

The ^{77}Se High-Resolution NMR in the Single Crystals of Potassium and Rubidium Hydrogen Selenites

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High-resolution ^{77}Se NMR spectra in single crystals of potassium and rubidium hydrogen selenites have been studied using the cross-polarization method. The chemical shift tensors of selenium nuclei are determined from the angular dependences of the position of lines relative to liquid H_2SeO_4 . The parameters of the tensors are typical for the HSeO_3^- configuration. The spectra are measured at different temperatures to search for the phase transitions. No phase transitions were found, confirming our previous results. © 1989 Academic Press, Inc.

The ^{77}Se high-resolution NMR spectra in single crystals have been studied earlier for the selenious acid and the salts of selenious acid—trihydrogen selenites $\text{MH}_3(\text{SeO}_3)_2$ (1-4). The parameters of the ^{77}Se chemical shielding tensor for the pyramidal SeO_3 group were determined from angular dependences of the ^{77}Se chemical shifts relative to liquid H_2SeO_4 .

Two significantly different ^{77}Se chemical shielding tensors were found for every crystal of the trihydrogen selenite family. An attempt was made to assign the experimental tensors to the structure. The structures of the trihydrogen selenites in the ordered phases can be described as being composed of hydrogen-bonded chains of H_2SeO_3 molecules and HSeO_3^- ions. It may be expected that the difference in the hydrogen-bond network around selenium atoms in H_2SeO_3 molecules and HSeO_3^- ions results in different degrees of SeO_3 group distortion and, consequently, in different ^{77}Se chemical shielding tensors.

The two experimentally determined chemically shielding tensors of the trihydrogen selenite crystals correspond to HSeO_3^- and H_2SeO_3 configurations, respectively. It will be a good idea to find the criterion for the assignment of the experimental ^{77}Se chemical shift tensors to the specific configurations. In previous papers (1-4) such an assignment was carried out from the analysis of the asymmetry parameters η or shielding anisotropy $\Delta\sigma$.

Studies of ^{77}Se NMR spectra in crystals with phase transitions have shown that these experiments can give useful information about the phase transition mechanism (3, 4). In our study of phase transitions in crystals of the hydrogen selenite family MHSeO_3 we have used ^{77}Se spectra along with ^1H , ^2D , and alkali ion NMR spectra.

At present the crystal structures of hydrogen selenites of lithium (5), sodium (6, 7), potassium (8), and rubidium (9) have been studied. Their unit cells consist of alkali ions and of pyramidal SeO_3 groups in-

terlinked by hydrogen bonds. The structural parameters of SeO_3 groups are similar in the crystals of both families (MHSeO_3 and $\text{MH}_3(\text{SeO}_3)_2$) and depend on the proton position in the hydrogen bonds. Thus, a pure Se-O bond is about 1.65 Å in length whereas Se-OH bond is about 1.75 Å. For the disordered case the Se-O bond length is approximately 1.70 Å (10).

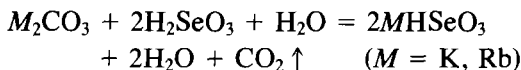
There are some typical peculiarities in the structures and properties of the MHSeO_3 hydrogen selenites. The first is the existence of hydrogen-bonded centrosymmetric dimers $(\text{HSeO}_3^-)_2$. Such dimers are found in the sodium, potassium, and rubidium salts. The only known exception is the LiHSeO_3 , whose crystal structure consists of hydrogen-bonded spiral chains of HSeO_3^- ions.

The second peculiarity of hydrogen selenites, in comparison with trihydrogen selenites, is the exclusive presence in the structure of HSeO_3^- ions. So, if ^{77}Se chemical shift tensors are studied in single crystals of MHSeO_3 with the different alkali ions, these tensors will result from HSeO_3^- exclusively. The parameters for the experimental tensors of the HSeO_3^- ion may be used to analyze these tensors. This can verify the corrections of the earlier assignment of tensors to the spectra of $\text{MH}_3(\text{SeO}_3)_2$.

