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INFRARED SPECTRUM OF SILVER SACCHARINATE : STRUCTURAL INFERENCES

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In an attempt to obtain some information about the character of the metal-to-ligand bonding in silver saccharinate and to make other structural inferences, the infrared spectrum of the title compound was studied, particularly in the region of the CO and SO_2 vibrations. Judging from the CO stretching frequency, the silver-to-saccharin bond in silver saccharinate appears to be mainly ionic in character. Because various factors determine the frequency difference of the two SO_2 stretching modes, the position of the SO_2 bands cannot be used to make conclusions about the type of metal-to-ligand bonding.

Key words: silver saccharinate; metal-to-ligand bonding; CO and SO_2 vibrations

INTRODUCTION

In order to obtain information on the crystal chemistry of various metals as well as on the complexing properties of saccharin, we have undertaken a broad research of the structural [1–7] and spectroscopic [8–12] characteristics of several metal saccharinates. In the meantime, data related to the structures of additional metal saccharinates have been published [13–15]. The crystal-structure analysis revealed differences in the type of the metal-to-ligand bonding in various metal saccharinates. It was found that some complexes are mainly ionic [1, 5, 14], others are covalent [2, 4, 6] and in still other cases the bonding appears to be intermediate between ionic and covalent [3, 13, 15].

For a number of metal saccharinates, the correlations between the structures, on the one hand, and the infrared spectra, on the other [9,10], have shown that irrespective of whether or not the CO and SO_2 oxygens participate in the coordination sphere around the metal atoms and/or take part in hydrogen bonding, the frequency of the CO and SO_2 stretching vibrations in the spectra of the saccharinates is *lower* than in saccharin itself but the *magnitude* of the frequency lowering depends on the type of the metal-to-saccharin bond. Thus, the shift to lower frequencies in the case of the ionic or intermediate metal saccharinates (those of Mn, Fe, Co, Ni, Zn, Cd, Pb, Mg and Na) is more pronounced than that observed in the case of the covalently bonded compounds (mercury saccharinate and chloromercury saccharinate) [9, 10].

The structural relevance of the *number* of observed C=O stretching bands is considerably less in the case of a saccharinate of unknown structure. It was found that in the spectrum of the highly deuterated $Na_3(sac)_3 \cdot 2H_2O$ (sac denotes saccharinate ion), *only one* carbonyl stretching band exists [9, 10], in spite of the existence of *three* crystallographically different C=O distances in the structure [1]. It is true that these three distances are very close to each other but, on the other hand, *two clearly separated bands* are found [9, 10] in the infrared spectrum of the highly deuterated analogue of $Mg(sac)_2 \cdot 7H_2O$, despite the fact that in the structure of the protiated compound the two carbonyl distances are also very close [1]. Furthermore, two C=O stretching bands are present (for reasons of symmetry) in the spectra of the isomorphous series of the saccharinates of Mn, Fe, Co, Ni, Zn and Cd [10], whereas *only one type* of C=O group is present in the structure [3].

The main structural inferences which could be made by analyzing the bands which are due to the SO_2 stretching modes are related to the values of the O-S-O angles and, perhaps, the number of crystallographically non-equivalent SO_2 groups. It has been shown [16] that the increase of the O-S-O angle in the structure is expected to produce an increase in the frequency difference between the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes in the spectra, the general conclusion being supported by the results of the spectra-structure correlations for various saccharinates [12, 17]. On the other hand, the number of pairs of SO_2 stretching bands [i.e. bands due to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes] may be indicative of the number of non-equivalent SO_2 groups. This too has been shown in the course of our previous studies on saccharinates [12, 17].

Since, to the best of our knowledge, neither crystallographic nor infrared studies have been performed on silver saccharinate, we decided to try to get some preliminary information about the metal-to-ligand bonding character in silver saccharinate and about other structural characteristics of this compound. As a basis, the analysis of the CO and SO_2 stretching regions of the spectrum of silver saccharinate was used, the spectral characteristics in the present case being compared to those of previously studied saccharinates with known structures.

EXPERIMENTAL

The crystals of silver saccharinate were prepared by mixing equimolar aqueous solutions of $AgNO_3$ and saccharin (or sodium saccharinate) and keeping the resulting mixture at a high temperature (~ 350 K) for 10 min. After cooling the reaction system to room temperature, transparent needle-shaped crystals were obtained. The crystals were recrystallized from aqueous solution.

The infrared spectra were recorded from AgCl 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. The room temperature (RT) and LNT infrared spectra of the title compound in the 4000 – 300 cm^{-1} region are shown in Fig. 1.

