

Molecular Spectra and X-Ray Study of the Alkali Hydrogen Selenites $M\text{HSeO}_3$

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A study of the molecular spectra confirmed that the protons are localized close to one of the oxygen atoms in the hydrogen bonds in the compounds LiHSeO_3 , KHSeO_3 , RbHSeO_3 , and CsHSeO_3 . The character of the NaHSeO_3 spectrum indicates that part of the protons are in ordered positions, which is in agreement with the results of the structural analysis published earlier. Down to a temperature of 77 K, no phase transition connected with a change in the proton ordering was found during the study of the molecular spectra of the test compounds. X-ray diffraction confirmed structural isomorphy of RbHSeO_3 with KHSeO_3 , with the $P\bar{1}$ space group, $a = 5.192(2)$ Å, $b = 5.876(3)$ Å, $c = 6.578(3)$ Å, $\alpha = 110.8(1)^\circ$, $\beta = 94.5(1)^\circ$, $\gamma = 88.8(1)^\circ$, $Z = 2$. CsHSeO_3 belongs to the orthorhombic system, with the $Pna2_1$ space group, $a = 6.431(3)$ Å, $b = 14.031(7)$ Å, $c = 4.820(2)$ Å, $V = 434.9$ Å³, $Z = 4$. The structure of this compound was determined using X-ray diffraction for 1053 independent reflections with $R = 0.071$. The independent part of the unit cell contains the Cs^+ cation, to which 10 oxygen atoms are coordinated from 6 different HSeO_3^- anions and the pyramidal HSeO_3^- anion. The hydrogen selenite anions are hydrogen bonded to form spiral chains along the c -axis. The Se-O(H) distance corresponds to an asymmetrical arrangement of the hydrogen bond. The space group found and the asymmetrical position of the proton in the hydrogen bond are in agreement with the pyroelectric behavior of the compound and do not exclude ferroelectric properties of this compound even at laboratory temperature. © 1988 Academic Press, Inc.

Introduction

Studies of the physical properties and crystal structures of alkali hydrogen selenites $M\text{HSeO}_3$ have been stimulated by the discovery of ferroelectric and antiferroelectric properties of the alkali trihydrogen selenites $M\text{H}_3(\text{SeO}_3)_2$ ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}$,

Cs) and their deuterated analogs. Cody *et al.* (1) assumed, on the basis of the position and shape of the vibrational bands, that the protons of the hydrogen bonds in LiHSeO_3 and NaHSeO_3 are in ordered positions at laboratory temperature, whereas those in KHSeO_3 and CsHSeO_3 are dynamically disordered. They explained the changes in

the low-temperature spectra of $KHSeO_3$ and $CsHSeO_3$ by a phase transition of the order-disorder type.

However, these conclusions are in agreement with X-ray diffraction study only for $LiHSeO_3$ (2). The results of structural analysis (3, 4) and NMR (5, 6) indicate that only part of the protons is in ordered positions. On the other hand, neutron diffraction (7) and NMR (8) suggest that all the protons are in ordered positions in $KHSeO_3$, even at laboratory temperature and exclude a phase transition down to a temperature of 77 K. Results similar to those for $KHSeO_3$ have been obtained by NMR of the isostructural compound $RbHSeO_3$ (8).

In view of the above facts, we devoted the present work to a repeated study of the molecular spectra of the alkali hydrogen selenites $MHSeO_3$, with a particular emphasis on the behavior of the protons in the hydrogen bonds and the possibility of an order-disorder phase transition at lower temperatures. To compliment the interpretation of the vibrational spectra by factor-group analysis and to discuss possible physical properties, $RbHSeO_3$ and $CsHSeO_3$ crystals were studied using X-ray diffraction.

