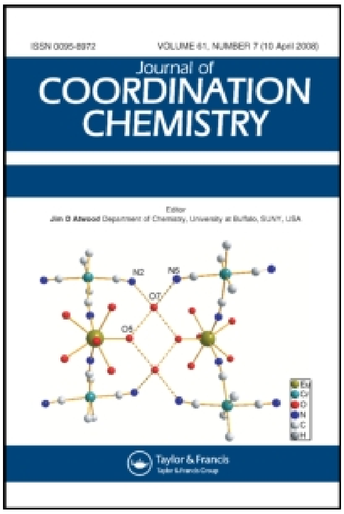

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SUGAR INTERACTION WITH ALKALI METAL IONS. SYNTHESIS AND VIBRATIONAL SPECTRA OF CRYSTALLINE SUCROSE AND ITS SODIUM HALIDE ADDUCTS

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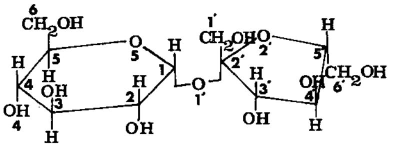
Sucrose interacts with NaCl, NaBr and NaI to give adducts of the type Na(sucrose)Cl·$2H_2O$ Na(sucrose)Br·$2H_2O$ and Na_3(sucrose)$_2I_3$·$3H_2O$. A comparison between the infrared spectra of free sucrose and its metal adducts has been made and a correlation between spectral changes and the binding sites used by the sugar molecule has been established. X-ray structural information shows that the Na^+ ion is six-coordinated in the structurally identified compound Na(sucrose)Br·$2H_2O$ and its isomorphous analogue Na(sucrose)Cl·$2H_2O$, but differs from this in the Na_3(sucrose)$_2I_3$·$3H_2O$ compound. The sodium ion binds through 0(4), 0(6), 0(6′) of the sugar and to two water molecules as well as to a halide anion, resulting a six-coordinated metal ion based on a distorted octahedron geometry. The strong sugar hydrogen bonding network is rearranged upon sugar metallation and the assignments of the absorption bands in the OH stretching region of the spectra have been made based on the X-ray structural analysis and neutron diffraction measurements.

Keywords: Alkali metals, sucrose, complexes, infrared, halides

INTRODUCTION

The interaction of the alkali and alkaline earth metal ions with carbohydrates is generally presumed to be of the simple ionic type, with metal ion binding non-specifically to such anionic residues as sugar hydroxyl groups. The X-ray structural analysis of Na(sucrose)Br·$2H_2O$ by Beevers and Cochran,[1] and several other alkaline earth metal-sugar complexes by Einspahr and Bugg[2] demonstrated the non-ionic nature of such metal-sugar interactions. It was therefore of interest to study the effects of the alkali and alkaline earth metal ions interactions on the vibrational spectra of several sugars such as *D*-glucuronic acid,[3–5] *L*-arabinose[6–7] and *D*-fructose,[8] as reported earlier. In the present report, having unambiguous structural information on Na(sucrose)Br·$2H_2O$,[1] we have tried to examine the FT–IR spectra of the compound, hoping to detect the characteristic features of each structural type of complex formed between sucrose and NaCl and NaI salts. The comparison of the spectra of the free sugar with that of the sodium halide adducts allowed us to establish a correlation between the spetral changes and the binding sites used by the sugar molecule. Furthermore, assignments of the sugar vibrational frequencies have been carried out using the structural information reported[9–10] and the Raman spectral analysis of the sucrose molecule.[11,12] The structure of sucrose with the numbering of the atoms is shown below.



sucrose

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EXPERIMENTAL

The sodium halide-sucrose adducts were prepared as reported by Cohran[13] by the addition of the sodium halide (3 mmol) to a solution of sucrose (2 mmol) in H_2O. The solution was left for a period of several weeks until the crystalline product deposited. The infrared spectra were recorded in potassium chloride pellets using a DIGI-LAB FTS-15/C fourier transform interferometer, equipped with a high sensitivity HgCdTe detector and a KBr beam-splitter, and having a spectral resolution of 2 to 4 cm^{-1}.

