

SYNTHESIS AND COMPARATIVE VIBRATIONAL STUDY OF TWO NOVEL CESIUM SACCHARINATES: SPECTROSCOPIC EVIDENCE FOR A SACCHARIN ADDUCT

Pance Naumov, Gligor Jovanovski

Institut za hemija, PMF, Univerzitet "Sv. Kiril i Metodij", POB 162, MK-91001 Skopje, Macedonia; spance@iunona.pmf.ukim.edu.mk

Abstract: Two novel saccharinates were synthesized and characterized as Cs(Hsac)(sac)·H₂O (**1**) and Cs(sac)·0.5H₂O (**2**). Their protiated and partially deuterated analogues were studied by FT IR spectroscopy at various temperatures.

Contrary to all studies to date of saccharinates, the frequency of one $\nu(\text{CO})$ mode in the spectrum of **1** is significantly *higher* than the corresponding value of the saccharin itself in the solid state and an absorption due to the NH stretching modes is also present in its spectrum. These findings represent spectroscopic evidence that **1**, besides a single compound reported previously [1], is an adduct of *molecular* saccharin. The present case confirms that, besides the other modes of bonding (as an ion and/or a ligand), saccharin can be also incorporated as a neutral molecule in its compounds, which could eventually be of some physiological significance.

Key words: Cesium salt, FT IR spectra, saccharinates, saccharin adduct

1. Introduction

Deprotonated form of saccharin shows an extraordinary variety of the types of bonding in the metal saccharinates (ionic, monodentate – ligated via the CO or SO₂ groups, amidato-like bidentate bridging or several of these modes within the same structure). A single compound, [VO(OH)(sac)(Hsac)(H₂O)], was reported to include saccharinato *molecules* in its structure [1]. Within our studies of the properties of the alkali saccharinates, two novel saccharinates, Cs(Hsac)(sac)·H₂O (**1**) and Cs(sac)·0.5H₂O (**2**), were synthesized. Since the two forms of saccharin in **1** (ionic and molecular) differ from each other by a single proton, we used FT IR spectroscopy and the partial isotopic substitution technique to characterize the compounds. In order to elucidate structural criteria for distinction between the ionic and molecular saccharin species in the saccharin adduct, the earlier spectra-structural correlations in a number of saccharinates were employed to make structural predictions about the title compounds.

2. Experimental

Cs carbonate dissolved in water/EtOH (1:1 vol) mixture and saccharin solution in EtOH in 1:1 mole ratio were mixed, while gently heating the stirred reaction mixture. The solution was then left at RT. Colorless, needle-shaped crystals of **1** appeared after several days.

Compound **2** was initially obtained as prismatic colorless crystals from the mother liquor after the removal of the solid **1**. In another preparation, large crystals of **2** were synthesized similarly as **1**, using carbonate to saccharin mole ratio of 1:2 and reducing the volume of the reaction mixture by slow evaporation until almost the entire solute was removed.

Deuterated samples of **1** and **2** were obtained by their recrystallization from the appropriate D₂O/EtOH and D₂O/H₂O mixtures, respectively. The FT IR spectra in the 6000-70 cm⁻¹ frequency range were recorded with a System 2000 interferometer (Perkin Elmer) using a P/N 21525 (Graseby Specac) variable-temperature cell.

3. Results and Discussion

The room (RT) and liquid-nitrogen temperature (LNT) FT IR spectra of the studied compounds in the middle infrared region are shown in Fig. 1.

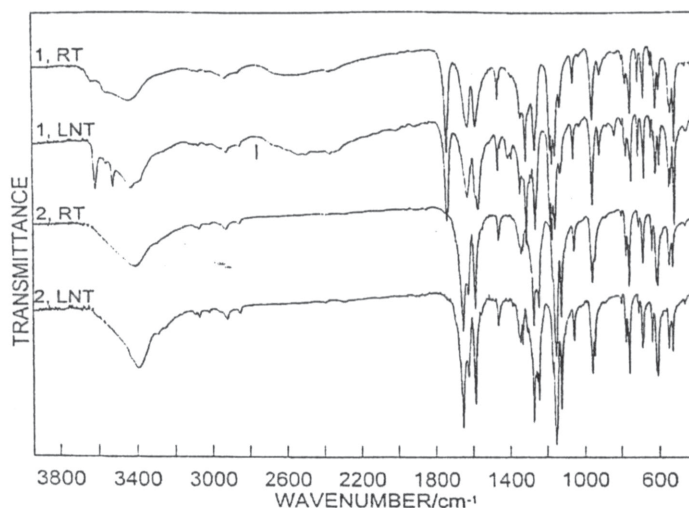


Fig. 1. The FT IR Spectra of Cs(Hsac)(sac)· H₂O (**1**) and Cs(sac)· 0.5H₂O (**2**)

3.1. Water Stretchings

The *two* $\nu(\text{OD})$ bands present in the LNT difference¹ spectrum of **1** show the existence of two non-equivalent OD oscillators in the corresponding structure. It is to be expected, therefore, that either a single water molecule with two non-equivalent proton sites, or possibly, two crystallographically non-equivalent C₂ water molecules exist in the structure of **1**. The presence of a *single* $\nu(\text{OD})$ band of isotopically isolated HOD species in H₂O matrix in the difference spectrum of **2**, on the other hand, reveals the existence of a single type of water molecules placed on C₂ axis in its structure. The frequency of the band (2490 cm⁻¹) implies that the two equivalent protons are included in hydrogen bonding of moderate strength.