Experimental

The hydrogen selenites $MHSeO_3$ were prepared by the reaction of an aqueous solution of selenious acid with the alkali carbonates followed by free crystallization from the solution. The crystals obtained were washed with chloroform and dried over concentrated H_2SO_4 at 273 K. Transparent, well-developed crystals were obtained; those of the potassium, rubidium, and cesium salts were strongly hygroscopic and thermolabile. The selenium content was determined iodometrically (9). The infrared absorption spectra were obtained on a Perkin-Elmer 684 instrument with a 3600 IR on-line data station, from 4000 to 350

cm^{-1} in nujol mulls and from 4000 to 1500 cm^{-1} in triprene suspension using KBr or NaCl windows. The samples were placed in a low-temperature cell and the measurements were carried out at laboratory temperature and at the liquid nitrogen temperature (77 K). The absorption maxima values were determined with a precision of ± 1 cm^{-1} for narrow bands and ± 20 cm^{-1} for wide bands.

The Raman spectra of polycrystalline materials were measured at laboratory temperature on a Coderg LRDH-850 instrument with a Tracor Northen on-line computer, from 50 to 1500 cm^{-1} . The green line of a Coherent CR-3 argon ion laser was used for excitation. The values of the scattering maxima were determined with a precision of ± 2 cm^{-1} .

Single crystals of $RbHSeO_3$ and $CsHSeO_3$ with dimensions of $0.25 \times 0.25 \times 0.4$ mm and a sphere-shaped crystal with a diameter of 0.20 mm were placed in Lindenmann capillaries and the Weissenberg and precession photographs were obtained using $CuK\alpha$ (Ni-filter) or $MoK\alpha$ (Zr-filter) radiation. The lattice parameters of $RbHSeO_3$ were obtained from the Weissenberg and precession photographs, those of $CsHSeO_3$ were refined from 16 independent diffractions on a Syntex P₂₁ four-circle diffractometer ($MoK\alpha$, graphite-monochromated). Analogously, the integral intensities were obtained on the Syntex P₂₁ diffractometer using the $\omega - 2\theta$ scan method and the Mo radiation, together with the appropriate standard deviations ($\lambda = 0.71069$ Å, $\mu = 17.47$ mm⁻¹, $T = 295 \pm 1$ K), in a range of $h = 0-10$, $k = 0-22$, $l = -7-0$ and up to a value of $\sin \theta/\lambda = 0.704$ Å⁻¹. The stability of the crystals was checked by monitoring three standard diffractions after 30 measured reflections. During the measurement on the first crystal, the intensities of the standard reflections increased by an average of 44% (a lamp with a voltage of 46 kV and a current of 20 mA; exposure time,

40 hr). Therefore, another crystal was measured independently and the reference reflection intensities were increased by an average of 128% (exposure time, 105 hr). The differences in the lattice parameters obtained for these two crystals were less than $\pm 1 \sigma$. The structure was determined from the measurements on the former crystal. The reflection intensities were corrected for the above increase, for absorption using the semiempirical method (10) on the basis of 15 symmetrically coupled reflections and their ϕ -scan and a correction was made using the Lp-factor. Of the 1053 independent reflections, 97 were unobserved with $|F_o| < 3.29\sigma(|F_o|)$. The tabulated values of the atomic scattering factors and the correction factors for anomalous dispersion for Se and Cs were used (11). The position of the Cs atom was obtained from the Patterson map and the positions of the other atoms were determined from calculated F -maps. The hydrogen atom position could not be found in the ΔF -map. All positional parameters, coefficients of anisotropic temperature factors, and the coefficient of isotropic secondary extinction were refined using the full-matrix least-squares method. The minimized function had the form, $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma^2(|F_o|) + 0.0009|F_o|^2)$. The refinement yielded $R = 0.071$, $R_w = 0.070$, $(\Delta/\sigma)_{\max} = 0.18$. The maximal and minimal heights on the ΔF -map amounted to 3.0 and $-6.3 \text{ e}\text{\AA}^{-3}$, respectively. The programs CAMEL JOCKEY (10), SHELX 76 (12), and ORTEP (13) were employed with ICL 4-72 and Siemens 7536 computers. The lists of observed and calculated structure factors, as well as the anisotropic thermal parameters, are available from the authors on request.

