Crystal structure, infrared and Raman spectra of tripotassium trisaccharinate dihydrate, $\text{K}_3(\text{C}_7\text{H}_4\text{NO}_3\text{S})_3 \cdot 2\text{H}_2\text{O}$

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Abstract: The crystal structure of tripotassium trisaccharinate dihydrate, $\text{K}_3(\text{C}_7\text{H}_4\text{NO}_3\text{S})_3 \cdot 2\text{H}_2\text{O}$, is triclinic, space group $P \bar{1}$, $Z = 2$. It consists of three crystallographically independent potassium and saccharinato ions as well as two structurally different water molecules. Potassium coordination polyhedra are irregular, with K1 and K3 six-coordinated and the third one K2 seven-coordinated. The K–O distances range from 2.652(9) to 3.100(2) Å (mean: 2.790 Å) whereas the K–N distance is 3.025(3) Å. The water molecules W2 is disordered over three positions with occupancies of approximately 0.6, 0.2 and 0.2. The hydrogen atom (H1W1) of the ordered water molecule (O1W) is hydrogen bonded to the sulfonyl oxygen atom (O11) ($R(\text{O} \cdots \text{O}) = 2.976(3)$ Å), whereas the other hydrogen atom (H2W1) is bifurcated to the carbonyl oxygen atom (O13) ($R(\text{O} \cdots \text{O}) = 2.851(3)$ Å) and the disordered water molecules (O23W) ($R(\text{O} \cdots \text{O}) = 3.067(12)$ Å). The carbonyl oxygens (O13, O23 and O33) and one of the disordered water molecules (O22W) are involved in C–H $\cdots$ O hydrogen bonds ($R(\text{C} \cdots \text{O}) = 3.027(4) - 3.304(9)$ Å). Structural characteristics of the studied compound are compared with the analogous trisodium trisaccharinate dihydrate and dipotassium sodium trisaccharinate monohydrate. Infrared and Raman spectra of the title compound have been analyzed in relation to the structure, and compared with the spectra of trisodium trisaccharinate dihydrate.

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Keywords: Potassium saccharinate dihydrate; crystal structure; vibrational (infrared and Raman) spectra; structure-spectral correlations

1 Introduction

Mainly due to the suspected carcinogenic nature ([1], [2]) of saccharin (systematic name: 1,2-benzisothiazole-3(2H)-one 1,1-dioxide; Figure 1), its use as a food additive, and the versatile coordination properties of its deprotonated form in its salts and complexes with various metals, extensive studies have been devoted to saccharinates during the last few decades. Among them, the alkali saccharinates have received the widest commercial use in the food industry, by reason of their high solubility in water compared to saccharin itself.

Fig. 1 Structural formula of saccharin.

In spite of that, reported structural and vibrational spectroscopic data on the alkali and pseudoalkali saccharinates are still rather scanty. Crystal structures of $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ [3], $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ [4] and $\text{NH}_4(\text{sac})$ [5] have been reported (sac = saccharinato anion). A tentative assignment of the room temperature (RT) infrared spectra of the saccharinates of Na and K has also been given [6] and a more detailed study of the OH and OD stretching vibrations in the infrared spectra of these two compounds has been reported [7]. The infrared spectrum of Li saccharinate in the region of the CO, SO_2 and water stretching vibrations has also been studied [8]. Recently, results of the vibrational (IR and Raman) study and spectra-structure correlations in ammonium saccharinate were published [9].

In order to obtain additional structural data concerning the ligation properties of saccharin in the salts with various alkali metals, we have undertaken a systematic and detailed structural and spectroscopic study of the alkali saccharinates. In the present comparative study, we report the results of structural and vibrational investigations of potassium saccharinate in comparison with the analogous sodium and mixed potassium sodium salts. Thereby, the complete assignment of the infrared and Raman spectra in the $1700\text{--}1100\text{ cm}^{-1}$ is performed, paying special attention to the C = O and SO_2 stretchings and their correlation with the structural data. The O–H and O–D stretching vibrations of the protiated and partially deuterated samples related to the presence of one ordered and one disordered water molecule in the structure are studied as well.

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2 Experimental

2.1 Preparation

The crystals of tripotassium trisaccharinate dihydrate, $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, were prepared from warm aqueous solution of saccharin and potassium carbonate. Recrystallization from aqueous and ethanolic solutions afforded an identical crystalline phase, with crystals suitable for X-ray diffraction. Deuterated analogues were obtained by recrystallization of the protiated sample from D_2O .