In the present paper ^{77}Se NMR spectra are measured using single crystals of KHSeO_3 and RbHSeO_3 . Earlier we studied these crystals by ^1H and ^2D NMR (11) and ESR (12) methods. We have found the triclinic symmetry and the isomorphism of both crystals. The parameters of hydrogen bonds also have been determined. Now we set out to find the parameters of the ^{77}Se chemical shielding tensor and to carry out a temperature measurement to search a phase transition.

Experimental

Potassium and rubidium hydrogen selenites were prepared by the reaction



Single crystals were grown by evaporation from saturated solutions close to room temperature.

The ^{77}Se high-resolution NMR spectra were obtained using the cross polarization of ^{77}Se nuclei (natural abundance 7.5%) by protons with a Bruker pulse spectrometer operating at 90.02 MHz for ^1H and at 17.187 MHz for ^{77}Se . A ^1H rotating radio frequency field of 10 G was employed in the experiments. The linewidths of separate lines in the ^{77}Se NMR spectrum were about 100 Hz. To determine the magnetic shielding tensor of ^{77}Se nuclei we chose three mutually orthogonal axes X , Y , Z that were based on the crystal habit and triclinic symmetry of the unit cell (8). The crystals of KHSeO_3 and RbHSeO_3 possess a cleavage plane (the 001 plane). Thus, the Z -axis was chosen perpendicular to this cleavage plane, the X -axis was chosen parallel to the a -axis, and the Y -axis was situated in the (001) plane, perpendicular to the X and Z axes. The crystal habit and the axis system are described in detail in (11).

NMR spectra were taken every 10° to study the angular dependences of the line shifts relative to liquid H_2SeO_4 at the rotation of the single crystal samples about X , Y , and Z . The experimental data were analyzed using the Volkoff method (13).

Results and Discussion

The crystal structures of KHSeO_3 and RbHSeO_3 have been determined by neutron diffraction and X-ray (8, 9) methods. The crystals were found to be isomorphous, as was predicted from NMR and ESR data. They have triclinic unit cells with the centrosymmetric point group $P\bar{1}$ and the parameters $a = 5.003$ Å, $b = 5.726$ Å, $c = 6.729$ Å for KHSeO_3 and $a = 5.231$ Å, $b = 5.903$ Å, $c = 7.748$ Å for RbHSeO_3 .

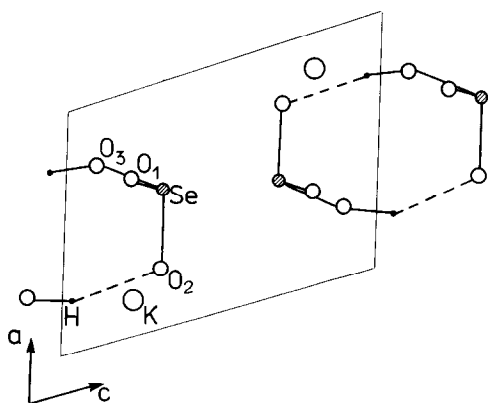


FIG. 1. The dimers $[\text{HSeO}_3]_2$ of KHSeO_3 crystals projected on the (ac) plane. Dotted lines indicate hydrogen bonds.

The unit cell of each crystal is found to be very small and contains two formula units. The structure consists of HSeO_3^- ions form-

ing centrosymmetric dimers $[\text{HSeO}_3]_2$ (Fig. 1). The HSeO_3^- ion is pyramidal, with two shorter Se-O bonds and one longer Se-OH bond. In the crystal KHSeO_3 the Se-O(1) bond length is 1.649 Å, Se-O(2) is 1.674 Å, and Se-O(3) is 1.748 Å. In RbHSeO_3 , Se-O(1) is 1.681 Å, Se-O(2) is 1.660 Å, and Se-O(3) is 1.781 Å. Protons are found ordered in hydrogen bonds in a single minimum potential well near O(3) and this extends the Se-O(3) bond length in comparison with the other. Disorder is not observed (8, 11).

