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STRUCTURAL CHARACTERISTICS OF THE HYDRATES OF THE SACCHARINATES OF CALCIUM, STRONTIUM AND BARIUM

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ABSTRACT

The infrared spectra of the hydrates of the saccharinates of calcium, strontium and barium in the region of the OH, OD, CO and SO_2 stretching modes as well as their X-ray powder diffractograms were studied. The analysis of the infrared spectra in the region of the CO stretching vibrations indicates that the metal-to-saccharin bonds in the studied compounds are mainly ionic in character.

INTRODUCTION

Continuing our structural studies on metal compounds of saccharin with various metals [2-13], we investigated the hydrates of saccharinates of calcium, strontium and barium. The investigated compounds are known for a long time (Defournel [1] was apparently the first to prepare and characterize the saccharinates of calcium and strontium, describing them as undecahydrate and dihydrate, respectively). To the best of our knowledge, neither infrared nor crystallographic studies on the saccharinates of Ca, Sr and Ba have been performed. In order to get preliminary information about some of the

structural characteristics (the metal-to-ligand bonding character, the hydrogen bonding in which the water molecules are involved, the structural similarities or dissimilarities, etc.) of the title compounds, we decided to study their infrared spectra in the regions of the OH, OD, CO and SO_2 stretching modes as well as their X-ray powder diagrams.

EXPERIMENTAL

The studied compounds were prepared by gradually adding an equimolar quantity of calcium, strontium or barium carbonate to a warm aqueous solution of saccharin. Needle-shaped crystals of all three compounds were obtained after cooling the reaction mixtures to room temperature (RT). Deuterated samples were prepared similarly, using appropriate solutions in D_2O.

The water content in the protiated samples was determined by electrometric Karl Fisher titration on a DTS800 multi-titration system.

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

The X-ray powder diagrams were obtained on a JEOL diffractometer using Cu$K\alpha$ radiation (λ = 154.178 pm).

RESULTS AND DISCUSSION

The collected data on the water content in the samples are given in Table I. As can be seen, the experimental results suggest that the saccharinates of calcium and strontium would be best described as tetrahydrates and the corresponding barium compound as an octahydrate.

The LNT infrared spectra of the studied saccharinate compounds of Ca, Sr and Ba in the region from 4000 to 300 cm^{-1} are shown in Fig. 1, the region of the OD stretching vibrations of the isotopically isolated HDO molecules is presented in Fig. 2 and the X-ray diffraction patterns for the three studied compounds of Ca, Sr and Ba are given in Fig. 3.

Table I. Analytical data on the water content in the hydrates of the saccharinates of calcium, strontium and barium

M-saccharinate*	M_r	Water content (in mass %)	
		Theoretical	Experimental
$Ca(sac)_2 \cdot 4H_2O$	477.24	15.10	14.31
$Sr(sac)_2 \cdot 4H_2O$	524.06	13.75	14.75
$Ba(sac)_2 \cdot 8H_2O$	646.04	22.31	23.10

* The abbreviation sac stands for saccharinate.

The values for the CO stretching frequencies in the infrared spectra of various metal saccharinates (including the studied title compounds) are given in Fig. 4, while the frequencies of the stretching SO_2 modes in the spectrum of saccharin and the studied metal saccharinates are compiled in Table II.

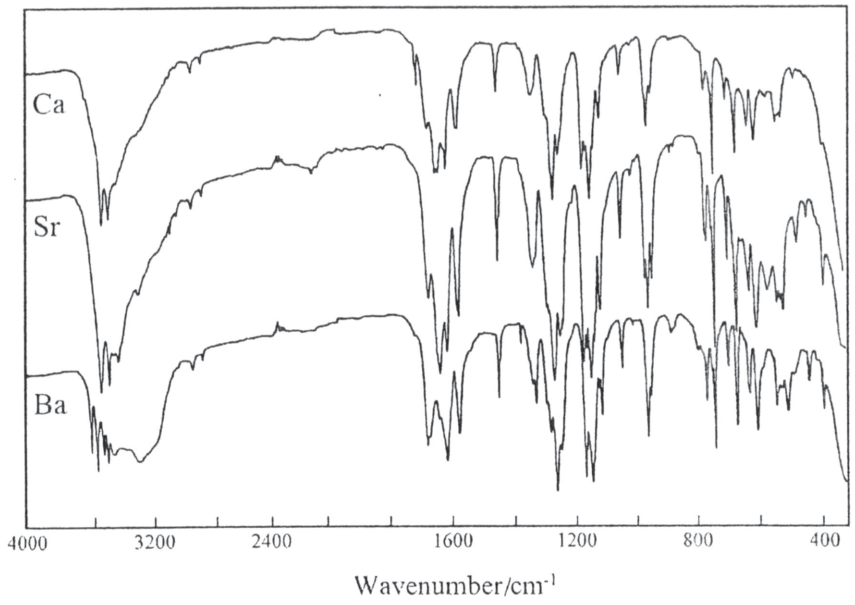

Fig. 1. The LNT infrared spectra of the hydrates of the saccharinates of calcium, strontium and barium

O-H and O-D stretchings

As seen from Fig. 1, the LNT infrared spectra of the saccharinates of Ca and Sr, in spite of some minor differences, are rather similar to each other. It can be taken as an indication that these two compounds are structurally alike. On the other hand, the LNT infrared spectrum of Ba saccharinate is significantly dissimilar, the differences being especially pronounced in the H_2O and CO stretching regions (see Fig. 1). The comparison of the spectra of the studied compounds in the ν(OH) region shows that some of the water molecules in the Ba compound are not hydrogen bonded (or participate in the formation of very weak hydrogen bonds) while others are more strongly hydrogen-bonded than in the saccharinates of Ca and Sr.

