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MONOHYDRATES OF THE THIOSACCHARINATES OF SODIUM AND POTASSIUM : SPECTRA-STRUCTURE CORRELATIONS

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ABSTRACT

The infrared spectra of the monohydrates of sodium and potassium thiosaccharinates and of some of their partially deuterated analogues were recorded at room and liquid-nitrogen temperatures.

The spectral features in the O-H and O-D stretching regions were correlated with the crystallographic data on the geometry of the water molecules and their nearest neighbours.

In an attempt to assign the bands due to the SO_2 stretching modes, the spectra of the thiosaccharinates were compared with those of the hydrate of sodium saccharinate, $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$.

INTRODUCTION

Contrary to the numerous reports about the structural and spectral properties of saccharin and its complexes with different metals [1-9], less seems to be known about the structural characteristics of the thiosaccharin itself and its complexes with various metals [10-13]. Continuing our studies of such compounds [10-13], we report the results of the investigation of the infrared spectra of the hydrates of sodium and potassium thiosaccharinates in the region of O-H, O-D and SO_2 stretching vibrations as well as the correlation of the spectral characteristics with the crystallographically determined [12,13] $O_w \cdots O$ and $O_w \cdots S$ distances for the two compounds.

EXPERIMENTAL

The title compounds were prepared by addition of an equimolar ethanolic solution of thiosaccharin to an aqueous solution of the corresponding metal hydroxyde. The transparent yellow prismatic crystals obtained after cooling to room temperature of the previously heated reaction mixture were recrystallized from water or ethanol.

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The partially deuterated analogues were prepared by the action of D_2O vapor on the crystals of the hydrate. Alternatively, the compounds were prepared from D_2O solution kept for several days in a sealed glass tube heated to 70 °C.

The infrared spectra were recorded from KBr discs on a Perkin-Elmer 580 infrared spectrophotometer. A VLT-2 variable-temperature cell cooled with liquid nitrogen was used for the low-temperature (LNT) measurements.

STRUCTURAL DATA

The details about the crystal structures of the monohydrates of sodium and potassium thiosaccharinate are given in refs. 12 and 13, respectively. Only the data concerning the H_2O and SO_2 groups and their immediate environment will be briefly summarized in the present paper.

In the structure of sodium thiosaccharinate monohydrate [12], all Na cations, thiosaccharinate anions and water molecules are equivalent. The water oxygen atom and the oxygen atoms belonging to the SO_2 groups from the thiosaccharinate anion take part in the coordination polyhedra around the sodium cations. The two S-O distances are 145.8(5) and 143.9(5) pm, while the O-S-O angle has value of 113.5(3)°. Only one of the water protons forms a hydrogen bond (of the O-H···S type), the $O_w \cdots S$ distance being 324.2(7) pm.

The structure of potassium thiosaccharinate monohydrate [13] also consists of crystallographically equivalent K cations, thiosaccharinate anions and water molecules. As in the case of the previously discussed sodium compound, the water oxygen atom and the oxygen atoms from the SO_2 groups are coordinated to the K cations. The S-O distances are 144.3(2) and 144.2(2) pm, while the value of the O-S-O angle is 113.7(1)°. The water molecules participate in the formation of hydrogen bonds (of the O-H···S and the O-H···O type) with the S atoms from the C=S group and with one of the O atoms from the SO_2 group. The $O_w \cdots S$ and $O_w \cdots O$ distances are 338.1(3) and 302.7(4) pm, respectively.

INFRARED DATA AND CORRELATIONS WITH THE STRUCTURES

As seen in Fig. 1, the LNT infrared spectra of the two title compounds are very similar with the exception of the regions of the O-H stretching vibrations and of the water librations.