RESULTS AND DISCUSSION

X-ray structural analysis had shown that the Na^+ ion in Na(sucrose)Br·$2H_2O$ is six-coordinate, binding to 0(6), 0(6') and 0(4) of the sugar and to two H_2O molecules as well as to the Br^- anion.[1] A strong hydrogen bonding network exists between the sugar OH groups, the H_2O molecules and the halide anion, and this stabilizes the crystal structure of the sodium halide-sucrose adduct.[1] This compound is isomorphous with Na(sucrose)Cl·$2H_2O$, but is different to the $Na_3(\text{sucrose})_2I_3\cdot 3H_2O$ compound. The infrared spectra of free sucrose and three of its sodium halide adducts have been studied in the region of 4000–500 cm^{-1} and the results of the spectral analysis are separated into sugar OH and CH stretching vibrations and sugar ring vibrational frequencies.

Sugar OH and CH stretching vibrations

The hydrogen bonding structures of sucrose reported from neutron[9] and X-ray diffraction measurements[10] are given in Table I. The data show that there are seven crystallographically distinct hydrogen bonds, two of which are intramolecular and five of which are intermolecular.[9] The hydrogen bonding involves ring oxygen 0(5) as an acceptor and each OH group except 0(4)-H(04) and 0(6)-H(6) as both donor and acceptor. The 0(6)-H(06) group is a donor only and the 0(4)-H(04) group and ring 0'(2) do not participate.[9] The strongest hydrogen bonding interaction is 0'(4)-H···0' with an

TABLE I
Intermolecular O···O distances and hydrogen bonds in sucrose together with O-H stretching frequencies

Hydrogen Bond (Neutron Diffraction)	O-H (A)	H···O (A)	O···O (A)	ν(OH)[a] (cm^{-1})
Intramolecular				
0'(1)-H···0(2)	0.974	1.851	2.781	3254 s
0'(6)-H···0(5)	0.972	1.895	2.850	3300 sh
Intermolecular				
0(2)-H··0'(6)	0.972	1.892	2.855	3335 bs
0(3)-H···0'(3)	0.959	1.907	2.862	3389 bs
0(6)-H···0(3)	0.956	1.921	2.848	3280 s
0'(3)-H···0'(4)	0.969	1.908	2.864	3412 sh
0'(4)-H···0'(1)	0.976	1.760	2.716	3200 s
Non-participating OH				
0'(2)		2.309	2.838	
0(4)-H 0(3)	0.912	2.534	2.879	3561 s
0(6)			3.373	

[a] Present work.

