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INFRARED SPECTRA OF PROTIATED AND DEUTERATED LEAD(II) SACCHARINATE MONOHYDRATE : SPECTRA-STRUCTURE CORRELATIONS

Key words: Infrared spectra, saccharinate, spectra-structure correlations

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ABSTRACT

The infrared spectra of protiated and deuterated lead(II) saccharinate monohydrate, $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ were studied in the OH, OD, CO and SO_2 stretching regions. The spectral characteristics of the HOH and HOD stretching fundamentals were correlated with the structural data on the geometry of the water molecules. Also correlated were the appearance of the spectrum in the CO stretching region, on the one hand, and the number of non-equivalent carbonyl groups in the structure, on the other. An attempt was made to assign the bands which are mainly due to the antisymmetric and the symmetric SO_2 stretching vibrations.

INTRODUCTION

Saccharin [1,2-benzisothiazol-3(2H)-one 1,1-dioxide] belongs to the group of cyclic imides and is commonly used as a sweetening agent. Its chemical properties and especially the physiological and biochemical activity are being extensively investigated because of its suspected carcinogenic nature.

Saccharin forms several types of metal saccharinates. In order to obtain informations on the ligation properties of saccharin, we have undertaken a systematic structural[1-6] and spectroscopic[7-10] study of a series of metal saccharinates. In the present paper we report the results of the infrared study of lead(II) saccharinate monohydrate and correlate the observed frequencies in the regions of the OH, OD, CO and SO_2 stretching fundamentals with the crystallographically determined distances and angles for the water molecules and for the CO and SO_2 groups belonging to the saccharinate ions.

EXPERIMENTAL

The studied compound was prepared by gradually adding an equimolar quantity of $PbCO_3$ to a warm aqueous solution of saccharin. Transparent colourless prismatic crystals were obtained after cooling the reaction mixture to room temperature (abbreviated RT henceforward). Samples deuterated to various degrees were prepared similarly, using appropriate mixtures of H_2O and D_2O.

The infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer, using Nujol or Fluorolube mulls and NaCl discs. A variable temperature cell (RIIC VLT-2) cooled with liquid nitrogen was used for the low-temperature (LNT) measurements.