2.2 FT-IR and Raman measurements

The room temperature (RT) and liquid nitrogen temperature (LNT) FT-IR absorption spectra in the $4000\text{--}400\text{ cm}^{-1}$ range were recorded on a Perkin-Elmer System 2000 instrument (32 background and 64 sample spectra averaged at resolution of 4 cm^{-1}). Since no differences were found between spectra recorded in paraffin oil and KBr pellets, the latter technique was employed. A Graseby Specac P/N 21525 variable-temperature cell with KBr windows was used for the low-temperature infrared measurements. The Raman spectrum was recorded on a Renishaw 2000 instrument equipped with a Leica microscope, using a 514 nm argon-ion or a 780 nm diode laser.

2.3 Crystallographic measurements

The colourless prismatic crystals with dimensions $0.80 \times 0.35 \times 0.35\text{ mm}$ were used for X-ray data collection. The crystallographic measurements were performed by the ω -scan method on a Philips PW1100 diffractometer using graphite monochromatized $\text{Mo-}K\alpha$ radiation. Details of the crystal data and refinement parameters for the studied compound $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (**1**) compared with the corresponding values for the analogous $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (**2**) [3] and $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ (**3**) [4] are presented in Table 1. The semi-empirical ψ -scan absorption correction was applied to the data set [10]. The structure was solved by direct methods and refined by full-matrix least-squares calculations with all non-hydrogen atoms allowed anisotropic motion. The saccharinato hydrogen atoms were positioned geometrically $0.95\text{ \AA}$ from the atom to which they were bonded and included (but not refined) in the final rounds of calculations. The hydrogen atoms (H1W1 and H2W1) belonging to the ordered water molecule (W1) were taken from the difference Fourier map and included as riding atoms in the structure factor calculations. The hydrogen atom positions of the disordered water molecule (W2) were not determined. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974) [11]. Computing was carried out on a personal computer using SHELXL97 integrated in WinGX [12], [13]. The ORTEP-III [14] and PLUTON [15] programs were used to generate the illustrations.

3 Results and discussion

At first sight, the crystal data of the studied $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (**1**) differ from the previously published values of the analogous $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}^\ddagger$ (**2**) [3] as well as of the double potassium sodium salt with very similar formula $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ (**3**) (see [4] and Table 1). However, transformation of the crystal data for compounds in (**2**) and (**3**) (using transformation matrix of type: 0 0 1; 0 -1 0; 1 0 0 - for the axes, and $\alpha(\text{new}) = 180^\circ - \gamma(\text{old})$; $\beta(\text{new}) = \beta(\text{old})$; $\gamma(\text{new}) = 180^\circ - \gamma(\text{old})$ - for the angles) shows that, in addition to their crystallization into the same crystal system (triclinic) and space group ($P \bar{1}$), they have comparable unit cell parameters and consequently are isostructural with the studied compound (**1**).

3.1 Crystal structure description

The final atomic parameters as well as the complete list of data concerning bond lengths and angles are available in CIF format as Electronic Supplementary Information (CCDC reference number 218495). Comparison of the interatomic distances of the K^+ and Na^+ ions for (**1**)-(**3**) is given in Table 2. Table 3 presents the selected bond lengths (Å) and angles (°) in the saccharinato anions of the studied compound $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ compared with the corresponding values in the analogous $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ [3] and $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ [4]. The hydrogen bonds of $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ are listed in Table 4. The crystal structure packing is shown in Figure 2. The "surrounding" of the potassium cations is illustrated in Figure 3.

Similarly to the previously studied trisodium trisaccharinate dihydrate [3], the structure of the potassium compound (**1**) consists of three crystallographically independent potassium and saccharinato ions as well as two structurally different water molecules (Figure 2). One of the water molecules (W2) is disordered, the corresponding occupation factors being 0.66(3), 0.190(5) and 0.147(5) for O21W, O22W and O23W, respectively. Two of the K^+ cations are six-coordinated; K1 is surrounded by five saccharinato oxygens and one water oxygen atom, whereas K3 has as nearest neighbours four saccharinato oxygens, one saccharinato nitrogen atom and one water oxygen atom (Figure 3). The third K^+ cation (K2) is seven-coordinated by five saccharinato oxygens and two water oxygen atoms (Figure 3). All coordination polyhedra are irregular. The K–O distances range from 2.652(3) to 3.100(2) Å (mean value: 2.790 Å) whereas the K3–N distance is 3.025(3) Å. The shorter mean K–O distance (2.790 Å) in (**1**) compared to the mean K–O value (2.818 Å) in (**3**) suggests stronger interaction between the K^+ cations and saccharinato anions in the compound (**1**) (Table 2). This observation is not supported by the comparison of the unique K–N distance in (**1**) (3.025 Å) with the corresponding mean

[‡] Recrystallization of the commercially available sodium saccharinate from water and ethanol yields two different forms: The crystals recrystallized from ethanol are triclinic with formula $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ [3], whereas the crystals obtained from aqueous solution are monoclinic. The composition of the latter has not been determined with certainty yet, but it has been assured that the compound is a higher hydrate [7] than that obtained from ethanol.