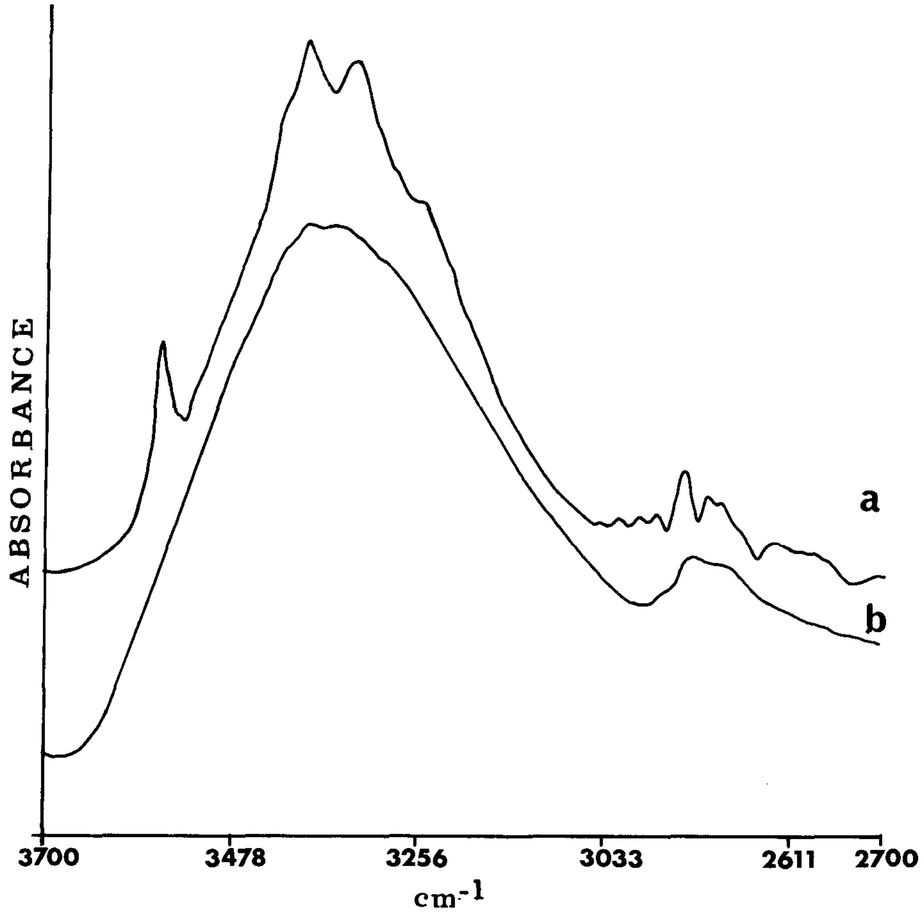

FIGURE 1 FT-IR spectra of sucrose and its sodium halide adduct in the region of 3700–2700 cm^{-1}; a: sucrose and b: Na(sucrose)Br·2H_2O.

0···0 distance of 2.716 A and the weakest interaction is 0(4)-H···0(3) with an 0···0 distance of 2.879 A (Table I).

According to the order of hydrogen bonding strengths, based on the 0···0 distances obtained from the structural analysis given in Table I, the following relationship can be proposed:

0'(4)-H > 0'(1)-H > 0(6)-H > 0'(6)-H > 0(2)-H > 0(3)-H > 0'(3)-H > 0(4)-H

Thus, the eight infrared absorption bands, observed in the spectrum (Fig. 1) of the free sucrose in the present work, are assigned as follows: the sharp absorption band at 3561 cm^{-1} to the weakly hydrogen bonded 0(4)-H; the strong band at 3412 cm^{-1} to the 0'(3)-H; the strong and broad bands at 3389 and 3335 cm^{-1} to the 0(3)-H and 0(2)-H stretching frequencies, respectively. The absorption bands with medium intensity at

TABLE II

FT-Infrared absorption frequencies (cm^{-1}) for free sucrose and its sodium halide adducts in the region 4000–500 cm^{-1} together with possible assignments