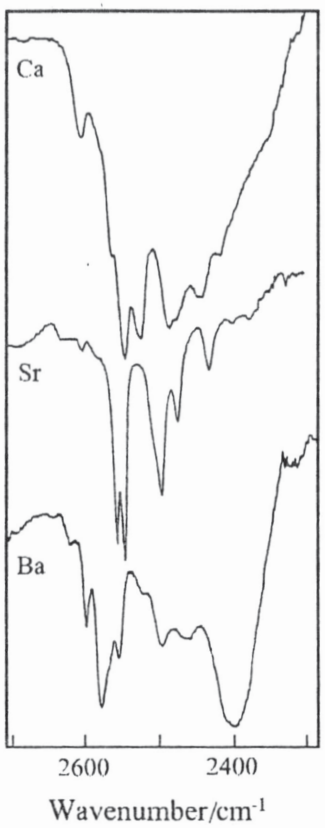

Fig. 2. The region of the OD stretching vibrations in the LNT infrared spectra of the studied samples containing isotopically isolated HDO molecules

Additional evidence about the above-mentioned structural characteristics of the studied compounds was obtained from the study of the infrared spectra of samples containing isotopically isolated HDO molecules in the region of the O-D stretching vibrations. As seen in Fig. 2, the spectra of the Ca and Sr compounds in this spectral region are again similar (although the similarity here is less pronounced than in the region of the O-H stretching vibrations) while the spectrum of the Ba compound in the same spectral region is completely different, in agreement with the conclusion based on the appearance of the spectra in the ν(O-H) region.

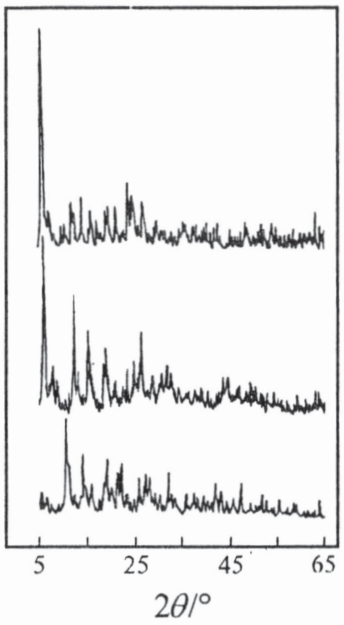

Fig. 3. The X-ray diagrams for the hydrates of the saccharinates of calcium, strontium and barium

Powder X-ray diffraction

The indication about the structural similarity between the hydrates of the saccharinates of Ca and Sr and the rather noticeable difference between the structure of these two compounds and the hydrate of Ba saccharinate obtained from the analysis of the infrared spectra is confirmed by their X-ray diffraction patterns (see Fig. 3). As expected,

the X-ray diagram of the Ba compound evidently differs from the mutually rather similar diffractograms of the Ca and Sr compounds.

Metal-to-ligand bonding

CO stretchings

The correlation between the structure and the infrared spectrum for the number of metal saccharinates [6,10,12] has shown that, irrespective of whether or not the CO oxygen participate in the coordination sphere around the metal atoms and/or take part in hydrogen bonding, the frequency of the CO stretching vibrations in the spectra of the saccharinates is lower than in saccharin itself. However, the ν(CO) frequency depends on the type of the metal-to-saccharin bond, the shift towards lower frequencies being less pronounced in the case of the covalently bonded compounds (mercury saccharinate and chloromercury saccharinate) than that observed for the ionic or intermediate metal saccharinates (those of Na, Mg, Mn, Fe, Co, Ni, Zn, Cd and Pb) [6,10,12]. This kind of spectral behavior was used to predict the metal-to-ligand bonding type in the saccharinates of Ca, Sr and Ba whose structures are unknown.

The location of the CO stretching bands in the spectra of the saccharinates of Ca, Sr and Ba was accompanied by some difficulties 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 as well as of bands originating from the water bending vibrations. However, the bands due to the benzenoid ring stretches were usually found to be much sharper than those arising from the CO stretches and are expected to appear at frequencies lower than 1600 cm^{-1} [14,15], while those originating from the water bending vibrations were almost completely eliminated by preparing highly deuterated samples of the studied compounds.