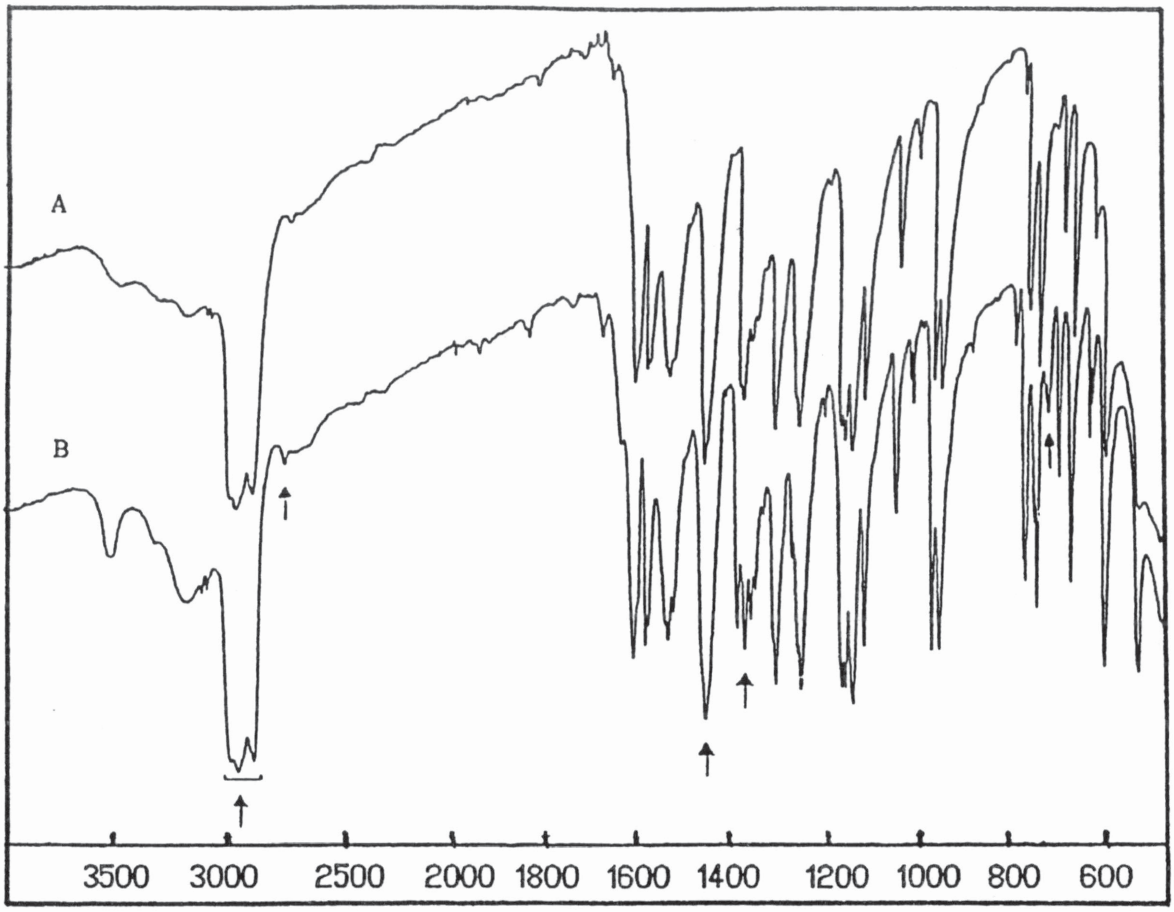

FIG. 1. Room-temperature (A) and low-temperature (B) infrared spectra of Nujol mulls of lead(II) saccharinate monohydrate (the bands due to the mulling agent are marked by arrows).

RESULTS AND DISCUSSION

Spectral data

The RT and LNT infrared spectra of protiated $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ are given in Fig 1. Fig. 2 shows the spectral changes in the OH stretching region of the protiated sample on lowering the temperature, whereas the appearance of the spectra in the OH and OD stretching regions of partially deuterated analogues containing

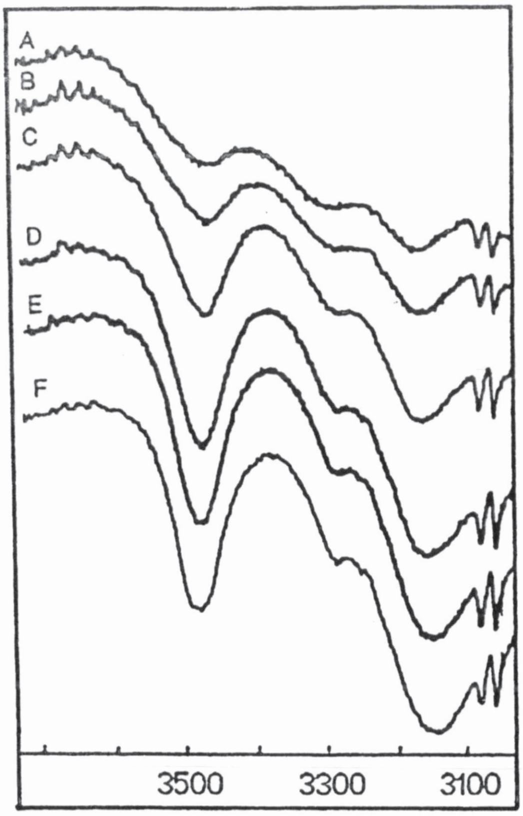

FIG. 2. The effect of the temperature lowering on the appearance of spectra of $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ in the O-H stretching region (curve A - room temperature; curve F - liquid-nitrogen temperature).

isotopically diluted HDO molecules are given in Figs. 3 and 4. The C=O and SO_2 stretching regions are shown in Figs. 5 and 6, respectively.