Sucrose	Na(sucrose)Cl·2H$_2$O	Na(sucrose)Br·2H$_2$O	Na$_3$(sucrose)$_2$I$_3$·3H$_2$O	Assignments (Refs 8,9,11,12,14)
3561 s				ν0(4)-H
3412 sh	2400 sh	2404 sh	2400 sh	ν0′(3)-H···0′(4)
3390 bs	3375 bs	3377 bs	3370 bs	ν0(3)-H···0′(3)
3335 bs	3345 bs	3340 bs	3340 bs	ν0(2)-H···0′(6)
3300 sh	3290 s	3280 s	3285 s	ν0′(6)-H···0(5)
3280 sh				ν0(6)-H···0(3)
3255 s				ν0′(1)-H···0(2)
3220 sh				ν0′(4)-H···0′(1)
3035 w	3035	3030 w	3030 w	νasy (CH$_2$)
2990 w				νasy (CH$_2$)
2983 w				νC-H
2970 w				νC-H
2940 m	2935 m	2935 m	2930 m	νsy (CH$_2$)
2895 sh	2890	2895 m	2890 m	νsy (CH$_2$)
2790 w				overtone
2750 w				
1640 mb	1650 mb	1636 mb	1635 mb	δ(H$_2$O)
1473 sh	1470 sh	1470 sh	1469 sh	δ(CH$_2$)
1460 m	1459 m	1455 sh	1455 sh	w(CH$_2$)
1430 s	1427 m	1420 s	1419 s	δ(COH)
1400 sh	1410 sh			
1385 w	1380 sh	1385 w	1383 w	r(CH$_2$)
1366 m	1367 m	1362 w	1360 w	t(CH$_2$)
1346 s	1345 m	1335 m	1336 m	δ(COC)
1322 m	1320 m	1300 vw	1300 sh	δ(COH)
1279 m	1275 m	1263 vw	1262 m	δ(COH)+δ(CCH)
1238 s	1235 m	1230 vw	1230 vw	δ(CCH)
1208 m	1200 w	1206 m	1207 m	
1150 sh	1164 m			δ(COH)
1129 vs	1131 sh	1134 s	1131 s	δ(COH)
1118 sh	1122 s			
1105 sh	1106 sh	1109 s	1107 s	ν(CO)
1070 vs	1065 vs	1060 sh	1058 sh	ν(CO)
1054 vs	1150 vs	1151 vs	1049 vs	ν(CO)
1014 sh				δ(COC)
1005 s	1009 s			
991 vs	990 s	993 vs	990 vs	δ(CCH)+δ(CH)
942 m	941 m	940 sh	940 sh	
920 sh		927 s	921 s	ν(CO)+δ(CH)
910 sh	912 s			
868 m	867 m	867 w	867 m	δ(CH)+δ(COH)
851 m	848 m	857 w	855 m	δ(CH)+ν(CC)
732 m	731 m	730 w	730 w	δ(CCO) endo (fru)
694 m	690 sh	690 sh	691 vw	δ(CCO) exo (fru)
680 sh	682 m	665 vw	665 vw	δ(OCO)
641 .	637 m	640 vw		δ(CCO) endo (glu)
610 sh	614 m	598 vw	591 m	δ(CCO) exo (glu)
587 m	583 m	585 vw	583 w	δ(CCC) (fru)
567 vw				
538 vw	540 w	549 w	550 m	δ(CCC) (glu)
527 vw				δ(COC)

s: strong m: medium. b: broad, w: weak: sh: shoulder: v: very: ν: stretching δ: bending: w: wagging r: rocking t: twisting fru: fructose: glu: glucose: endo: endocyclic and exo: exocyclic.

3300, 3280 and 3254 cm^{-1} correspond to 0′(6)-H, 0(6)-H and 0′(1)-H stretching vibrations, respectively and finally the band at 3220 cm^{-1} is attributed to the strongly hydrogen bonded 0′(4)-H group.

In the present work, all the O-H stretching vibrations of free sucrose exhibited considerable changes (shifting and intensity), upon sugar metallation (Fig. 1 and Table II). The sharp band at 3561 cm^{-1} in the spectrum of the free sugar and related to the 0(4)-H stretching vibration, shifted towards lower frequency (possibly under the strong and broad absorptions of the other sugar OH stretches and coordinated H_2O molecules). Similarly, the other OH stretching vibrations related to 0(6)-H and 0′(6)-H at 3335 and 3250 cm^{-1} also showed shift and intensity changes on sugar complexation (Fig. 1). The changes observed are consistent with the X-ray structural analysis of Na(sucrose)Br·$2H_2O$, which demonstrate the participation of the 0(4)-H, 0(6)-H and 0′(6)-H groups, in metal-sugar bond.[1] Similar spectral changes were observed in the infrared spectra of several alkali metal ion-sugar compounds containing the *D*-glucuronate anion.[4]

It is interesting to note that the rearrangement of the inter- and intramolecular hydrogen bonding of free sucrose to that of the sugar OH· · ·H_2O· · ·Br^- system in Na(sucrose)Br·$2H_2O$ is also responsible for the modification of the sugar OH stretching frequencies, but it is difficult to differentiate the effects of the metallation and the alteration of the hydrogen bonding network.

Due to the overlapping of the OH stretching vibration of the bonded water molecule with those of the sugar hydroxyl groups in the region 3500–3200 cm^{-1}, it is difficult to draw a certain conclusion as to the nature of the metal-water bonding. However, the presence of the bonded water molecule could be identified from the H_2O bending vibrations, observed in other regions of the spectra (1800–500 cm^{-1}).