K–N distance in **(3)** (3.001 Å). As seen from Table 2, the delta value 0.372 obtained by subtraction of the mean Na–N distance (2.635 Å) in **(2)** and **(3)** from the mean K–N distance (3.007 Å) in **(1)** and **(3)** corresponds very closely to the delta value 0.36 obtained by subtraction of the $r(\text{Na}^+) = 1.02$ Å (for CN = 6) from the $r(\text{K}^+) = 1.38$ Å (for CN = 6) [16]. The corresponding delta value obtained by subtraction of the mean Na–O distance (2.469 Å) in **(2)** and **(3)** from the mean K–O distance (2.780 Å) in **(1)** and **(3)** is smaller (0.311), but still close to $r(\text{K}^+) - r(\text{Na}^+) = 0.372$.

There are no significant differences between the interatomic distances and angles in the crystallographically different saccharinato anions of the studied compound (Table 3). Comparison also shows that the corresponding interatomic distances and angles in the five-membered rings of the deprotonated saccharins in compounds **(1)**, **(2)** and **(3)** are very closely similar.

The carbonyl and sulfonyl saccharinato oxygen atoms are involved in hydrogen bonds with the water molecules and with some of the saccharinato C–H groups. In particular, the hydrogen atom H1W1 belonging to the water molecule O1W is hydrogen bonded to the sulfonyl saccharinato oxygen atom O11 ($R(\text{O} \cdots \text{O}) = 2.976(3)$ Å), whereas the other hydrogen atom H2W1 is bifurcated to the carbonyl saccharinato oxygen atom O13 ($R(\text{O} \cdots \text{O}) = 2.851(3)$ Å) and to O2W oxygen atom belonging to water molecule with population parameter 0.147(5) (the position O23W) ($R(\text{O} \cdots \text{O}) = 3.067(12)$ Å). The carbonyl saccharinato oxygen atoms (O13, O23 and O33) and the O2W oxygen atom belonging to water molecule with population parameter 0.190(5) (the position O22W) are involved in C–H $\cdots$ O hydrogen bonds ($R(\text{C–H} \cdots \text{O}) = 3.027(4) - 3.304(9)$ Å) (Table 4).

3.2 Vibrational studies

3.2.1 General considerations

Contrary to the existence of two different hydrates of sodium saccharinate (*triclinic* from ethanol and *monoclinic* from aqueous solution [3], [7]), the IR spectra and the powder diffractograms showed that identical hydrate of potassium saccharinate is obtained both from water and ethanol. The XRD and thermal data [17] confirmed that the potassium compound **(1)** corresponds to the triclinic form of trisodium trisaccharinate dihydrate, $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ **(2)** [3], having the analogous formula, $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$. Although their room temperature (RT) IR spectra are very similar, significant differences exist between the O–H and O–D stretching region of the infrared spectra of **(1)**, on the one hand, and **(2)**, on the other hand, recorded at the nitrogen boiling temperature (LNT) [7]. This was taken as a serious indication that, in spite of the fact that these two compounds are isostructural, significant differences exist in the structural arrangement of the water molecules. This presumption has been now confirmed by the crystal structure determination of **(1)**.

The assignment of the experimental frequencies in the RT and LNT IR and RT Raman spectra of tripotassium trisaccharinate dihydrate is given in Table 5. This assignment is based on theoretical calculations on deprotonated saccharin (saccharinate anion) in the

1700 -1000 cm^{-1} region. Some of the characteristic saccharinate vibrations, such as the C=O and SO₂ stretches belonging to the five-membered ring as well as the O–H and O–D stretches of the water molecules will be discussed here. The number of bands arising from these vibrations, and their frequencies, will be correlated with the crystallographic values of the corresponding interatomic distances.

3.2.2 The O–H and O–D stretches

The O–H stretching region of protiated (**1**) and the O–D stretching region of its partially deuterated analogue are shown in figures 3 and 4, respectively. In the region of the O–H stretches, two strong and complex RT bands with maxima at 3557 and 3397 cm^{-1} are accompanied by a shoulder around 3258 cm^{-1} (Figure 4a). Sharpening, splittings and shifts of the bands are observed with decrease of the temperature, resulting in at least seven overlapped bands with frequencies ranging from 3585 down to 3254 cm^{-1} (Figure 4b). The band positions are consistent with the existence of non-hydrogen bonded and weakly to medium hydrogen bonded water molecules in the structure (see Table 4).