The densities of the two salts were determined pycnometrically, obtaining $D_m = 3.78(1)$ and $D_x = 3.791$ for RbHSeO_3 and $D_m = 4.06(2)$ and $D_x = 3.984 \text{ Mgm}^{-3}$ for CsHSeO_3 .

Results and Discussion

Molecular Spectra

The IR absorption spectra obtained at laboratory temperature in nujol mulls are given in Fig. 1; the Raman spectra are given in Fig. 2. The values of the absorption and scattering maxima are listed in Tables I to V. Narrow bands corresponding to the HSeO_3^- anion with the C_s symmetry have been found in the molecular spectra of LiHSeO_3 , KHSeO_3 , RbHSeO_3 , and CsHSeO_3 . It is evident from the positions and shapes of the absorption bands that the protons in the hydrogen bonds of the crystals are localized close to one of the oxygen atoms, even at laboratory temperature. This corresponds to the results of the structural analy-

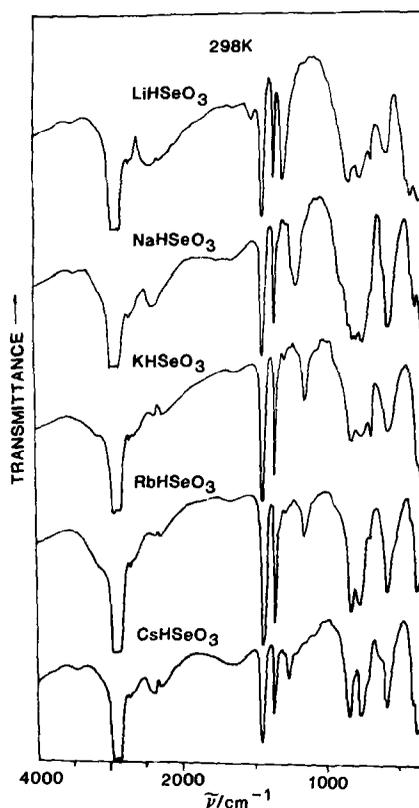
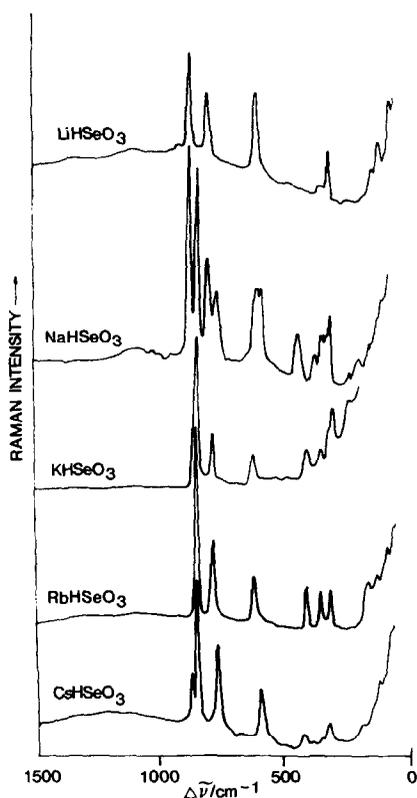


FIG. 1. Infrared absorption spectra of MHSeO_3 at 298 K.

FIG. 2. Raman spectra of $M\text{HSeO}_3$ at 298 K.

sis of LiHSeO_3 and KHSeO_3 . In the LiHSeO_3 structure (2), the HSeO_3^- anions have been found to be hydrogen-bonded with a bond length of 2.62 Å to form spiral chains. In the KHSeO_3 structure (7), two HSeO_3^- anions form centrosymmetrical dimers $[\text{HSeO}_3]_2^{2-}$, hydrogen bonded with a bond length of 2.75 Å.