With respect to the ^{77}Se NMR spectra, we observed only one spectral line in all orientations of the crystals relative to the magnetic field. The angular dependences of the position of the ^{77}Se NMR lines in KHSeO_3 and RbHSeO_3 are shown in Fig. 2. They correspond to a triclinic symmetry of both crystals, to their isomorphism, and to

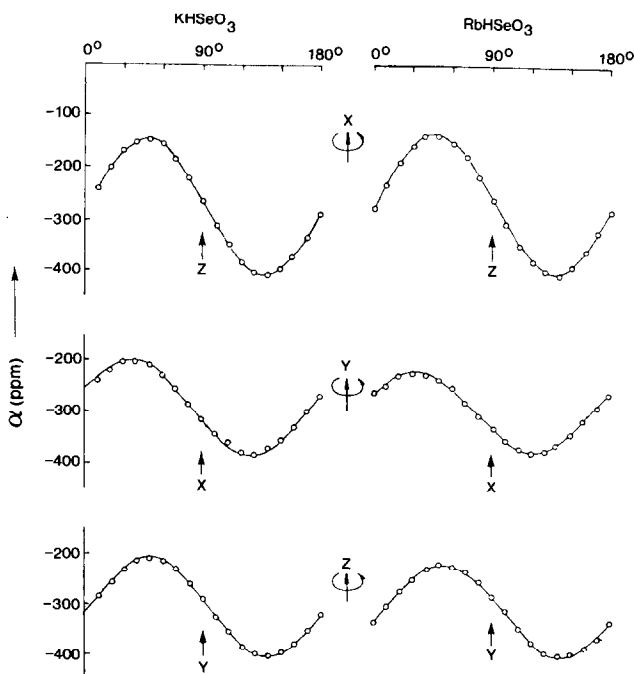


FIG. 2. Angular dependences of the ^{77}Se chemical shifts relative to liquid H_2SeO_4 in KHSeO_3 and RbHSeO_3 single crystals.

TABLE I
PARAMETERS OF THE ^{77}Se CHEMICAL SHIELDING TENSOR IN THE SINGLE CRYSTALS OF
 KHSeO_3 AND RbHSeO_3

Single crystal	Principal values (ppm) relative to liquid H_2SeO_4	Direction cosines of the principal tensor axes relative to			Isotropic average σ_{av}	Shielding anisotropy $\Delta\sigma$	Asymmetry η
		X-axis	Y-axis	Z-axis			
KHSeO_3	$\sigma_{xx} = -415$	0.3343	-0.7932	0.5089	-293	317	0.15
	$\sigma_{yy} = -382$	-0.8143	0.0287	0.5797			
	$\sigma_{zz} = -81$	0.4744	0.6082	0.6364			
RbHSeO_3	$\sigma_{xx} = -411$	0.4114	-0.7662	0.4935	-292	303	0.18
	$\sigma_{yy} = -375$	-0.8118	0.0619	0.5807			
	$\sigma_{zz} = -90$	0.4144	0.6396	0.6474			

one structurally nonequivalent SeO_3 group in the unit cell of each crystal.

From experimental angular dependences we calculated the parameters of the ^{77}Se magnetic shielding tensor: principal values σ_{xx} , σ_{yy} , σ_{zz} , their direction cosines relative to X , Y , Z axes, as well as the values of the isotropic average $\sigma_{av} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, the shielding anisotropy $\Delta\sigma = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$, and the asymmetry parameter $\eta = (\sigma_{yy} - \sigma_{xx})/(\sigma_{zz} - \sigma_{av})$. These parameters are given in Table I.