Because the extensive vibrational interactions preclude direct comparison of the number of bands in the O–H stretching region of protiated sample with the geometry of the water molecules, the LNT spectrum of the isotopically isolated HOD molecules in the partially deuterated (**1**) was studied. The data obtained can assist in correlating the spectrum with the hydrogen bonding. As seen from Figure 5, three intense and well separated bands (2615, 2548 and 2471 cm^{-1}) appear in the IR spectrum, the lowest-frequency one being the most intense. The three main bands are accompanied by at least four to five less intense bands or shoulders (2634, 2596, 2507, 2484 and 2416 cm^{-1}). At least qualitatively, the total number of eight registered bands with variable intensity in the $\nu(\text{OD})$ region of the partially deuterated sample corresponds with the presence of one ordered (W1) and one triply-disordered water molecule (W2) with the approximate occupation factors 0.6, 0.2 and 0.2. The *three* most intense bands (the one at 2471 cm^{-1} being considerably stronger than the other two) could be related to the four O–D stretching vibrations arising from the ordered water molecule W1 and the disordered water molecule W2 with occupancy 0.6. The other less intense bands or shoulders probably appear as a result of $\nu(\text{OD})$ vibrations of the *two* disordered water positions of W2, each with approximate occupancy of 0.2.

3.2.3 The C=O stretches

As has been shown by theoretical calculations ([9], [18]), and confirmed experimentally [9, 18-21] (see also Table 5), the stretching vibrations of the carbonyl and the sulfonyl groups can be considered as characteristic group vibrations, manifested as very strong bands in the vibrational (infrared and Raman) spectra of the corresponding compounds. Therefore they are often used to correlate the spectroscopic data with those obtained by structure determination.

The analysis of the bands originating from the C=O stretch mode in the infrared spectra of various metal saccharinates is complicated by the appearance, in the same

spectral region, of bands arising from the benzenoid ring stretches as well as from the water bending modes. According to *ab initio* calculations for deprotonated saccharin [18], the benzenoid stretching bands appear at somewhat lower frequencies (below 1610 cm^{-1}) and are sharper and less intense than the bands originating from the C=O stretches. Recording the spectra of samples with high deuterium content, however, eliminates the bands due to the H–O–H bending vibrations from the region where the $\nu(\text{CO})$ modes are expected.

As indicated in Figure 6, a pair of bands appears in the RT IR spectrum (1650 and 1641 cm^{-1}) and also in the Raman spectrum (1647 and 1636 cm^{-1}) (see also Table 5) of the studied compound in the region where $\nu(\text{CO})$ stretching mode is expected. Five bands (two well separated and three shoulders), however, are registered in this spectral region of the IR spectrum of the same compound recorded at LNT (see Figures 6 and 8 and Table 5). The reduced intensity of the bands at 1665 , 1643 and 1637 cm^{-1} in the LNT spectrum of the deuterated analogue (*ca.* 30 % deuterium content) in comparison with the protiated one (Figure 8) confirms that they belong to the $\delta(\text{HOH})$ modes. In addition to the strongest band at 1651 cm^{-1} , exception is the shoulder at 1626 cm^{-1} in the IR spectrum of the protiated sample which in the spectrum of the deuterated analogue separates as a sharp band. On the basis of these considerations, the uninfluenced by deuteration strongest single band at 1651 cm^{-1} could be attributed to the $\nu(\text{CO})$ modes. It corresponds with presence of three crystallographically different saccharinato CO groups in the structure of the studied compound with very short C–O distances ($1.234(3)$, $1.236(3)$ and $1.239(3)\text{ \AA}$). However, the origin of the second uninfluenced by deuteration weaker LNT band at 1626 cm^{-1} remains still unclear, although most probably its origin is other than the $\nu(\text{CO})$ mode.

3.2.4 The SO_2 stretches

Similarly to the C=O stretches, the assignment of the bands originating from the SO_2 (sulfonyl) stretching vibrations in the spectra of saccharinato salts and complexes is usually complicated by the appearance of additional bands originating from ring vibrations of the saccharinato ions (ligands) [22–24]. The bands arising from the benzenoid stretches, however, are found to be sharper and less intense than the sulfonyl stretching bands and thus the strongest bands in the $1300\text{--}1150\text{ cm}^{-1}$ spectral region are usually attributed to the antisymmetric and symmetric $\nu(\text{SO}_2)$ modes. A detailed analysis of infrared spectra of metal saccharinates in the SO_2 stretching region has shown that the $\nu(\text{SO}_2)$ frequency depends on the O–S–O angles rather than on the S–O distances [19].