The absorption bands exhibit pronounced splitting into doublets in the NaHSeO_3 spectra, which corresponds to the results of structural analysis (3, 4) and NMR (5, 6). Two nonequivalent $[\text{HSeO}_3]_2^{2-}$ species have been found in the structure of this salt, with different behavior of the protons in the hydrogen bonds. The protons are in ordered positions in the dimer with hydrogen bonds characterized by a length of 2.59 Å, while in the other dimer, with a bond length of 2.66 Å, the protons exhibit a tunnel effect.

Although one-half of the protons in NaHSeO_3 occurs in disordered positions, the bands obtained are relatively narrow, compared with the $M\text{H}_3(\text{SeO}_3)_2$ compounds with similar proton arrangements, which

TABLE I
VIBRATIONAL SPECTRA OF LiHSeO_3 (cm^{-1})

Infrared spectra		Raman spectrum	Assignment
298 K	77 K		
2820 sb	2850 sb	—	Hydrogen bond stretching
2500 sb	2500 sb		
1540 wb	1565 wb	—	$\delta(\text{SeOH})$
1318 vs	1335 vs		
868 vs	874 vs	860 vs	$\nu_s(\text{SeO}_2)$
835 vs	841 vs	792 m	$\nu_{as}(\text{SeO}_2)$
796 vs	796 vs		
619 s	625 s	592 s	$\nu(\text{SeOH})$
484 sh	490 sh	480 vw	$\nu(\text{Li-O})$
459 vs	467 vs	—	$\delta(\text{SeO}_2)$
419 m	426 m		
409 sh	413 sh		
356 w	365 w	354 w	$\delta_{as}(\text{HSeO}_3)$
—	—	314 w	$\delta_s(\text{HSeO}_3)$
—	—	248, 148, 126, 98, 82	External vibrations

TABLE II
VIBRATIONAL SPECTRA OF NaHSeO₃ (cm⁻¹)

Infrared spectra		Raman spectrum	Assignment
298 K	77 K		
2850 sb	2850 sb	—	Hydrogen bond stretching
2410 mb	2460 mb		
1700 vw b	1700 wb		
1256 sh	1266 s		δ(SeOH)
1231 m	1241 s	—	
920 sh	938 s		ν _s (SeO ₂)
867 sh	852 vs	868 vs	
843 vs	838 vs	838 s	ν _{as} (SeO ₂)
819 vs	814 vs	800 m	
777 vs	777 vs	770 m	ν(SeOH)
613 s	617 vs	616 m	
598 sh	602 sh	598 m	δ(SeO ₂)
449 sh	449 sh	448 w	
426 m	427 m		δ _{as} (HSeO ₃)
376 m	385 m	382 w	
352 w	352 w	350 w	δ _s (HSeO ₃)
—	—	332 sh	
—	—	324 m	External vibrations
—	—	208, 122, 78	

can be explained by different interconnection of the basic building units through a system of hydrogen bonds. In MH₃(SeO₃)₂, the HSeO₃⁻ and H₂SeO₃ species are connected by hydrogen bond chains. On the other hand, the [HSeO₃]₂⁻ dimers in NaH

SeO₃ are relatively isolated and thus significant coupling of vibrational motions of several anions and consequent distribution of the frequencies for each mode cannot occur.

A factor-group analysis has further been

TABLE III
VIBRATIONAL SPECTRA OF KHSeO₃ (cm⁻¹)

Infrared spectra		Raman spectrum	Assignment
298 K	77 K		
2900 sh	2900 sh	—	Hydrogen bond stretching
2340 mb	2340 mb		
1650 wb	1650 wb		
1173 m	1190 m	—	δ(SeOH)
851 vs	848 vs	844 vs	
790 vs	781 vs	780 m	ν _{as} (SeO ₂)
615 s	612 s	620 w	
412 s	412 s	413 w	ν(SeOH)
371 m	370 m	356 w	
—	—	327 m	δ(SeO ₂)
—	—	178, 130, 110, 80	
—	—		δ _{as} (HSeO ₃)
—	—		
—	—		δ _s (HSeO ₃)
—	—		
—	—		External vibrations
—	—		