Structural data

The detailed discussion of the structure of lead(II) saccharinate monohydrate is given in ref. 4. Only the data referring to the H_2O molecules and the CO and SO_2 groups and to their immediate surrounding will be briefly summed up here.

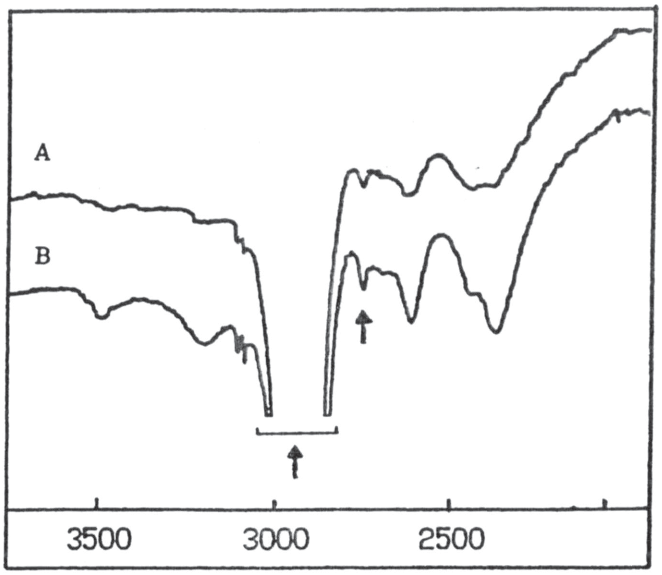

FIG. 3. RT (A) and LNT (B) spectra of highly deuterated $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ containing HDO molecules isotopically isolated with D_2O molecules (the arrows denote Nujol bands).

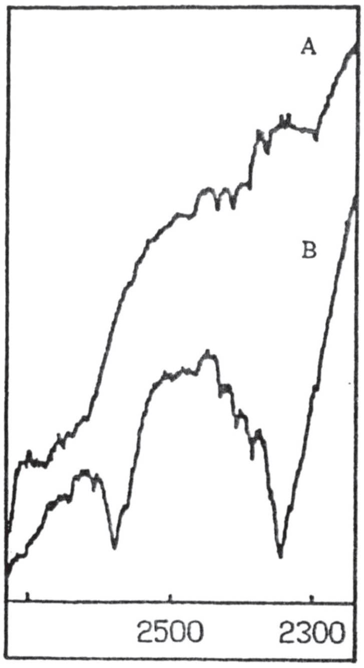

FIG. 4. LNT spectra of protiated (A) and slightly deuterated (B) $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ in the O-D stretching region.

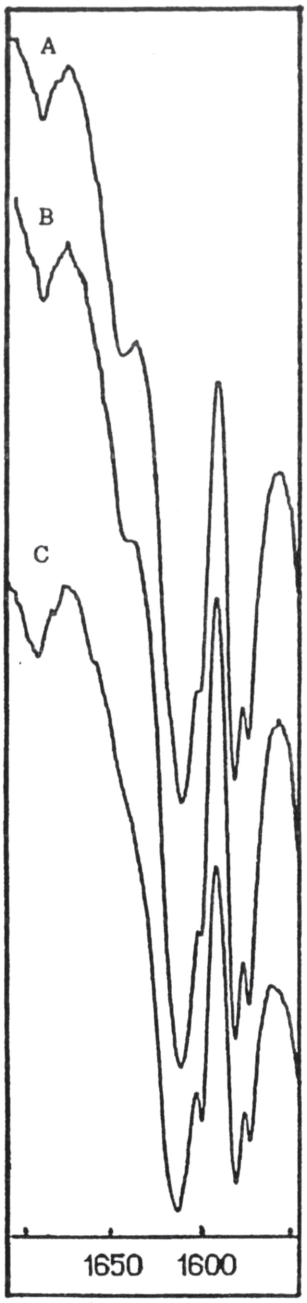

FIG. 5. The C=O stretching region in the spectra of protiated $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ (A) and its partly deuterated (B) and highly deuterated (C) analogues (the band denoted by an arrow is due to the H-O-H bending vibration).

