	118(6)	113(5)	118(7)
X	19	1.76(2)	–	2.63(8)	–	1.65(3)	–	–	–	113(9)	121(8)

[a] Superscripts *d* and *a* denote donor and acceptor atoms, *S* denotes the X-ray (X) or neutron(N) diffraction, *n* is the number of values used in calculation. The value in parentheses are e.s.d.'s of arithmetic means.

TABLE V
Values V/Z_{obs} and V/Z_{calc} (Å^3)

Symbol	HH	LiH	NaH	KH	RbH	CsH	CsLiH2	LiH3	NaH3	KH3	RbH3	CsH3	NH_4H3	TlH3	CsH5	NaH7
V/Z_{obs}	69.6	73.9	78.9	86.3	95.1	108.7	186.4	129.2	144.7	159.1	166.1	172.3	164.1	164.5	240.8	278.0
V/Z_{calc}	–	–	–	–	–	–	182.6	143.5	148.5	155.9	164.7	178.3	–	–	241.9	283.9

$$\mathrm{DISQ} = \left[\sum_n (T_n - X_n)^2 / \sum_n T_n^2\right] K \ , \qquad (1)$$

where the T_n values are the average values of distances Se–O (T_1 = 1.65, T_2 = 1.71, T_3 = 1.75) or of angles O–Se–O (T_1 = 103, T_2 = 101, T_3 = 99), the X_n values are the values of Se–O or O–Se–O of the individual SeO_3 formations (n = 1–3, X_1 = a or *a–b* etc.) and K is a constant (equal to 1 . 10^6 for distances and 1 . 10^5 for angles). The greater the index value, the more the formation differs from the average geometry. The average DISQ index for Se–O distances equals 190(132), the minimum index 6 has the RbH3lt *B1* formation, the maximum index 535 has CsH formation. The average DISQ index for O–Se–O angles equals 49(42), the minimum index 6 has the CsH3 *D1* formation, the maximum index 183 has HH formation. This index is greater than the $\bar{x} + 3\sigma$ value.

5. BOND VALENCES

The bond valences s are calculated according to Brown and Altermatt[18] from the relationship

$$s = \exp\left[(r_0 - r)/B\right] \ , \qquad (2)$$

where r is an interatomic distance (Å) and r_0 and B are calculated parameters r_0[Se(IV)–O] = 1.811 and B = 0.37. Ideally, Σs equals the value of the oxidation state of cation, in the Se(IV) case equals 4. The shorter the distance r, the greater is the bond valence expressed in terms of the bond valence unit. The average Σs(Se–O) value equals 4.03(9), the minimum value 3.85 has the RbH3lt *A4* formation, the maximum value 4.19 has NaH7 *A1* formation. All values are smaller than the $\bar{x} \pm 2\sigma$ values.

6. CONNECTING OF SeO_3 FORMATIONS

Connecting of SeO_3 formations in the structure are given in Table IV and can be described by the formulae mentioned in the same table.

Comparison of values V/Z_{obs} and V/Z_{calc} (Å^3) is interesting for the packing, where V is the volume of cell (Å^3) and Z is the number of formula units in the cell. The calculated values were obtained as the sum of the pertinent observed values, see Table V.

7. CORRELATIONS

Very good correlations are found between the ionic radii r of elements M (Å, ICSD, ref.[20]) and the values V/Z (Å^3). Correlations are described by the relations

TABLE IV
Connection of the SeO_3 formations. *A* = $SeO(OH)_2$, *B* = SeO_2OH^-, *C* = $SeO(OH_{0.5})_2^-$, *D* = $Se(OH_{0.5})_3^{0.5-}$, *E* = $SeO(OH)(OH_{0.5})^{0.5-}$