TABLE IV
VIBRATIONAL SPECTRA OF $RbHSeO_3$ (cm^{-1})

Infrared spectra		Raman spectrum	Assignment
298 K	77 K		
3000 mb	3000 mb	—	Hydrogen bond stretching
2350 wb	2350 wb		
1700 wb	1700 wb		
1173 w	1195 m	—	$\delta(\text{SeOH})$
853 vs	854 vs	846 vs	$\nu_3(\text{SeO}_2)$
796 s	788 s	782 m	$\nu_{as}(\text{SeO}_2)$
611 s	618 s	618 w	$\nu(\text{SeOH})$
404 m	403 m	410 w	$\delta(\text{SeO}_2)$
365 m	371 m	356 w	$\delta_{as}(\text{HSeO}_3)$
—	—	316 w	$\delta_s(\text{HSeO}_3)$
—	—	174, 138, 98, 72	External vibrations

carried out on the basis of the crystallographic data (Table VI) for the crystals of the lithium to cesium salts, obtaining the following irreducible representations for the crystal internal vibrations:

$$\text{LiHSeO}_3: \Gamma_{\text{vib}}^{\text{int}} = 9A(\text{R}) + 9B(\text{R,IR}) \\ + 9B_2(\text{R,IR}) + 9B_3(\text{R,IR})$$

$$\text{NaHSeO}_3: \Gamma_{\text{vib}}^{\text{int}} = 18g(\text{R}) + 18g(\text{R}) \\ + 18A_u(\text{IR}) + 18B_u(\text{IR})$$

$$\text{K(Rb)HSeO}_3: \Gamma_{\text{vib}}^{\text{int}} = 9A_g(\text{R}) + 9A_u(\text{IR})$$

$$\text{CsHSeO}_3: \Gamma_{\text{vib}}^{\text{int}} = 9A_1(\text{R,IR}) + 9A_2(\text{R}) \\ + 9B_1(\text{R,IR}) + 9B_2(\text{R,IR})$$

TABLE V
VIBRATIONAL SPECTRA OF $CsHSeO_3$ (cm^{-1})

Infrared spectra		Raman spectrum	Assignment
298 K	77 K		
2800 mb	2800 mb	—	Hydrogen bond stretching
2430 mb	2420 mb		
1660 wb	1710 wb		
1277 w	1291 m	—	$\delta(\text{SeOH})$
	926 w	872 w	
849 vs	849 vs	850 vs	$\nu_3(\text{SeO}_2)$
820 sh	821 sh		
	785 sh	782 sh	$\nu_{as}(\text{SeO}_2)$
771 vs	768 vs	766 m	
606 sh	609 sh		
592 s	595 s	594 m	$\nu(\text{SeOH})$
422 sh	426 m	430 w	$\delta(\text{SeO}_2)$
414 m	414 m	420 sh	
387 m	389 w	358 vw	$\delta_{as}(\text{HSeO}_3)$
—	—	324 w	$\delta_s(\text{HSeO}_3)$
—	—	198, 150, 126, 82	External vibrations