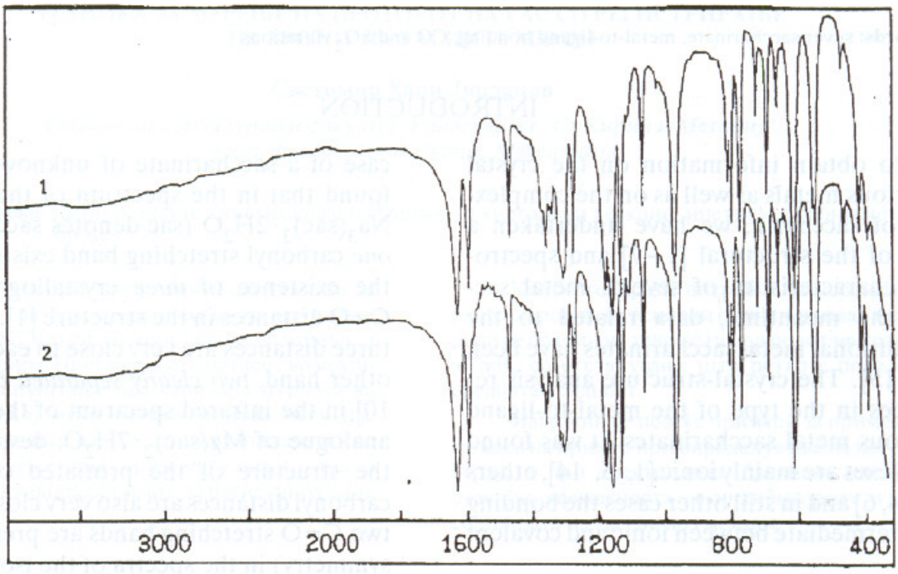

Fig. 1. RT (1) and LNT (2) infrared spectra of silver saccharinate

RESULTS AND DISCUSSION

CO stretchings

In general, the location of the carbonyl stretching bands in the spectra of metal saccharinates is not always straightforward because of the existence, in the same spectral region, of bands due to some of the vibrations localized mainly in the six-membered aromatic ring and, in the case of the crystallohydrates, of bands originating from the water bending vibrations [9, 10]. Fortunately, silver saccharinate is *anhydrous,* while the bands due to the benzenoid ring stretches are expected to appear lower than 1600 cm^{-1} [18, 19] and to be *much sharper* than those arising from the CO stretches.

As seen in Fig. 2, only one strong band appears in the C=O stretching region of the LNT spectrum of silver saccharinate, the sharp band around 1582 cm^{-1} being undoubtedly due to one of the benzenoid ring stretching modes. The frequency of the ν(CO) band (1628 cm^{-1}) is 97 cm^{-1} *lower* than that of the corresponding band in the spectrum of saccharin (see Fig. 2) and falls in the region of the frequencies of the C=O stretching modes of *ionic* saccharinates of Mg, Na, Pb, Mn and its isomorphous analogues of Fe, Co, Ni, Zn and Cd [9, 10] (see Fig. 3). This is a serious indication that the silver-to-saccharin bond in the title compound is *mainly ionic* in character.

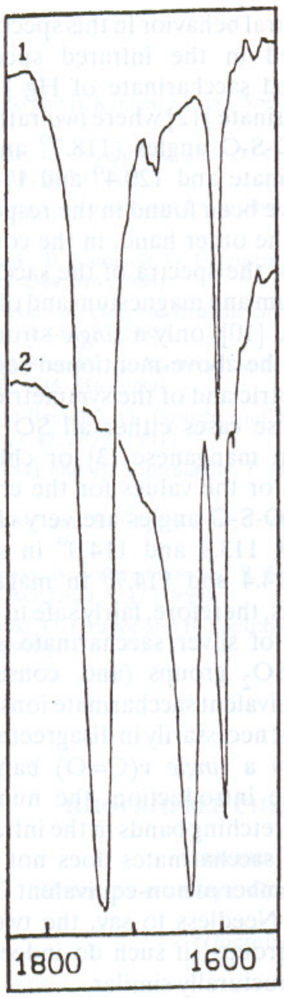

Fig. 2. The C=O stretching region in the LNT infrared spectra of saccharin (1) and silver saccharinate (2)

SO_2 vibrations

As is well known [e.g. 20–23], the bands due to the two SO_2 stretching vibrations are expected in the region from 1350 to 1100 cm^{-1}.

As seen in Fig. 4, *eight* bands of various intensity appear in the room-temperature spectrum of silver saccharinate in the region (1400-1100 cm^{-1}) where the antisymmetric and symmetric SO_2 stretchings are expected. When the temperature is lowered, a new band separates (at around 1316 cm^{-1}) on the high-frequency side of the band around 1305 cm^{-1} where at RT only a shoulder is seen. Thus, all together *nine* bands (at 1370, 1358, 1341, 1316, 1305, 1272, 1178, 1155 and 1130 cm^{-1}) appear in the LNT spectrum of the title compound in the region where the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes are expected, the bands at 1305, 1178 and 1155 cm^{-1} being broader and far more intense than the rest.