Two strong bands are registered in the RT infrared spectrum of the studied compound in the region where the $\nu(\text{SO}_2)$ modes are expected (Figure 6). There is no doubt that the band at 1255 cm^{-1} can be assigned as the $\nu_{as}(\text{SO}_2)$ mode, whereas the band at 1150 cm^{-1} can be attributed to the $\nu_s(\text{SO}_2)$ mode (Table 5). As expected, the band corresponding to the antisymmetric stretching SO_2 mode in the Raman spectrum is of a weak intensity (at 1257 cm^{-1}) compared to the strong band arising from the symmetric SO_2 mode (at 1151 cm^{-1}) (Figure 7 and Table 5). The Raman frequencies of these two modes are

practically the same as those found in the RT infrared spectrum. The appearance of only one pair of RT infrared and Raman $\nu(\text{SO}_2)$ bands, in contrast to the existence of three crystallographic types of sulfonyl groups in the studied compound, is due to the similarity between the interatomic distances and especially the O–S–O angles in the different SO_2 groups (Table 3). The presence, however, of three crystallographically different types of SO_2 groups in the structure of the studied compound could be the reason for splitting of the $\nu(\text{SO}_2)$ bands into two components and, consequently, appearance of two pairs of SO_2 stretching bands in its LNT infrared spectrum (Figure 6 and Table 5).

4 Conclusion

The study of the crystal structure and the vibrational (infrared and Raman) spectra has shown that, by contrast with the previously confirmed existence of two different hydrates of sodium saccharinate (*triclinic* from ethanol and *monoclinic* from water), identical crystal phases of potassium saccharinate are obtained by its recrystallization from aqueous and ethanolic solutions. Although at first sight the crystal data for $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (**1**) differ from the published values for the analogous triclinic $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (**2**) [3] and $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ (**3**) [4], the more detailed analysis has shown that compounds (**1**), (**2**) and (**3**) have comparable unit cell parameters. In spite of that, one of the water molecules (W2) in the studied potassium compound (**1**) was found to be triply-disordered, the corresponding occupation factors being 0.66(3), 0.190(5) and 0.147(5) for O21W, O22W and O23W, respectively. This has been confirmed, at least qualitatively, by analysis of the infrared spectrum of partially deuterated $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ in the O–D stretching region.

Despite the presence of three crystallographically different saccharinato ions in the structure of $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, the corresponding interatomic C–O and S–O distances and especially the O–S–O angles in the CO and SO_2 groups are very similar. Accordingly, a single band in the region where the $\nu(\text{CO})$ are expected as well as only one pair of infrared and Raman $\nu(\text{CO})$ bands in the SO_2 stretching region are observed.

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	<div>K₃(sac)₃·2H₂O</div> <div>1</div> <div>(this work)</div>	<div>Na₃(sac)₃·2H₂O [3]</div> <div>2</div>	<div>K₂Na(sac)₃·H₂O [4]</div> <div>3</div>
Empirical formula	C ₂₁ H ₁₂ N ₃ O ₉ S ₃ K ₃ · ·2H ₂ O	C ₂₁ H ₁₂ N ₃ O ₉ S ₃ Na ₃ · ·2H ₂ O	C ₂₁ H ₁₂ N ₃ O ₉ S ₃ K ₂ Na· ·H ₂ O
Formula weight	699.85	651.54	665.74
Temperature/K	293	293	294
Crystal System	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.619(1)	15.237(8) [7.346(3)]*	16.428(5) [6.954(1)]*
<i>b</i> /Å	12.325(1)	11.640(5) [11.640(5)]	12.122(4) [12.122(4)]
<i>c</i> /Å	15.521(1)	7.346(3) [15.237(8)]	6.954(1) [16.428(5)]
α /°	72.29(1)	96.31(3) [72.45(3)]	97.61(2) [69.91(2)]
β /°	86.58(1)	87.64(3) [87.64(3)]	77.36(2) [77.36(2)]
γ /°	81.27(1)	107.55(3) [83.69(3)]	110.09(2) [82.39(2)]
<i>V</i> /Å ³	1372.2(2)	1234.7	1266.5
<i>Z</i>	2	2	2
$\mu(M_0K\alpha)/cm^{-1}$	7.89	4.22	6.3
θ range/°	2.5 - 27	2 - 30	
Reflection collected	6200	6641	5647
Independent reflections <i>R</i> _{int}	5978/0.0127	5365	4724
Goodness-of-fit (<i>F</i> ²)	1.057		
Final <i>R</i> ₁ /w <i>R</i> ₂ indices (<i>I</i> > 2σ _{<i>I</i>}) (<i>I</i> > 3σ _{<i>I</i>})	0.0389/0.1252	0.039	0.054/0.075

* Data given in squared brackets correspond to the transformed original data using the transformation matrix of type: (0 0 1; 0 -1 0; 1 0 0 - for axes and $\alpha(\text{new}) = 180^\circ - \gamma(\text{old})$; $\beta(\text{new}) = \beta(\text{old})$; $\gamma(\text{new}) = 180^\circ - \gamma(\text{old})$ - for angles).