TABLE VI
 CRYSTALLOGRAPHIC DATA FOR $MHSeO_3$

	$LiHSeO_3^a$	$NaHSeO_3^b$	$KHSeO_3^c$	$RbHSeO_3$	$CsHSeO_3$
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
Lattice parameters	$a = 5.058 \text{ \AA}$ $b = 11.187 \text{ \AA}$ $c = 5.221 \text{ \AA}$ $V = 295.4 \text{ \AA}^3$ $Z = 4$	$a = 21.980 \text{ \AA}$ $b = 5.791 \text{ \AA}$ $c = 10.280 \text{ \AA}$ $\beta = 105.11^\circ$ $V = 1263.2 \text{ \AA}^3$ $Z = 16$	$a = 5.003 \text{ \AA}$ $b = 5.726 \text{ \AA}$ $c = 6.729 \text{ \AA}$ $\alpha = 108.95^\circ$ $\beta = 107.31^\circ$ $\gamma = 91.27^\circ$ $V = 172.6 \text{ \AA}^3$ $Z = 2$	$a = 5.192(2) \text{ \AA}$ $b = 5.876(3) \text{ \AA}$ $c = 6.578(3) \text{ \AA}$ $\alpha = 110.8(1)^\circ$ $\beta = 94.5(1)^\circ$ $\gamma = 88.8(1)^\circ$ $V = 187.0 \text{ \AA}^3$ $Z = 2$	$a = 6.431(3) \text{ \AA}$ $b = 14.031(7) \text{ \AA}$ $c = 4.820(2) \text{ \AA}$ $V = 434.9 \text{ \AA}^3$ $Z = 4$
Factor group	D_2	C_{2h}	C_i	C_i	C_{2v}
Site symmetry of the anion	C_1	C_1	C_1	C_1	C_1

^a Ref. (1).

^b Ref. (2).

^c Ref. (7).

(activity in the Raman and infrared spectra is specified in the parentheses). The results of the factor-group analysis have confirmed the multiplet character of the vibrational bands for $LiHSeO_3$, $NaHSeO_3$, and $CsHSeO_3$, caused by coupling of the vibrational motion of the species in the unit cell; as expected, the bands for $KHSeO_3$ and $RbHSeO_3$ are singlets.

To verify the possibility of phase transitions, IR spectra of $MHSeO_3$ were obtained at the liquid nitrogen temperature (Fig. 3, Tables I to V). The changes in the low-temperature IR spectra are mainly caused by the temperature effect leading to narrowing and partial separation of the bands. However, no change corresponding to a new proton arrangement connected with a phase transition was found in the spectra within the studied temperature range, 298 to 77 K. This finding is in agreement with the results of measurements by other methods, published for $LiHSeO_3$ (2), $NaHSeO_3$ (4, 5), $KHSeO_3$ (7, 8), and $RbHSeO_3$ (8). The differences in the spectrum character, primarily for the potassium and cesium salts, published by Cody *et al.* (1), are probably

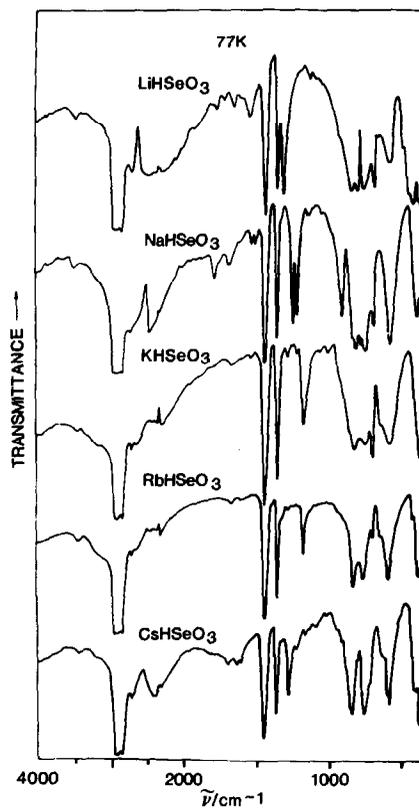


FIG. 3. Infrared absorption spectra of $MHSeO_3$ at 77 K.

TABLE VII

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC PARAMETERS FOR THE NONHYDROGEN ATOMS, WITH STANDARD DEVIATIONS IN PARENTHESES

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^4$) ^a
Cs	-0258(1)	1505(1)	0	265(3)
Se	0116(1)	3688(1)	5223(5)	211(5)
O1	2064(13)	4602(7)	4797(46)	335(48)
O2	1679(12)	2742(7)	4749(35)	282(40)
O3	-0334(18)	3745(11)	8535(30)	303(47)

$$^a U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

caused by unsuitable use of the KBr pellet technique with which conversion to diselenite occurs, especially for heavier salts.