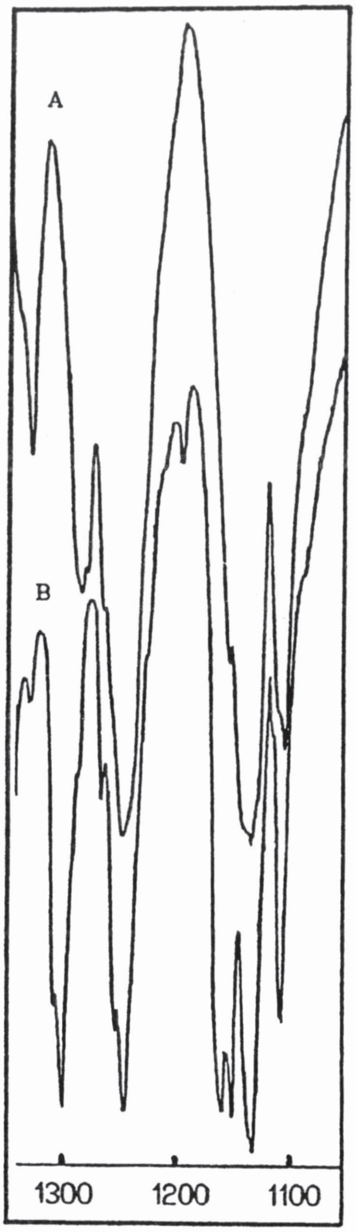

FIG. 6. The comparison of the SO_2 stretching regions in the spectra of $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$ (A) and $Pb(C_7H_4NO_3S)_2 \cdot H_2O$ (B).

The structure of the title compound consists of lead(2+) cations, saccharinate anions and water molecules. The Pb^{2+} ions are eight coordinated by one water O atom, three carbonyl oxygens, two O atoms from the SO_2 groups and two nitrogen atoms belonging to the saccharinate ions.

One of the carbonyl oxygen atoms from one of the two crystallographically independent saccharinates [denoted saccharinate(1) henceforth] is coordinated to *two* Pb^{2+} ions, while the carbonyl oxygen from the other saccharinate [denoted saccharinate(2)] is coordinated to *only one* Pb(2+) cation, at the same time participating in hydrogen bonding with the water molecule [$R(O_w...O)$ = 271(2) pm]. The second proton acceptor involved in hydrogen bonding is one of the SO_2 oxygen atoms [$R(O_w...O)$ = 296(1) pm]. The C-O distances are 120.4(15) and 125.5(15) pm.

Contrary to the SO_2 oxygen atoms from saccharinate(1), those from the saccharinate(2) anion are not coordinated to the Pb cations and do not participate in hydrogen bonding either. The four S-O distances are 143.9(9) and 143.3(9) in saccharinate(1) and 146.3(19) and 142.9(22) pm in saccharinate(2), while the O-S-O angles have values of 111.8(6) and 120.4(10)°, respectively.

Spectra-structure correlations

Water modes. As seen in Fig. 2 (curve A), three rather broad bands with almost equal intensity appear in the O-H stretching region at room temperature. Their frequencies are around 3469, 3288 and 3169 cm^{-1}.

The bands sharpen gradually and change position when the temperature is lowered (curves B-F). The high-frequency band (its RT value is 3469 cm^{-1}) shifts to *higher* frequencies (to around 3482 cm^{-1}), while the two low-frequency bands shift to *lower* frequencies (from 3288 and 3169 cm^{-1} to 3282 and 3139 cm^{-1}, respectively).