3.2. NH Stretching Region in the Spectrum of Cs(Hsac)(sac)· H₂O

The broad absorption between 3100 and 2200 cm⁻¹ with a minimum around 2775 cm⁻¹ in the spectrum of **1** (Fig. 1) is due to the $\nu(\text{NH})$ mode of the saccharinato molecules. Both the spectral appearance and the frequency range of the $\nu(\text{NH})$ absorption show the characteristics of strongly hydrogen bonded imino groups. Only *one* weak band corresponding to the first overtone of the $\nu(\text{NH})$ mode is present at 5203 cm⁻¹ in the LNT spectrum, giving roughly 2600 cm⁻¹ (or somewhat higher) for the frequency of the corresponding $\nu(\text{NH})$ mode and, therefore, a value in the vicinity of the $\nu(\text{NH})$ centroid. It seems probable that the region of low

¹ The difference spectra were obtained by subtraction of the (appropriately scaled) LNT spectrum of the protiated samples from the corresponding spectra of the slightly deuterated samples.

absorption around 2775 cm^{-1} in the spectrum of **1** (marked in Fig. 1) is a transmission window on the broad NH stretching band.

3.3. Carbonyl Stretchings

A unique feature of the IR spectrum of **1** (Fig. 2) is the high frequency of the IR carbonyl stretching band (1732 cm^{-1} at RT). Contrary to all studies to date of saccharinates, the band frequency is *higher* than that of the saccharin in the solid state (1725 cm^{-1}) and even higher than the corresponding band in the RT spectrum of the only known saccharin adduct, $[\text{VO}(\text{OH})(\text{sac})(\text{Hsac})(\text{H}_2\text{O})]$ (1727 cm^{-1}) [1]. The presence of this carbonyl band in the spectrum of **1** inevitably confirms the existence of *molecular* saccharin in the corresponding structure. Its higher frequency compared to the frequency of the corresponding band of saccharin, on the other hand, might be taken as an indication that the carbonyl groups of saccharin molecules in **1** participate in a weaker hydrogen bonding than that between the C–O and N–H groups in saccharin. The pronounced frequency differences between the two lower-frequency carbonyl stretchings in **1** and saccharin (104 and 158 cm^{-1} , Fig. 2) go along with the presence of saccharinato *ions* in its structure.

As many as *three* prominent and relatively broad RT bands, at 1647 , 1619 and 1582 cm^{-1} (1649 , 1620 and 1582 cm^{-1} at LNT), can be prescribed to the carbonyl stretching modes in the spectrum of **2** (Fig. 2). As can be expected, the differences between the band frequencies and the corresponding saccharin value (76 , 105 and 143 cm^{-1}) are consistent with the existence of solely *ionic* saccharinato species in **2**. As it was noted earlier [2, 3], however, the number of the bands, even in case of much simpler spectral appearance of the carbonyl stretching region, cannot be relied upon to make predictions concerning the number of structurally different saccharinato anions.

3.4. Sulfonyl Stretchings

Three pairs of bands in the sulfonyl stretching region correspond to $\nu(\text{SO}_2)$ modes in the LNT IR spectrum of **1**. The pair of the highest-frequency antisymmetric and symmetric infrared $\nu(\text{SO}_2)$ bands (1342 and 1177 cm^{-1}) can be prescribed to the sulfonyl stretchings of the saccharinato *molecules*.

Upon conversion of **1** into mixture of **2** and saccharin (by dissolution of **1** in water and evaporation of the solute) the weak antisymmetric SO_2 stretching band of **1** (1342 cm^{-1}) shifts to the saccharin value (1336 cm^{-1} , the spectrum denoted "Mix" in Fig. 3) and two more $\nu_{\text{as}}(\text{SO}_2)$ bands appear (1271 and 1241 cm^{-1}). The latter bands are also present in the spectrum of **2** (Fig. 3) and can undoubtedly be assigned as the $\nu_{\text{as}}(\text{SO}_2)$ modes of **2**. The strong and apparently complex band in the spectrum of **2** (with a maximum at 1148 cm^{-1}), on the other hand, corresponds to the $\nu_{\text{s}}(\text{SO}_2)$ mode.