Table 1 Crystal data and structure refinement for K₃(sac)₃·2H₂O, and the respective data for Na₃(sac)₃·2H₂O [3] and K₂Na(sac)₃·H₂O [4].

K ₃ (sac) ₃ ·2H ₂ O (This work)		Na ₃ (sac) ₃ ·2H ₂ O [3]		K ₂ Na(sac) ₃ ·H ₂ O [4]	
1		2		3	
K1:CN=6		Na1:CN = 6		Na1:CN=6	
K1–O13	2.735(2)	Na(1)–Ow(1)	2.344(2)	Na(1)–O(13) ^{iv}	2.295(4)
K1–O21 ⁱ	2.707(2)	Na(1)–Ow(2)	2.345(2)	Na(1)–O(21) ^v	2.353(4)
K1–O31 ⁱⁱ	7 2.878(2)	Na(1)–O(32)	2.580(2)	Na(1)–O(1) ^{vi}	2.412(4)
K1–O31 ⁱⁱⁱ	2.855(2)	Na(1)–O(11)	2.674(2)	Na(1)–O(12) ^v	2.290(4)
K1–O32 ^{iv}	2.741(2)	Na(1)–O(12)	2.602(2)	Na(1)–O(1) ^v	2.841(4)
K1–O1W ⁱ	2.797(2)	Na(1)–O(13) ⁱ	2.365(2)	Na(1)–N(31) ^{vi}	2.538(4)
K2:CN=7		Na2:CN=6		K1:CN=8	
K2–O12 ⁱⁱⁱ	2.808(2)	Na(2)–Ow(2) ⁱⁱ	2.400(2)	K(1)–O(12)	2.749(3)
K2–O21 ⁱⁱⁱ	2.780(2)	Na(2)–O(21) ⁱ	2.431(2)	K(1)–O(23) ⁱ	3.113(4)
K2–O22 ⁱⁱⁱ	3.070(2)	Na(2)–O(22)	2.796(2)	K(1)–O(1) ⁱⁱⁱ	2.928(4)
K2–O23 ^{iv}	2.705(2)	Na(2)–O(22) ⁱⁱ	2.527(2)	K(1)–O(32) ⁱⁱⁱ	2.959(3)
K2–O31 ⁱ	3.100(2)	Na(2)–O(33) ⁱⁱⁱ	2.349(2)	K(1)–O(22) ⁱ	2.865(3)
K2–O1W ⁱⁱⁱ	2.776(2)	Na(2)–O(12) ⁱⁱ	2.430(2)	K(1)–N(11) ⁱⁱ	2.889(4)
K2–O21W*	2.702(3)			K(1)–O(31) ⁱⁱ	2.817(3)
K2–O23W*	2.652(9)			K(1)–N(31) ⁱⁱⁱ	3.236(6)
K3:CN=6		Na3:CN=6		K2:CN=6	
K3–O11 ^v	2.891(2)	Na(3)–Ow(1) ⁱⁱⁱ	2.331(2)	K(2)–O(11)	2.728(4)
K3–O12 ^{vi}	2.821(2)	Na(3)–N(3)	2.731(3)	K(2)–O(31)	2.802(3)
K3–N1 ^v	3.025(3)	Na(3)–O(31)	2.681(2)	K(2)–O(23) ^v	2.654(4)
K3–O33 ^{vii}	2.767(2)	Na(3)–O(32) ⁱⁱⁱ	2.534(2)	K(2)–N(21)	2.878(4)
K3–O33 ^{iv}	2.654(2)	Na(3)–O(23)	2.304(2)	K(2)–O(22) ^{iv}	2.786(3)
K3–O21W ^{iv*}	2.704(3)	Na(3)–O(23) ^{iv}	2.437(2)	K(2)–O(11) ^{iv}	2.599(4)
K3–O22W ^{iv*}	2.711(8)				
K3–O23W ^{iv*}	2.726(9)				
(K–O) _{mean}	2.790			(K–O) _{mean}	2.818
(K–N) _{mean}	3.025			(K–N) _{mean}	3.001
		(Na–O) _{mean}	2.478	(Na–O) _{mean}	2.438
		(Na–N) _{mean}	2.731	(Na–N) _{mean}	2.538

^a Symmetry transformations used to generate equivalent atoms: (none) x, y, z ; (i) $x, -1+y, z$; (ii) $x, -1+y, 1+z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, 2-z$; (vi) $1+x, y, z$; (vii) $x, y, 1+z$.

^b Symmetry transformations taken from references 3 and 4, respectively.

* Disordered water molecule with occupation factors 0.663(3), 0.190(5) and 0.147(5) for O21W, O22W and O23W, respectively.

Table 2 Interatomic distances (Å) involving the K^+ and Na^+ ions in the structures of $K_3(sac)_3 \cdot 2H_2O^a$, $Na_3(sac)_3 \cdot 2H_2O^b$ and $K_2Na(sac)_3 \cdot H_2O^b$.