The region of deformation vibrations of the Se-O-H group (1170 – 1320 cm^{-1}) is interesting in the $MHSeO_3$ spectra. The frequency δ (SeOH) correlates with the H bond length and with the thermal stabilities toward conversion into $M_2Se_2O_5$ (14). On cooling to 77 K, the absorption maxima shift by 10 to 20 cm^{-1} toward higher wavenumbers; an analogous shift has been observed for the torsion vibration γ (SeOH). This phenomenon can be explained by an increase in the hydrogen bond stability independence on a decrease in the temperature.

The character and temperature behavior of the valence vibrational bands of the hy-

drogen bond are the same as with the other alkali selenites of the type $MH_3(SeO_3)_2$ (15, 16).

Crystallographic Study

The Weissenberg and precession photographs have confirmed the triclinic symmetry of $RbHSeO_3$ and the fact that it is isostructural with $KHSeO_3$, as assumed on the basis of NMR (8). The $CsHSeO_3$ compound belongs to the orthorhombic system; however, it is impossible to distinguish between the $Pna2_1$ and $Pnma$ space groups on the basis of systematic absent reflections $0kl$: $k + l = 2n$; $h0l$: $h = 2n$. As compounds with the noncentrosymmetrical space group $Pna2_1$ satisfy the conditions for the presence of a spontaneous polarization vector and thus for pyroelectric or ferroelectric behavior, the $CsHSeO_3$ compound was subjected to X-ray structural analysis.

The principal crystallographic data for $RbHSeO_3$ and $CsHSeO_3$ are given in Table VI, together with the data for the other hydrogen selenites. The results of X-ray structural analysis of $CsHSeO_3$ are listed in Table VII (the final values of the atomic parameters) and Table VIII (interatomic distances and angles). The atomic arrangement is represented in Fig. 4 and the molecule with the cesium atom surroundings in

TABLE VIII
INTERATOMIC DISTANCES (\AA) AND ANGLES ($^\circ$)

Ionic bond (up to 5 \AA)			
Cs-O(2)	3.13(1)	Cs-O(2 ⁱⁱ)	3.31(1)
Cs-O(2 ⁱ)	3.20(1)	Cs-O(3 ^{iv})	3.36(1)
Cs-O(3 ⁱⁱ)	3.22(1)	Cs-O(1 ^v)	3.370(9)
Cs-O(3 ⁱⁱⁱ)	3.26(2)	Cs-O(2 ^{iv})	3.38(1)
Cs-O(1 ⁱ)	3.27(2)	Cs-O(1 ^v)	3.42(2)
Covalent bond			
Se-O(1)	1.805(8)	O(1)-Se-O(2)	97.5(5)
Se-O(2)	1.680(8)	O(2)-Se-O(3)	106.2(7)
Se-O(3)	1.624(15)	O(1)-Se-O(3)	101.5(9)

Note. Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (ii) $x, y, z - 1$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - 1$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$.

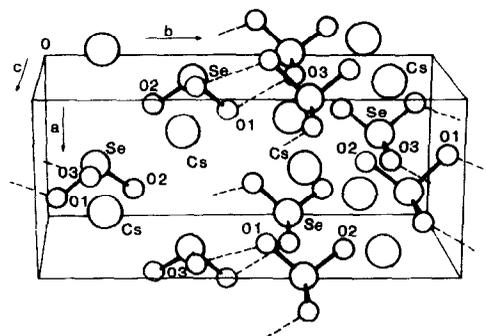


FIG. 4. Particle arrangement in the $CsHSeO_3$ unit cell. Only the atoms located inside the unit cell are marked. The covalent bonds are marked by solid lines, the hydrogen bonds by dashed lines.