Compound	Connecting
H_2SeO_3	*A* type molecules are connected by four hydrogen bonds and constitute two-dimensional double layer parallel to the (100) plan → $\{SeO(OH)_2\}_{2\infty}$
$LiHSeO_3$	*B* type anions are linked together by hydrogen bonds forming spiral chains running in the [100] direction → $\{SeO_2OH^-\}_{1\infty}$
$NaHSeO_3$	*B* and *C* type anions are hydrogen bonded to form two different centrosymmetric dimers, which are connected to the layers → $\{[SeO_2OH^-]_2 + [SeO(OH_{0.5})_2^-]_2\}_{2\infty}$
$KHSeO_3$	*B* type anions are hydrogen bonded to form centrosymmetric dimers → $\{SeO_2OH^-\}_2$
$RbHSeO_3$	*B* type anions are hydrogen bonded to form centrosymmetric dimers → $\{SeO_2OH^-\}_2$
$CsHSeO_3$	*B* type anions are linked together by hydrogen bonds to form spiral chains in the [001] direction → $\{SeO_2OH^-\}_{1\infty}$
$CsLi(HSeO_3)_2$	*B* type anions are linked together by hydrogen bonds to form waved chains in the [100] direction → $\{SeO_2OH^-\}_{1\infty}$
$LiH_3(SeO_3)_2$	Molecules *A* and anions *B* are connected in turn by hydrogen bonds to form S-shaped chains in the [001] direction → $\{SeO(OH)_2 + SeO_2OH^-\}_{1\infty}$
$NaH_3(SeO_3)_2$	*D* type anions are hydrogen bonded to form a three-dimensional network →$\{Se(OH_{0.5})_3^{0.5-}\}_{3\infty}$
$KH_3(SeO_3)_2$	*E* type anions are hydrogen bonded to form chains in the [001] direction → $\{SeO(OH)(OH_{0.5})^{0.5-}\}_{1\infty}$
$RbH_3(SeO_3)_2$ht	There are two types of chains in the structure: one chain in [001] is built up of *A* molecules and the other in [100] of *B* anions linked by hydrogen bonds. These two types of chains are cross-linked by the other hydrogen bonds thus forming a three-dimensional network → $\{[SeO(OH)_2]_{1\infty} + [SeO_2OH^-]_{1\infty}\}_{3\infty}$
$RbH_3(SeO_3)_2$lt	There are two types of chains in the structure: one chain in [001] is built up of *A* molecules and the other in [100] of *B* anions linked by hydrogen bonds. These two types of chains are cross-linked by the other hydrogen bonds thus forming a three-dimensional network → $\{[SeO(OH)_2]_{1\infty} + [SeO_2OH^-]_{1\infty}\}_{3\infty}$
$CsH_3(SeO_3)_2$	Two different *D* anions form two different chains, which are interlinked to a three-dimensional network → $\{[Se(OH_{0.5})_3^{0.5-}]_{1\infty}\}_{3\infty}$
$NH_4H_3(SeO_3)_2$	Connecting analogous to RbH3
$TlH_3(SeO_3)_2$	Connecting analogous to RbH3
$CsH_5(SeO_3)_3$	The layers of *A* molecules are connected through the *B* anions and form a three-dimensional network → $\{[SeO(OH)_2]_{2\infty} + SeO_2OH^-\}_{3\infty}$
$NaH_7(SeO_3)_4$	The *A* molecules and the *B* anions are connected by hydrogen bonds to form a three-dimensional network → $\{SeO(OH)_2 + SeO_2OH^-\}_{3\infty}$