The presence of *three* O-H stretching bands in the infrared spectrum is somewhat surprising in view of the existence of *only one* type of water molecules in the structure. It is reasonable to suppose, however, that the apparent disagreement is due to the fact that the overtone of the HOH bending vibration takes part in a vibrational interaction with the symmetric H_2O stretch. The doubled value of the H-O-H bending frequency, namely, is quite close to the value of the absorption *minimum* (around 3243 cm^{-1} at RT) between the two RT low-frequency bands at 3288 and 3169 cm^{-1}.

That only *two* water stretching fundamentals exist (in line with the expectations) is shown by the analysis of the O-H and O-D stretching regions of partially deuterated samples in which the deuterium content is either very low or very high and the HDO molecules can be considered to be isotopically isolated, i.e. having as neighbours only water molecules with different isotopic composition (D_2O or H_2O). It is well-known[11,12], namely, that the frequencies of the bands originating from the decoupled O-D stretchings of HDO molecules in the spectra of the solid hydrates containing isotopically isolated HDO molecules are an excellent probe of the structure and bonding of water molecules.

As seen in Fig. 3, *two* bands appear in the O-H stretching region of the spectra of *highly deuterated* samples where the HDO molecules are isotopically diluted with D_2O molecules. Three bands are seen in the O-D stretching region, however. Two bands (at 2585 and 2325 cm^{-1}) are also seen (cf. Fig. 4) in the O-D stretching region of the spectra of partially deuterated samples with *low deuterium content* (in such samples the HDO molecules are isotopically isolated with H_2O molecules). The small bands or shoulders at the high- and low-frequency side of the two O-D stretching fundamentals are *not* due to water. As seen in Fig. 4, namely, bands with the same shape and intensity are present in the same spectral region of the spectrum of the protiated compound (the upermost curve in Fig. 4). Since the O-D stretching region is free from interfering bands (those due to the mulling agent), the spectra of the samples with low deuterium content will be discussed in more detail.

There is little doubt that the more weakly hydrogen-bonded group [$R(O_w...O)$ = 296(1) pm] gives rise to the high-frequency OD stretching band (found around 2585 cm^{-1}), while the more strongly hydrogen-bonded OD group [$R(O_w...O)$ = 271(2) pm] is responsible for the band appearing at 2325 cm^{-1} (Fig. 4). Thus, the spectral picture agrees well with the existence of *only one type of water molecules* in the structure[4]. The large splitting of the two OD stretching fundamentals (about 260 cm^{-1}), on the other hand, confirms[13,14] the pronounced distortion and the asymmetry in the bonding of the water molecules found in the structure of the title compound[4].

The non-negligible *intensity difference* between the two bands is another point worth mentioning. Similar spectral behaviour has been found in the case of $Ba(NO_3)_2 \cdot H_2O$[14], $Li_2SO_4 \cdot H_2O$[15], $SrCl_2 \cdot 2H_2O$ and

$BaCl_2 \cdot 1/2H_2O$[16] as well as in the monohydrate of sodium thiosaccharinate[17] and in other hydrates. As pointed out by Lutz[16], the different intensity of the two OD stretching modes is probably mainly the result of the differences in the *nature of the normal coordinates* of the HDO vibrations for the asymmetrically bonded HDO molecules acquiring one of the two possible orientations (H-O-D...O and D-O-H...O, respectively).

CO stretchings. The assignment of the bands originating from the C=O stretching modes in the spectra of the title compound was, as in the case of other saccharinates[8,9] accompanied by at least two difficulties.

First of all, the bands which are due to the C=O stretching vibrations appear in the spectral region where modes localized mainly in the six-membered ring of the saccharinate anion are also expected. Secondly, the HOH bending bands may also be present in the same spectral region. The complications arising from the presence of the water bending band were almost entirely eliminated by recording the spectra of samples deuterated to a high degree, whereas the benzenoid ring stretching bands are sharper and with somwhat lower frequencies than the bands which originate from the carbonyl stretches (cf. Fig. 5).