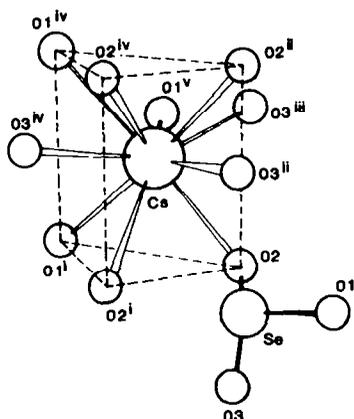


Fig. 5. The HSeO_3^- anion and the surroundings of the cesium atom. The trigonal prism from which the cesium coordination polyhedron is derived is shown by dashed lines. The covalent layers are denoted by solid wedges, the ionic layers by empty wedges.

Fig. 5. The HSeO_3^- anion has a pyramidal arrangement with the Se atom in the apex, with one longer Se–O(1)H bond and two shorter Se–O (2, 3) bonds. The HSeO_3^- anions are hydrogen bonded to form spiral chains along the [001] direction. The distance of the oxygen atoms O(1)–O(3^{vi}) ($V_i = -x, 1 - y, z - \frac{1}{2}$) belonging to the hydrogen bond amounts to 2.64(2) Å. Similar spiral chains have been found for LiHSeO_3 , with an O–O distance of 2.62 Å (2). Around the cesium atom, 10 oxygen atoms have been found with Cs–O distances ranging from 3.13 to 3.42 Å. Other oxygen atoms are at distances greater than 5 Å. The coordination polyhedron of cesium can be derived from a trigonal prism with the cesium atom in one rectangular face. Two oxygen atoms are located outside this wall and a single oxygen atom lies outside each of the two other rectangular faces. The Cs–O distances are in agreement with the values found for the compounds $\text{CsH}_3(\text{SeO}_3)_2$ (17) and $\text{CsH}_5(\text{SeO}_3)_3$ (18). However, the coordination environment of the cesium atom differs for these compounds. The Cs–O ionic bonds then connect the hydrogen se-

lenite chains into a three-dimensional network.

For the hydrogen bond with the $\text{O} \cdots \text{O}$ distance equal to 2.64 Å, a dynamically disordered, asymmetrically localized proton is assumed. This assumption is in agreement with the results of study of the vibrational spectra of this and other substances. The increase in the reflection intensities during the X-ray measurements was also not accidental, but probably reflected changes in the ferroelectric domain structure of the studied substance during the measurement. This change depended on the irradiation time (19). The *R*-factors have also been calculated for the structures of the two enantiomers, but they are not significantly different. This is apparently caused by an only 7% electron density on the O3 atoms which causes the structure to belong to the non-centrosymmetrical space group $Pna2_1$. The other atoms, Cs, Se, O1, and O2, are almost located in the 4c positions of the centrosymmetrical space group $Pnam$. For this reason, the absolute structure of the substance has not been determined.

The values of the interatomic distances and the coordination number of cesium are in agreement with the calculated bonding forces (20) (bond valences): For the sum of the Se–O bonding forces, $s = 4.099$ is obtained (instead of the theoretical value of 4) and for the sum of the Cs–O forces $s = 0.966$ (instead of unity). The values $s(\text{O}–\text{H}) = 0.773$ and $s(\text{H} \cdots \text{O}) = 0.227$ have been obtained for the hydrogen bond $\text{O}–\text{H} \cdots \text{O}$.

The crystal polar point group, i.e., a necessary condition for the presence of the spontaneous polarization vector and thus for the possibility of pyroelectric or ferroelectric properties, is satisfied with the MHSeO_3 compounds studied, only for CsHSeO_3 with the space group $Pna2_1$. A pyroelectric effect has been confirmed with this compound by measurement of changes in polarization on a plate cut from a large

crystal parallel with the (001) plane, within a temperature range of 293 to 393 K (A. Glanc, Physical Institute, Czechoslovak Academy of Sciences, Czechoslovakia, personal communication). Experiments are being carried out at present to verify the ferroelectric behavior of this salt.

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