Water modes

Two bands with similar intensity are observed (around 3570 and 3440 cm^{-1}) in the H_2O stretching region in the spectrum of the potassium compound, whereas *three* rather intense bands exist

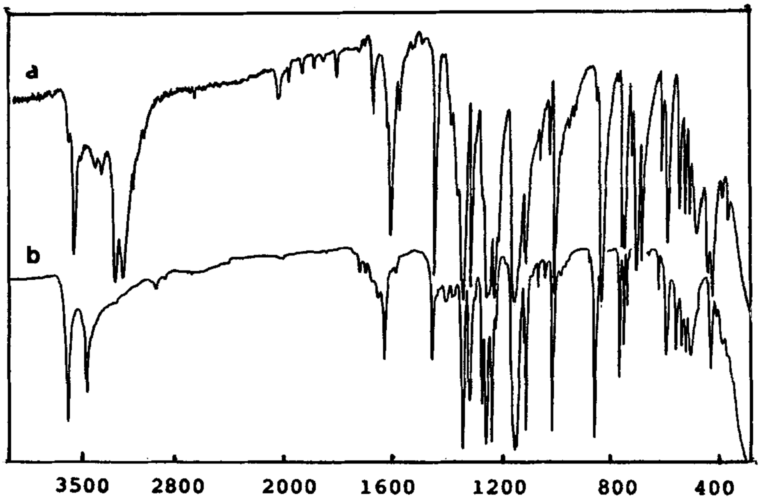

Fig. 1. LNT spectra of the monohydrates of the thiosaccharinates of sodium (a) and potassium (b)

in same spectral region of the analogous sodium compound (cf. Fig. 1). Their frequencies are around 3540, 3240 and 3180 cm^{-1}, the latter two bands being more intense than the 3540 cm^{-1} one.

The appearance of the spectrum in the former case is in agreement with the existence of only one type of unsymmetrically bonded and quite distorted H_2O molecules in the structure of the potassium compound [13]. The spectra-structure correlations are less straight-forward in the case of the sodium compound, the presence of three O-H stretching bands being, at first sight, in contradiction with the existence of a single type of water molecules. The apparent contradiction is resolved, however, if the possibility of vibrational interaction of the overtone of the bending HOH vibration with one of the fundamental O-H stretches is taken into account. The doubled value of the HOH bending frequency, namely, is quite close to that of the absorption minimum between the two lower-frequency bands (those at around 3240 and 3180 cm^{-1}).

As is well-known [14,15], a better structural probe is provided by the study of the O-D stretching region in the spectra of partially deuterated samples which contain HDO molecules isotopically isolated with ordinary water molecules. Under such conditions, namely, the two water stretches are decoupled, the probability of vibrational interactions is strictly reduced and the stretch of each non-equivalent O-D bond gives rise to a separate infrared band. The frequency separation between these bands will, obviously, depend on the degree of distortion of the water molecules.

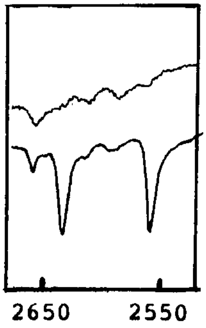

Fig. 2. O-D stretching region in the spectrum of slightly deuterated potassium thiosaccharinate monohydrate

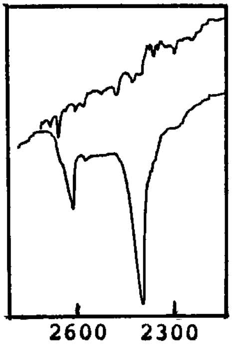

Fig. 3. O-D stretching region in the spectrum of slightly deuterated sodium thiosaccharinate monohydrate

The situation in the O-D stretching region of the spectra of potassium thiosaccharinate recorded under the discussed conditions is simple and in agreement with the spectral picture in the O-H stretching region of the protiated analogue. As seen in Fig. 2, namely, two bands with almost equal intensity and shape are found in this region (at approximately 2625 and 2540 cm^{-1} respectively)*. The non-negligible frequency difference between the two bands (approximately 85 cm^{-1}) is in agreement with the existence of distorted water molecules forming two different hydrogen bonds.