Compounds 1 and 3:	$(\text{K-O})_{\text{mean}}$	2.780	
			$\Delta = (\text{K-O})_{\text{mean}} - (\text{Na-O})_{\text{mean}} = 0.311$
Compounds 2 and 3:	$(\text{Na-O})_{\text{mean}}$	2.469	
Compounds 1 and 3:	$(\text{K-N})_{\text{mean}}$	3.007	
			$\Delta' = (\text{K-N})_{\text{mean}} - (\text{Na-N})_{\text{mean}} = 0.372$
Compounds 2 and 3:	$(\text{Na-N})_{\text{mean}}$	2.635	
$r(\text{K})^+ = 1.38 \text{ \AA}$ (for CN = 6) [16]			
			$\Delta'' = r(\text{K})^+ - r(\text{Na})^+ = 0.36$
$r(\text{Na})^+ = 1.02 \text{ \AA}$ (for CN = 6) [16]			

Table 2 (continue) Interatomic distances ($\text{\AA}$) involving the K^+ and Na^+ ions in the structures of $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}^a$, $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}^b$ and $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}^b$.

	$\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ 1 (this work)	$\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ [3] 2	$\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$ [4] 3
Bond lengths			
Anion 1			
C–O	1.234(3)	1.230(3)	1.227(5)
C–N	1.360(3)	1.354(3)	1.351(5)
S–N	1.607(2)	1.596(2)	1.596(5)
C–S	1.766(3)	1.764(2)	1.760(5)
S–O	1.446(2)	1.443(2)	1.432(3)
	1.453(2)	1.450(2)	1.440(3)
Anion 2			
C–O	1.236(3)	1.241(4)	1.237(4)
C–N	1.355(4)	1.346(3)	1.348(5)
S–N	1.599(3)	1.606(2)	1.604(5)
C–S	1.766(3)	1.767(2)	1.753(5)
S–O	1.453(2)	1.446(2)	1.444(3)
	1.439(2)	1.456(2)	1.440(3)
Anion 3			
C–O	1.239(3)	1.237(3)	1.244(4)
C–N	1.355(4)	1.357(4)	1.353(4)
S–N	1.601(2)	1.603(2)	1.608(4)
C–S	1.765(3)	1.764(3)	1.770(5)
S–O	1.448(2)	1.445(2)	1.441(4)
	1.442(2)	1.455(2)	1.433(4)
Bond angles			
Anion 1			
C–C–N	113.2(2)	113.0(2)	113.2(3)
C–N–S	110.9(2)	111.4(2)	111.2(3)
C–S–N	98.1(1)	97.9(1)	97.7(2)
O–S–O	114.0(2)	112.9(1)	112.4(2)
Anion 2			
C–C–N	112.7(2)	113.7(2)	113.8(3)
C–N–S	111.6(2)	111.3(2)	110.8(3)
C–S–N	97.8(1)	97.5(1)	97.8(2)
O–S–O	113.3(1)	113.9(1)	112.8(2)
Anion 3			
C–C–N	113.3(2)	113.5(2)	113.5(3)
C–N–S	111.1(2)	111.0(2)	111.3(3)
C–S–N	97.8(1)	97.8(1)	97.2(2)
O–S–O	113.6(1)	114.0(1)	114.9(3)

Table 3 Selected bond lengths (Å) and angles (°) in the saccharinato ions for $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Na}(\text{sac})_3 \cdot \text{H}_2\text{O}$.

D-H...A	D...A	D-H	H...A	< D-H...A
O1W-H1W1...O11	2.976(3)	0.82(3)	2.23(3)	152.1(2.3)
O1W-H2W1...O23W ⁱⁱⁱ	3.067(12)	0.82(2)	2.70(3)	109.5(2.4)
O1W-H2W1...O13 ^{viii}	2.851(3)	0.82(2)	2.06(2)	163.0(3.1)
C15-H15...O13	3.043(4)	0.930(3)	2.872(2)	91.6(2)
C25-H25...O23	3.027(4)	0.930(3)	2.851(2)	91.8(2)
C35-H35...O33	3.038(4)	0.930(3)	2.862(2)	91.9(2)
C24-H24...O22W ^{ix}	3.304(9)	0.930(3)	2.561(9)	137.2(3)

^a Symmetry transformations used to generate equivalent atoms: (none) x, y, z ; (*iii*) $-x, 1-y, 1-z$; (*viii*) $-x, 1-y, 2-z$; (*ix*) $x, 1+y, z$.

Table 4 Lengths (Å) and angles (°) of hydrogen bonds in $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}^a$.