According to the normal-coordinate analysis for phtalimide, potassium phtalimide and its tetrachloro analogue, at least *four* [18] or, perhaps, as many as *six* [19] bands due to the ring stretches should be present in the 1360–1130 cm^{-1} region. Consequently, it is reasonable to assume that the sharp bands in the spectrum of the title compound whose frequencies are similar to those calculated for the ring stretch modes in potassium phtalimide and its tetrachloro analogue could be similarly assigned to the ring stretches. Such are the bands at 1370, 1358, 1341, 1272 and 1130 cm^{-1} (and probably the shoulder at 1310 cm^{-1} as well), leaving the remaining two pairs of intense bands (those at 1316 and 1305 cm^{-1} and 1178 and 1155 cm^{-1} respectively) to be attributed to the antisymmetric and symmetric SO_2 stretching vibrations.

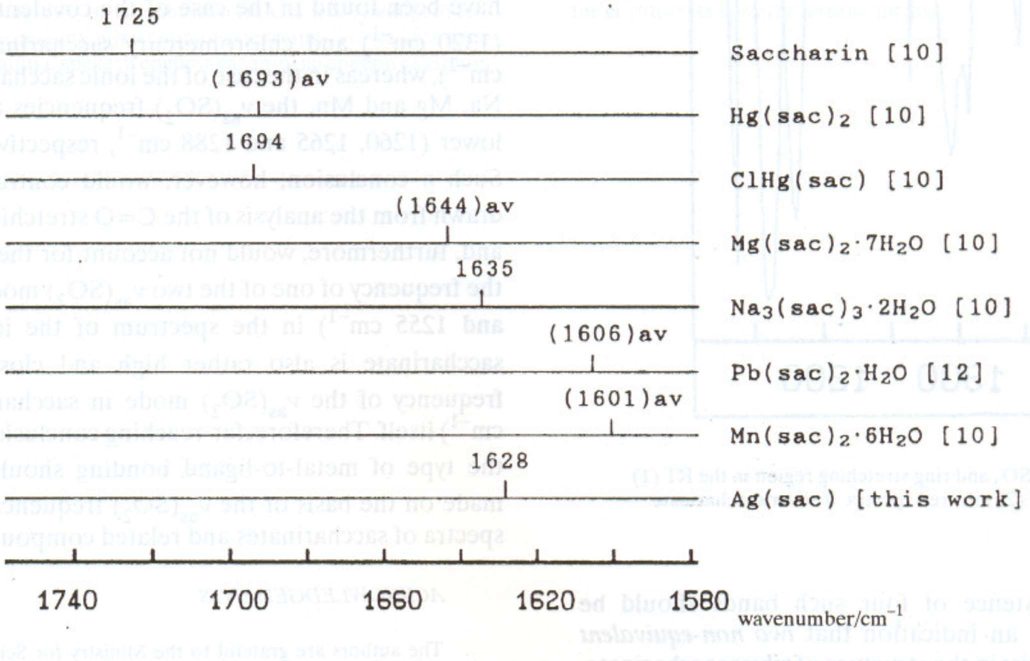

Fig. 3. The C=O stretching frequencies in the LNT infrared spectra of various metal saccharinates