Two peaks appear (at ≈ 2620 and 2405 cm^{-1}) in the O-D stretching region of the spectra of slightly deuterated samples of sodium thiosaccharinate monohydrate as well, but the low-frequency band is, this time, far more intense (see Fig. 3). There is little doubt that the high-frequency band (2620 cm^{-1}) is due to the stretch of the non-bonded OD group of the water molecule, while the low-frequency one (2405 cm^{-1}) originates from HDO molecules in which the deuterons participate in the formation of hydrogen bonds. The question of the unequal intensities of the two bands is open for discussion. One possible explanation would involve the assumption of preferential deuteron-for-proton substitution at the sites of hydrons involved in hydrogen bonding [16]. As an alternative, the difference in the nature of the normal coordinates in the case of the H-O-D···S and the D-O-H···S systems may be taken into account as a possible reason for the observed spectral picture [17,18].

In any case, the smaller frequency difference of the two OD stretching bands in the spectrum of the potassium compound than in that of the sodium analogue shows that the water molecules in the former case are less distorted than those in the structure of the sodium analogue. This, it should be recalled, is in agreement with the crystallographic results [13].

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* The upper curve in this figure and in Fig. 3 gives the appearance of the same region in the spectra of the protiated compounds.

There is one further unexpected spectral feature in the water stretching regions of the spectra of the two compounds. Namely, although one of the water hydrons in the case of the sodium compound is not involved in hydrogen bonding, the frequencies of the highest O-H stretch (3540 cm^{-1}) and the highest O-D stretch (2620 cm^{-1}) in the spectra of protiated and partially deuterated sodium thiosaccharinate monohydrate are *lower* than the corresponding frequencies (3570 and 2625 cm^{-1} respectively) in the spectra of the potassium compound.

S-O stretchings

Since the S-O distances and O-S-O angles in the presently investigated compounds (see above) are very similar to the corresponding S-O distances and O-S-O angles in the structure of trisodium trisaccharinate dihydrate, $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$ [2], the assignment of the infrared spectrum of the latter compound [19] was used to assign the bands which are due to the SO_2 stretching modes.

The assignment of the respective bands in the spectrum of $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$ is relatively simple and is possible solely on the basis of their intensities. As seen in Fig. 4, in the region of the SO_2 stretching vibrations, in the spectrum of $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$ (curve **a** in Fig. 4) only *two* bands (at 1260 and 1150 cm^{-1}) are strong enough to be assigned to such modes.

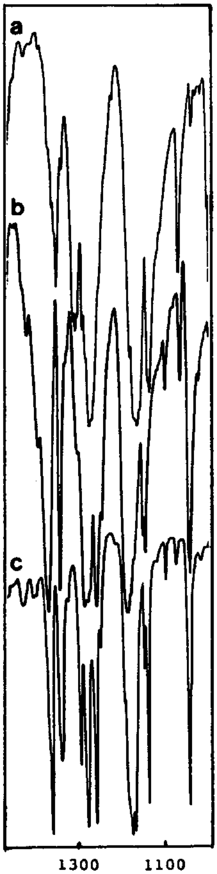

Fig. 4. SO_2 stretching region (see text)

The number of strong bands in the corresponding region of the spectra of sodium thiosaccharinate monohydrate (curve **b** in Fig. 4) and of the corresponding potassium compound (curve **c** in this figure) is considerably larger since bands due to modes with C=S stretching character appear in the same spectral region. The assignment of the SO_2 stretching bands on the basis of their intensities is thus not straight-forward. However, the comparison with the spectrum of $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$ makes the assignment quite simple.

On the basis of such a comparison, namely, the bands appearing (in the spectra of the two title compounds) at ≈ 1270 and

≈ 1160 cm^{-1} were attributed to the antisymmetric and the symmetric SO_2 stretching vibrations respectively.

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