4. Conclusions

In conclusion, the present work shows that in addition to the known diversity of the bonding modes of its deprotonated form in the metal saccharinates, saccharin can also form adducts in the solid state, even with the simple alkali saccharinato salts. This, eventually, can have some significance for understanding the mechanisms of the suspected pathological action of saccharin on the biological systems.

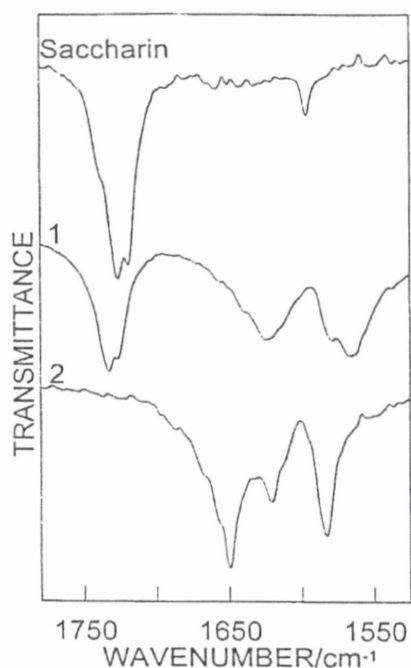


Fig. 2. The Carbonyl Stretching Region in the FT IR Spectra of the Two Cesium Saccharinates and Saccharin

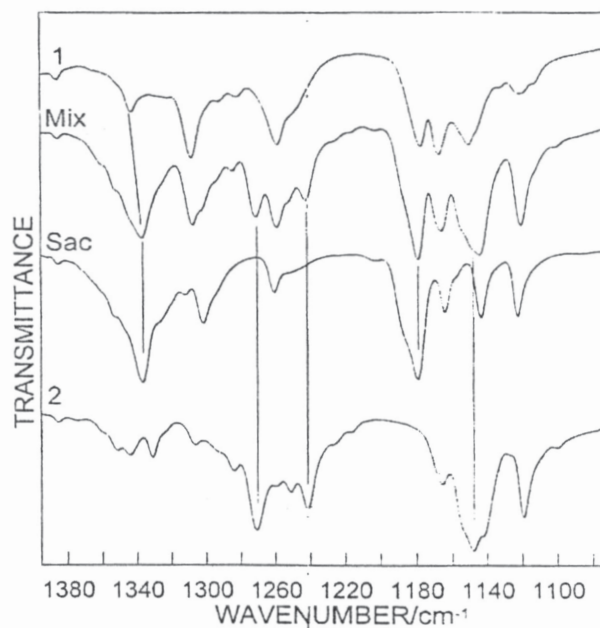


Fig. 3. The $\nu(\text{SO}_2)$ Region in the FT IR Spectra of the Two Cesium Saccharinates, Saccharin ("Sac") and the Mixture ("Mix") of $\text{Cs}(\text{sac}) \cdot 0.5\text{H}_2\text{O}$ and Saccharin obtained after Dissolution of $\text{Cs}(\text{Hsac})(\text{sac}) \cdot \text{H}_2\text{O}$ in Water

5. References

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СИНТЕЗА И КОМПАРАТИВНО ВИБРАЦИОНО ИЗУЧУВАЊЕ НА ДВА НОВИ ЦЕЗИУМ САХАРИНАТИ: СПЕКТРОСКОПСКИ ДОКАЗ ЗА АДУКТ НА САХАРИН

Панче Наумов, Глигор Јовановски

*Институт за хемија, Природно-математички факултет,
 Универзитет "Св. Кирил и Методиј", П Фак 162, МК-91001 Скопје, Македонија*

Апстракт: Синтетизирани и карактеризирани се два нови сахаринати на цезиум со формули $\text{Cs}(\text{Hsac})(\text{sac}) \cdot \text{H}_2\text{O}$ (1) и $\text{Cs}(\text{sac}) \cdot 0.5\text{H}_2\text{O}$ (2). Нивните протирани и парцијално деутерирани анализи се изучени со Фурие-трансформна инфрацрвена спектроскопија на различни температури.

Спротивно на сите досега изучени сахаринати, фреквенцијата на еден од $\nu(\text{CO})$ модовите во спектарот на **1** е значително повисока од соодветната вредност кај сахаринот во цврста состојба, а истовремено, во спектарот на ова соединение е присутна и лента што се припишува на NH валентната вибрација. Ова претставува спектроскопски доказ дека **1**, покрај единствениот ваков познат случај досега [1], претставува адукт на молекулскиот сахарин. Овој наод потврдува и дека, покрај останатите начини на сврзување (како јон и/или лиганд), сахаринот може да биде вклучен во структурата и како неутрална молекула, што од своја страна може да има и физиолошко значење.