To analyze these parameters of the tensors it can be noted that all parameters are similar in KHSeO_3 and RbHSeO_3 . They are similar also to the parameters of the ^{77}Se magnetic shielding tensor in the single crystal $\text{NH}_4\text{HSeO}_3 \cdot \text{H}_2\text{O}$ (our data) (14). These three tensors correspond to the HSeO_3^- configuration.

It is necessary to compare our results with the results obtained in $\text{MH}_3(\text{SeO}_3)_2$ single crystals which also contain HSeO_3^- ions. The experimental results for $\text{MH}_3(\text{SeO}_3)_2$ are given in Table II together with data for selenious acid. The results for potassium and cesium salts are for ordered phases.

Single crystals of selenious acid consist of H_2SeO_3 molecules (15), and the experi-

mental ^{77}Se magnetic shielding tensor in this crystal is typical for H_2SeO_3 . Its characteristic property is a large asymmetry parameter $\eta = 0.45$. In the crystals of KHSeO_3 , RbHSeO_3 and $\text{NH}_4\text{HSeO}_3 \cdot \text{H}_2\text{O}$ with the HSeO_3^- configuration η changes in the range 0.15–0.18. It must be expected that in M_2SeO_3 crystals with SeO_3^{2-} ions, η will be zero because all three Se–O bonds must be of equal length, but the experiments are necessary.

So, the asymmetry parameter η can be considered as the characteristic parameter for the assignment of the experimental tensor to SeO_3^{2-} , HSeO_3^- , or H_2SeO_3 species.

In the family of trihydrogen selenites only the data for $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$ satisfied this contention: η for H_2SeO_3 is twice as large as that for HSeO_3^- . In $\text{KH}_3(\text{SeO}_3)_2$ η is about equal for HSeO_3^- and H_2SeO_3 as that in $\text{CsH}_3(\text{SeO}_3)_2$. Because of this, in these crystals the assignment was taken from the analysis of the shielding anisotropy $\Delta\sigma$. The authors (3, 4) found that $\Delta\sigma$ is always less in HSeO_3^- and is changed from 274 to 301 for HSeO_3^- and from 390 to 534 for H_2SeO_3 (Table II). But our $\Delta\sigma$ values in MHSeO_3 crystals (317 for KHSeO_3 , 303 for RbHSeO_3 , and 345 for $\text{NH}_4\text{HSeO}_3 \cdot \text{H}_2\text{O}$) are between these limits of the change of $\Delta\sigma$ for

TABLE II
PARAMETERS OF THE ⁷⁷Se CHEMICAL SHIELDING TENSOR IN THE SINGLE CRYSTALS OF SELENIOUS ACID AND TRIHYDROGEN SELENITES

Single crystal	Configuration	Principal values (ppm) relative to liquid H ₂ SeO ₄	Isotropic average σ_{av}	Shielding anisotropy $\Delta\sigma$	Asymmetry η
H ₂ SeO ₃	H ₂ SeO ₃	$\sigma_{xx} = -450$ $\sigma_{yy} = -133$ $\sigma_{zz} = -1$	-261	390	0.45
NH ₄ H ₃ (SeO ₃) ₂	H ₂ SeO ₃	$\sigma_{xx} = -471$ $\sigma_{yy} = -311$ $\sigma_{zz} = -22$	-268	369	0.65
	HSeO ₃ ⁻	$\sigma_{xx} = -369$ $\sigma_{yy} = -315$ $\sigma_{zz} = -68$	-251	274	0.29
KH ₃ (SeO ₃) ₂ $T < T_c$ ordered phase	H ₂ SeO ₃	$\sigma_{xx} = -415$ $\sigma_{yy} = -359$ $\sigma_{zz} = -13$	-261	373	0.21
	HSeO ₃ ⁻	$\sigma_{xx} = -383$ $\sigma_{yy} = -351$ $\sigma_{zz} = -81$	-273	289	0.19
CsH ₃ (SeO ₃) ₂ $T < T_c$ ordered phase	H ₂ SeO ₃ (1)	$\sigma_{xx} = -430$ $\sigma_{yy} = -343$ $\sigma_{zz} = -47$	-242	433	0.30
	H ₂ SeO ₃ (2)	$\sigma_{xx} = -507$ $\sigma_{yy} = -353$ $\sigma_{zz} = -104$	-252	534	0.43
	HSeO ₃ ⁻ (1)	$\sigma_{xx} = -407$ $\sigma_{yy} = -307$ $\sigma_{zz} = -19$	-244	338	0.44
	HSeO ₃ ⁻ (2)	$\sigma_{xx} = -371$ $\sigma_{yy} = -340$ $\sigma_{zz} = -54$	-255	301	0.15