C-H stretching vibrations

Sucrose has fourteen fundamental C-H stretching vibrations. However, because of the inherent width of some bands and the consequent overlap, only some of these vibrational modes can be observed at room temperature. Several absorption frequencies are observed in the infrared spectrum of sucrose (Fig. 1), assigned to the asymmetric and symmetric CH_2 and C-H stretching vibrations, as given in Table 2.

Sugar ring vibrational frequencies

The Raman spectra of sucrose in aqueous solution, in the region of 1700–3000 cm^{-1} have been reported by Barret[12] and Mathlouthi *et al.*,[11] and possible assignments have been made. In this region, our infrared band assignment is in a good agreement with the above observations. A broad absorption band with medium intensity at about 1640 cm^{-1} in the spectra of the metal-sugar adducts is assigned to the bending of the bonded water molecule.[14] The presence of this band in the spectrum of the free sugar could be related to water of crystallization (Fig. 2).

The CH_2 bending vibrations[11,12] at 1473, 1460, 1383 and 1366 cm^{-1} in the free sucrose spectrum showed no major changes upon sugar metallation (Fig. 2 and Table II), whereas other absorption bands at 1430, 1400, 1346, 1322, 1279, 1150, 1129 and 1118 cm^{-1}, related to the COH and COC bending modes[15,16], exhibited considerable intensity changes and shifting in the spectra of the Na-sucrose adducts (Table II). The observed changes for these vibrational frequencies are due to the participation of the sugar hydroxyl groups in metal-ligand bonds[3,8]. Other strong absorption bands at 1105, 1070 and 1054 cm^{-1} in the spectrum of the free sugar assigned to the CO stretching vibrations[11,12,15,16] also showed major alterations on complex formation (Table II). The