TABLE VI
Phase transitions

Symbol	Point group	Phase transitions, some properties
HH	222	piezoelectric[1]
LiH	222	piezoelectric, by DTA and DSC none phase transition (PT) between 103 and 413 K, minor transition starting at 415 K, followed by decomposition starting at 425 K, the absolute structure determined[2], by IR none PT between 77 and 298 K (ref.[6])
NaH	$2/m$	by NMR (IR) none PT between 133 and 336 (77 and 298) K (refs[3,6])
KH	$\bar{1}$	by EPR, IR and microscopic method none PT between 77 and 298 K (refs[4,6])
RbH	$\bar{1}$	by EPR and dielectric permeability (NMR and DTA) none PT between 123 and 353 (293) K (ref.[21]), by IR none PT between 77 and 298 K (ref.[6])
CsH	$mm2$	by IR none PT between 77 and 298 K, pyroelectric effect confirmed[6]
CsLiH2	222	piezoelectric, by NMR and dielectric permeability none PT between 134 and 393 K (ref.[7])
LiH3	$m \rightarrow 2/m$	ferroelectric from 293 to 383 K (melting point) with a large pyroelectric signal at 293 K ($\boldsymbol{P}_s$ is antiparallel to $\boldsymbol{c}^*$), absolute structure determined[22]. The ferroelectric (m) to paraelectric ($2/m$) PT is induced by pressure 2.1 GPa at 296 K (extrapolating to zero pressure T_c = 420 K) (ref.[23]). Thermal decomposition studied by TGA, DTA, X-ray: transformation from crystalline to amorphous state at 353 K (ref.[24])
NaH3	$m \leftarrow 1 \leftrightarrow 2/m$	the paraelectric α phase ($2/m$) has PT of the second order at 194.5 K into the ferroelectric β phase (1) and vice versa. β phase has PT of the first order at 100.6 K into the ferroelectric γ phase (m) and vice versa at 111 K. PT of γ to α phase is at 194.5 K (ref.[25])
NaD3	$m \leftarrow 2/m$	paraelectric ($2/m$) → ferroelectric (m) PT temperature is 266.6 K (ref.[26]). For $Na(D_xH_{1-x})_3$ see (ref.[27])
KH3	$1 \leftarrow mmm$	PT of the second order from paraelectric phase to the pyroelectric phase at 211.5 K (ref.[28]). The statistical model of PT was published[29]
RbH3	$2 \leftarrow 222$	PT of the nearly second order from the hight-temperature paraelectric phase ($P2_12_12_1$) to the low-temperature improper ferroelectric phase ($P2_1$) with the doubled-cell ($c_{lt} = 2c_{ht}$) at about 158 K (ref.[30]). Structure of low-temperature phase determined[12]
CsH3	$\bar{1} \rightarrow \bar{1}$	PT of the first order from an antiferroelectric low-temperature phase at 145 K to a paraelectric high-temperature one. Lt-phase has superstructure with $P\bar{1}$ symmetry and $c_{lt} = 2c_{ht}$ (ref.[31])
NH4H3	222	linear dielectric in the range 200–300 K (ref.[30])
TlH3	$2 \leftrightarrow \beta \leftrightarrow 222$	PT of the second order from α phase to β phase and vice versa at 56.4 K, PT of the first order from β phase to γ phase at 51.6 K and from γ phase to β phase at 52.9 K. All phases are piezoelectric, pyroelectric effect has been confirmed by γ phase with the doubled cell[15]
CsH5	$2/m$	studied by TGA, DTA, DSC, IR (ref.[16])
NaH7	m	studied by TGA, DTA, DSC, IR (ref.[32])

$$V/Z = 52.3 + 30.0r_{\mathrm{M}} \tag{3}$$

for LiH, NaH, KH, RbH, CsH, correlation coefficient r equals 0.93 and

$$V/Z = 105.772 + 39.982r_{\mathrm{M}} \tag{4}$$

for LiH3, NaH3, KH3, RbH3, CsH3, TlH3, r equals 0.99994.

8. PHASE TRANSITIONS

Only in the case of RbH3 the structures of high- and low-temperature phases are known. In other cases phase transitions have been confirmed by non-structure methods. The phase transitions and some properties of compounds are given in Table VI.

9. DEUTERATED SELENITES

The list of deuterated selenites is given in Table VII. All deuterated compounds are isomorphic with the native ones.

TABLE VII
Deuterated selenites[a]

Compound	S	Reference
$NaDSeO_3$	N	3
$RbDSeO_3$	NMR	21
$LiD_3(SeO_3)_2$	ε	23
$NaHD_2(SeO_3)_2$	N	33
$NaH_2D(SeO_3)_2$	N	34
$Na(D_xH_{1-x})_3(SeO_3)_2$	ε	27
$NaD_3(SeO_3)_2$	X	35,26
$KD_3(SeO_3)_2$	N	10
$RbD_3(SeO_3)_2$	X, N, ε	35,36
$CsD_5(SeO_3)_3$	IR	16

[a] S denotes studies by the X-ray (X) or neutron (N) diffraction, nuclear magnetic resonance (NMR), dielectric measurement (ε) or infrared spectroscopy (IR).

10. DISCUSSION

The Se atoms can be described as being sp^3 hybridised, the lone electron pair repelling the three bonding pairs and thus reducing the bond angles from the tetrahedral value of 109.47° to the mean value of 101(3)°. This value is greater than the one equal to 98(4)° for analogous TeO_3 formations (n = 12, calculated from data published by Trömel[37]). From comparison of the V/Z_{obs} values with the V/Z_{calc} values follows that the V/Z_{obs} values of single components (e.g. $LiHSeO_3$ and $CsHSeO_3$) are not affected by packing into more composite molecules (e.g. $LiCsH_2(SeO_3)_2$). The correlation between radii r_M and the values V/Z of the MH compounds was to be expected. The correlation of the MH3 compounds is consistent with the comparison of the values V/Z. The structure of H_2SeO_3 deviates in the majority of indices from the average values (the angle a–b, 3 O^d...O^a distances and the O–Se–O DISQ index).

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