HSeO₃⁻ and H₂SeO₃ in trihydrogen selenites.

To summarize, we assume that η must be the characteristic parameter for the assignment of the experimental ⁷⁷Se magnetic shielding tensors to SeO₃²⁻, HSeO₃⁻, or H₂SeO₃ species. But for the final argument experimental data are necessary from single crystals of MHSeO₃ and M₂SeO₃ families. For the present the results in the trihydrogen selenites of potassium and caesium remain incomprehensible.

Earlier we attempted to discover a phase transition in KHSeO₃ which is reported in

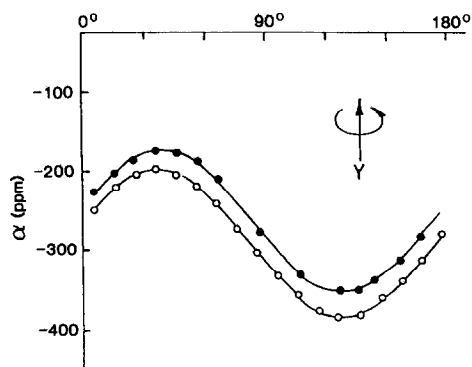


FIG. 3. Angular dependences of the ⁷⁷Se chemical shifts of KHSeO₃ at room temperature (O) and at 108 K (●).

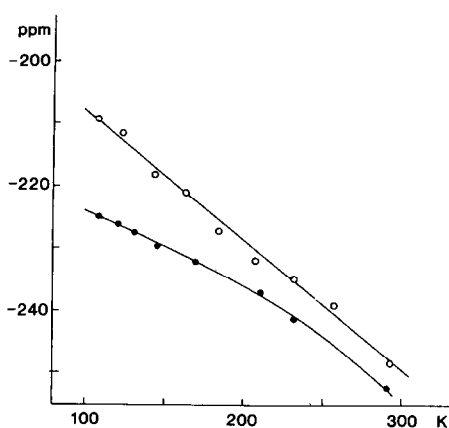


FIG. 4. Temperature dependences of the ^{77}Se chemical shifts in the single crystals of KHSeO_3 (●) and RbHSeO_3 (○), $H_0 \perp Y$, $\theta = 70^\circ$.

(16, 17) but without success (11). In the present paper we continue the search of the phase transition by recording the ^{77}Se NMR spectra of KHSeO_3 over a wide temperature range. We have studied the angular dependences of the chemical shifts not only at room temperature, but also at 108 K for the specimen rotated around the Y -axis (Fig. 3). At low temperature the values of the chemical shifts are decreased but the shape of the angular dependence is retained. The temperature change of the chemical shift is permanent as can be seen from Fig. 4. A phase transition was not discovered.

In the crystal of RbHSeO_3 we obtained a similar result: no phase transition was detected. We studied the temperature dependence of the chemical shift from room temperature to 108 K and found no evidence for a phase transition (Fig. 4).

Our results on ^{77}Se NMR confirmed earlier results of the absence of the phase transitions in KHSeO_3 and RbHSeO_3 single

crystals. Apparently the dimers $[\text{HSeO}_3^-]_2$ make rigid structures in MHSeO_3 families.

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