No	Experimental			Ab initio			Approximate		
	Infrared		Raman	Binev <i>et al.</i> [17]	Naumov, Jovanovski [9]		assignment ^e		
	RT	LNT	RT	<i>A</i> ^b	<i>A</i> ^c	<i>R</i> ^d			
1		1665 sh					$\nu(\text{H}_2\text{O})^f$		
2	1650 vs	1651 vs	1647 w	1700	495.6	1691	94.6	26.2	$\nu(\text{CO})+\nu(\text{CN})$
3	1641 vs	1643 vs							$\nu(\text{H}_2\text{O})^f$
4		1637 sh	1636 w						$\nu(\text{H}_2\text{O})^f$
5		1626 sh							
6	1587 s	1589 s	1595 m	1596	17.7	1599	50.8	175.9	$\nu(\text{CC})+\delta(\text{CCC})$
7	1543 vw	1546 vw		1584	13.8	1585	36.9	89.0	$\nu(\text{CC})+\delta(\text{CCC})$
8	1508 vw	1508 vw							
9		1498 vw							
10		1463 m		1468	4.5				$\delta(\text{HCC})+\nu(\text{CC})$
11	1459 m	1459 m	1458 w	1459	13.2				$\delta(\text{HCC})+\nu(\text{CC})$
12		1387 vw							
13		1365 sh				1366	35.0	59.4	$\delta(\text{HCC})+\nu(\text{CC})$
14		1345 sh							$\delta(\text{HCC})+\delta(\text{SCC})$
15	1332 s	1333 s	1331 w						$\delta(\text{HCC})+\nu(\text{CC})$
16	1288 s	1289 s	1292 w	1285	9.5				Benzenoid ^g
17	1255 vs	1258 vs	1257 w	1289	297.6	1268	324.7	8.4	$\nu_{as}(\text{SO}_2)$
18		1250 vs		1246	46.2				$\delta(\text{HCC})+\nu(\text{CC})$
19		1213 sh							
20	1164 s	1165 s	1166 m	1201	450.3				$\nu(\text{CN})+\delta(\text{CSN})$
21	1150 vs	1153 vs	1151 s	1160	349.4	1115	656.8	27.1	$\nu_s(\text{SO}_2)+\delta(\text{CSN})$
22		1144 vs		1135	2.4				$\nu(\text{CC})+\delta(\text{HCC})$
23	1120 s	1120 s	1123 vw	1117	40.9	1121	164.7	16.0	$\delta(\text{CCC})+\delta(\text{HCC})$
24		1116 sh							

^a Except for columns denoted by *A* and *R*, the data are given in cm^{-1} ; vw – very weak; w – weak; m – medium; s – strong; vs – very strong; sh – shoulder.

^b IR intensities (in km mol^{-1}) for saccharin anion.

^c IR intensities (in km mol^{-1}) for saccharin anion in ammonium saccharinate.

^d Raman scattering activities (in $\text{\AA}^4$ per amu) for saccharin anion in ammonium saccharinate.

^e Vibrational modes: ν , stretching; δ , bending (all kinds of); subscripts: as, antisymmetric; s, symmetric.

^f Assignment based on the band intensity decreasing in the spectrum of the deuterated sample (see Figure 8).

^g Internal mode of the saccharinato six-membered ring.

Table 5 Assignment of the experimental frequencies in the infrared and Raman spectra of tripotassium trisaccharinate dihydrate based on the literature theoretical infrared and Raman data for deprotonated saccharin (saccharin anion) in the $1700\text{--}1100\text{ cm}^{-1}$ region^a.

Fig. 2 The Crystal structure packing in $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$.

Fig. 3 The surroundings of potassium cations K1, K2 and K3 in $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$. The symmetry transformations are given in Table 2. In case of K2 and K3 only the oxygen atoms of the disordered water molecules, O21W, with the largest occupancy (0.663) are shown. The thermal ellipsoids are drawn as ORTEP plots at 50 % probability level.

Fig. 4 The O–H stretching region in (a) RT and (b) LNT IR spectrum of $K_3(sac)_3 \cdot 2H_2O$.

Fig. 5 The O–D stretching region in the LNT difference IR spectrum of partially deuterated analogue of $\text{K}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (the spectrum is obtained by subtracting the LNT spectrum of the protiated species from the corresponding spectrum of the sample deuterated to $w_D \approx 3\%$).

Fig. 6 The (a) RT and (b) LNT IR spectrum of $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ in the 2000–400 cm^{-1} region.

Fig. 7 The Raman spectrum of $K_3(sac)_3 \cdot 2H_2O$ in the 1750-50 cm^{-1} region.

Fig. 8 The LNT IR spectrum of the (a) protiated and (b) deuterated analogue of $K_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$ (*ca.* 30 % deuterium content) in the region where $\nu(\text{CO})$ mode is expected.