As seen from Fig. 4, the frequencies of the ν(CO) bands in the spectra of the saccharinates of Ca, Sr and Ba are for 80 to 100 cm^{-1} lower than the value of the corresponding band in the spectrum of saccharin and fall in the region of the ν(CO) frequencies

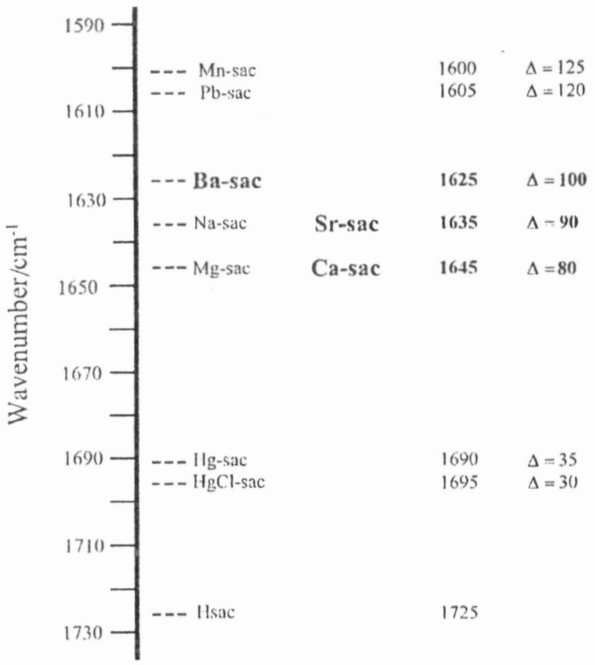

Fig. 4. The values (in cm^{-1}) for the CO stretching frequencies in the infrared spectra of various metal saccharinates including the studied title compounds and for the frequency difference between the value of ν(CO) in saccharin and in the given saccharinate. As before, Hsac denotes saccharin, while M-sac stands for metal saccharinate; the water content is not given

observed for the *ionic* saccharinates of Mg, Na, Pb and Mn, in agreement with the expectations that the metal-to-saccharin bonds in the studied compounds are mainly ionic in character. On the other hand, the above-mentioned fact provides an additional support for the conclusion that the value of the n(CO) frequency is a good probe for determining the character of the metal-to-ligand bonding.

SO_2 stretchings

The bands originating from the two SO_2 stretching vibrations are expected in the region from 1350 to 1100 cm^{-1} [see, for example, 16-18]. However, as in other metal saccharinates [13, 19, 20], the location of the bands due to the ν(SO_2) modes in the studied saccharinates of Ca, Sr and Ba was not straightforward. Namely, as already dis-

cussed in refs. 13 and 20, at least four to five bands [14,15] due to the ring stretches should be present in the region where the bands originating from the SO_2 stretching vibrations are also expected to appear. Fortunately, the benzenoid ring stretching bands are sharp and, at best, moderately intense, while the $\nu(SO_2)$ modes (which are rather good group vibrations [17]) give rise to very strong bands. Therefore, the strongest bands in the above-mentioned region in the spectra of the studied compounds were attributed to the corresponding antisymmetric and symmetric SO_2 stretching vibrations (see Fig. 1 and Table II).

Table II. The values for the frequencies (in cm^{-1}) of the SO_2 stretching modes in the spectrum of saccharin and the studied metal saccharinates

Compound	ν_{as}	ν_s	Δ	Δ'	Δ''
Hsac [19]	1335	1180	155		
$Ca(sac)_2 \cdot 4H_2O$	1270	1150	120	65	30
$Sr(sac)_2 \cdot 4H_2O$	1275	1150	125	60	30
$Ba(sac)_2 \cdot 8H_2O$	1270	1150	120	65	30

$\Delta = \nu_{as} - \nu_s$; $\Delta' = \nu_{as}$[H(sac)] - ν_{as}[M-sac]; $\Delta'' = \nu_s$[H(sac)] - ν_s[M-sac]; Hsac denotes saccharin.

As seen from Table II, the frequencies of the antisymmetric and symmetric SO_2 stretching vibrations in the spectra of the saccharinates of Ca, Sr and Ba are lower than in saccharin itself. The lowering of the more sensitive to external influences $\nu_{as}(SO_2)$ mode [16] is expectedly more pronounced. Various factors, however, determine the frequency difference of the SO_2 stretching modes [13, 20]. Namely, the analysis of the infrared spectra of various metal saccharinates in the region of the stretching SO_2 modes has shown [20] that, contrary to the case of the carbonyl stretching vibrations (the frequencies of which mainly depend on the type of the metal-to-saccharin bond), the lowering of the frequencies of the $\nu(SO_2)$ modes is additionally influenced by the value of the O-S-O angle in the structure. Therefore, the position of the bands arising from the

SO_2 stretching vibrations in the spectra of the saccharinates of Ca, Sr and Ba can not be used to predict the type of metal-to-ligand bonding in their structures.

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Povzetek

Preučevali smo infrardeče spektre hidratov saharinatov kalcija, stroncija in barija v področjih OH, OD, CO in SO_2 valenčnih nihanj ter rentgenske uklonske posnetke njihovih praškastih vzorcev. Analiza CO valenčnih nihanj kaže na to, da so vezi med kovino in saharinom v preučevanih spojinah pretežno ionskega značaja.

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