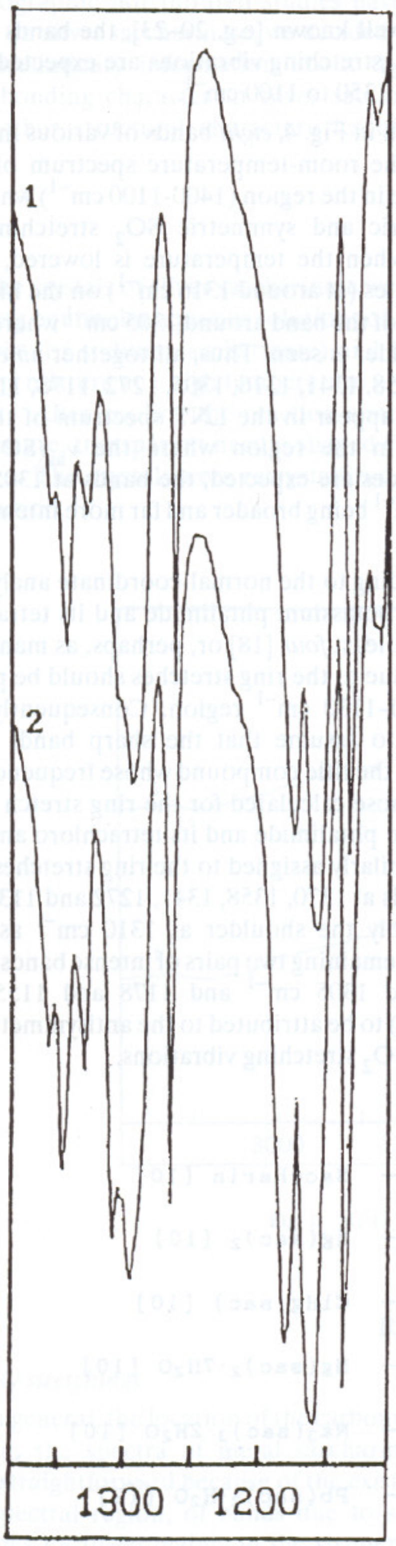

Fig. 4. The SO_2 and ring stretching region in the RT (1) and LNT (2) infrared spectra if silver saccharinate

The existence of four such bands should be considered as an indication that *two non-equivalent* SO_2 groups exist in the structure of silver saccharinate.

Very similar spectral behavior in this spectral region is, namely, observed in the infrared spectra of the covalently bonded saccharinate of Hg [17] and the ionic lead saccharinate [12] where *two* rather different values for the O-S-O angles (118.7° and 111.8° in mercury saccharinate and 120.4° and 111.8° in lead saccharinate) have been found in the respective structures [2, 5]. On the other hand, in the corresponding spectral region of the spectra of the saccharinates of manganese, sodium and magnesium and of chloromercury saccharinate [10], only a *single* strong band appears in each of the above-mentioned regions (those of the antisymmetric and of the symmetric SO_2 vibrations). In all these cases either all SO_2 groups are equivalent (as in manganese [3] or chloromercury saccharinate [4]) or the values for the crystallographically different O-S-O angles are very close to each other (*e.g.* 112.9, 113.9 and 114.0° in sodium saccharinate and 114.4 and 114.7° in magnesium saccharinate [1]). It is, therefore, fairly safe to assume that in the structure of silver saccharinate at least *two* non-equivalent SO_2 groups (and, consequently, at least two non-equivalent saccharinate ions) exist. Such a conclusion is not necessarily in disagreement with the existence of only a *single* $\nu(C{=}O)$ band since, as mentioned in the introduction, the number of the observed C=O stretching bands in the infrared spectra of various metal saccharinates does not always correspond to the number of non-equivalent C=O groups in the structure. Needless to say, the two non-equivalent carbonyl groups (if such do indeed exist) are expected to be structurally similar.

It is tempting to conclude that the relatively high frequency of the $\nu_{as}(SO_2)$ bands (1316 and 1305 cm^{-1}) is indicative of *covalent* metal-to-ligand bonding since such high frequencies for the corresponding mode have been found in the case of the covalent mercury (1320 cm^{-1}) and chloromercury saccharinate (1300 cm^{-1}), whereas in the case of the ionic saccharinates of Na, Mg and Mn, the $\nu_{as}(SO_2)$ frequencies are much lower (1260, 1265 and 1288 cm^{-1}, respectively [17]). Such a conclusion, however, would contradict that drawn from the analysis of the C=O stretching region and, furthermore, would not account for the fact that the frequency of one of the two $\nu_{as}(SO_2)$ modes (1308 and 1255 cm^{-1}) in the spectrum of the ionic lead saccharinate is also rather high and close to the frequency of the $\nu_{as}(SO_2)$ mode in saccharin (1335 cm^{-1}) itself. Therefore, far-reaching conclusions about the type of metal-to-ligand bonding should not be made on the basis of the $\nu_{as}(SO_2)$ frequencies in the spectra of saccharinates and related compounds.

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Резиме

ИНФРАЦРВЕН СПЕКТАР НА СРЕБРО САХАРИНАТ : СТРУКТУРНИ ЗАКЛУЧОЦИ

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Клучни зборови: сребро сахаринат; врска метал-лиганд; CO и SO_2 вибрации

Испитуван е инфрацрвениот спектар на сребро сахаринатот со цел да се добијат некои информации за карактерот на врската метал-лиганд кај ова соединение, како и да се направат други структурни заклучоци. Притоа, особено внимание е посветено на подрачјето на CO и SO_2 вибрациите. Заклучено е дека, судејќи според фреквенцијата на валентната CO вибрација, врската сребро-сахарин во сребро сахаринатот е главно јонска по својот карактер. Најдено е, исто така, дека, со оглед на тоа што разни фактори ја определуваат фреквентната разлика на двата SO_2 валентни мода, положбата на SO_2 лентите не може да послужи за донесување на заклучоци за типот на врската метал–лиганд.