Although it was shown[9] that, in principle, a precise correlation between the C=O stretching frequencies and CO distances in a series of different metal saccharinates is *not* possible, it seems that in the case of lead(II) saccharinate monohydrate the structural data concerning the CO group are in a rather good agreement with the appearance of the infrared spectrum. Namely, the existence of *two* rather different CO distances [120.4(15) and 125.5(15) pm] in the structure is manifested by the appearance of *two* strong bands at 1610 and 1601 cm^{-1} in the spectrum (the high-frequency band being far more intense) (see Fig. 5).

The frequency (around 1610 and 1601 cm^{-1}) of both carbonyl stretching vibrations in the spectrum of title compound is *lower* than in saccharin itself (1725) cm^{-1}). This shift of the CO stretch to lower frequencies for about 120 cm^{-1} agrees with the previously observed values in the spectra of a number of ionic saccharinates (those of Na, Mg, Mn, Fe, Co, Ni, Zn and Cd[8,9,18].

SO stretchings. As pointed out above, the SO_2 groups of the two saccharinate anions in the structure of $Pb(C_7H_4NO_3S)_2{\cdot}H_2O$, are appreciably different. This is especially true for the two O-S-O angles, but even the SO distances are not equal for the SO_2 groups in saccharinate(1) and saccharinate(2). Still, the SO distances in lead(II) saccharinate monohydrate[4] are not very different from those found in the structute of trisodium trisaccharinate dihydrate[1] (there are three pairs of such distances: 144.3(2) and 145.0(2) pm; 144.6(2) and 145.6(2) pm and 144.5(2) and 145.5(2) pm). Similarly, the value of the O-S-O angle in saccharinate(1) is close to the three such values reported[1] for $Na_3(C_7H_4NO_3S)_3{\cdot}2H_2O$ (the values there are 112.9(1), 113.9(1) and 114.0(1)°. So, the assignment[18] of the spectrum of $Na_3(C_7H_4NO_3S)_3{\cdot}2H_2O$ can be used as a guide for the assignment of the bands which are due to the SO_2 stretching modes in the spectrum of $Pb(C_7H_4NO_3S)_2{\cdot}H_2O$. It should be born in mind that, as mentioned, *two* non-equivalent SO_2 groups are present in the structure of

$Pb(C_7H_4NO_3S)_2 \cdot H_2O$ and thus at least *two pairs* of SO_2 stretching bands are expected in the spectrum of this compound. Since the value of the O-S-O angle in saccharinate(2) is appreciably larger than that in saccharinate(1), the frequency difference between the antisymmetric and the symmetric SO_2 stretch in the former case is expected to exceed that in the latter.

As seen in Fig. 6 (curve A), in the spectrum of trisodium trisaccharinate dihydrate there are only two bands (at 1260 and 1150 cm^{-1}) which are strong enough to be assigned to the antisymmetric and symmetric SO_2 stretching modes, respectively. In the spectrum of the title compound (curve B in Fig. 6), however, there are at least *five* strong bands in the corresponding region. Two of them (found at 1308 and 1255 cm^{-1}) lie in the region where the antisymmetric SO_2 stretchings are expected to appear, whereas those at around 1167, 1159 and 1142 cm^{-1} fall in the region of the symmetric SO_2 stretchings. It seems reasonable to assign the bands at 1308 and 1255 cm^{-1} (especially the latter one) to the antisymmetric SO_2 stretches of the two structurally non-equivalent SO_2 groups but it is difficult to decide which of the strong bands in the region below 1200 cm^{-1} are due to the symmetric SO_2 stretching vibrations. The comparison with the spectrum of $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$, however, seems to indicate that the band at 1142 cm^{-1} is most probably due to one of the expected symmetric SO_2 stretches.

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