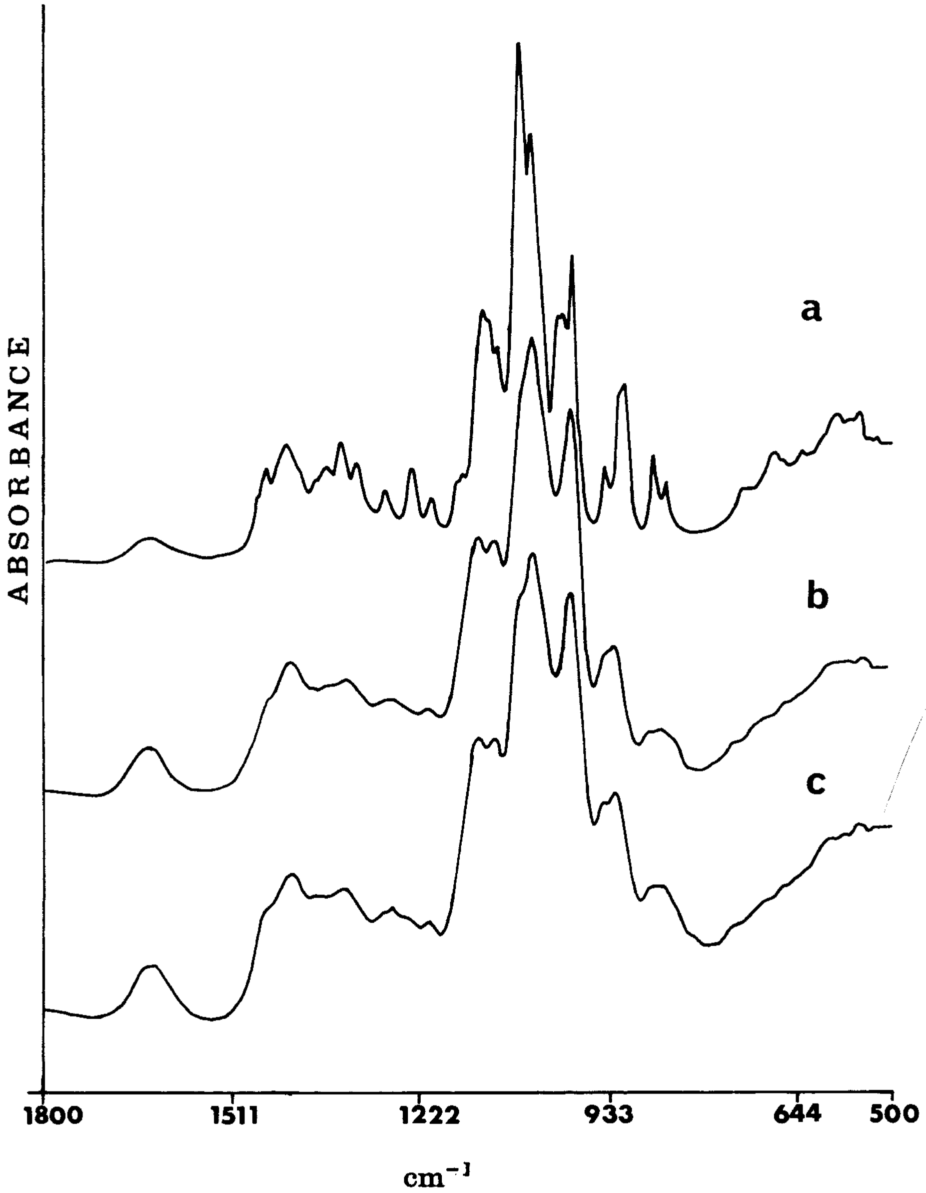

FIGURE 2 FT-IR spectra of sucrose and its sodium halide adducts in the region of 1800–500 cm^{-1}; a: sucrose, b: $Na(sucrose)Br \cdot 2H_2O$ and c: $Na_3(sucrose)_2I_3 \cdot 3H_2O$.

changes in the CO stretching vibrations of the free sugar upon metallation are indicative of metal-sugar binding *via* the oxygen atoms of the sugar hydroxyl groups. Similar behaviour is observed in the infrared spectra of *D*-fructose[8] and *D*-glucose[17] upon coordination to Mg(II) and Ca(II) ions. Several absorption bands in the region 1000–500 cm^{-1} of free sucrose showed shifts in the spectra of the sodium halide complexes (Table II). Since these vibrations are mainly related to the skeletal deformation of C–C–C, C–C–H and C–O–C groups, the changes are consistent with the rearrangement of the free sugar hydrogen bonding network and the participation of the sugar OH groups in metal complexation, which perturb the electron distribution in the sugar ring systems, where the vibrations are mostly localized. This finally results in ring distortion. This argument is consistent with the structural changes observed for this sugar, in the crystal stsructure of the Na(sucrose)Br·$2H_2O$ compound.[1]

CONCLUDING REMARKS

Correlation between structural analysis and infrared spectroscopy often helps to assign the sugar vibrational frequencies in these kinds of complexes. Recently, on the basis of X-ray and neutron diffraction measurements and the infrared spectra of the free sugars and their metal adducts, the assignments of the OH stretching vibrations of *D*-fructose and *D*-glucose have been achieved.[8,17] Similarly, in this work a correlation between structural information and infrared spectra of sucrose and its sodium halide adducts lead us to the following conclusions:

a. According to the OH hydrogen bonds strength the assignments of the sugar OH stretching frequencies can be made and a sharp band with medium intensity at 3561 cm^{-1}, in the free sugar spectrum can be assigned to the unperturbed 0(4)–H stretching vibration.

b. The spectral changes observed for the OH, CO stretches and the COH, COC bending modes upon sugar metallation, confirms the participation of the sugar OH groups and the H_2O molecules in metal-ligand bonding.

c. The Na–O (sugar) distances of 2.32–2.62 A should not be regarded as simple ionic interactions, since the metal-sugar bonds show direct interaction, with considerable effect on the sugar vibrational frequencies.

d. The infrared spectra of the 1:1 and 2:3 sodium-sugar adducts are virtually identical.

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