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MAGNESIUM-SUGAR INTERACTION

SYNTHESIS, SPECTROSCOPIC AND STRUCTURAL CHARACTERIZATION OF Mg-SUGAR COMPLEXES CONTAINING β-D-FRUCTOSE

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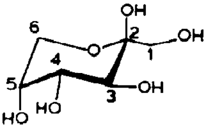
The interaction between β-D-fructose and hydrated magnesium salts has been studied and complexes of the type Mg(β-D-fructose)$Cl_2 \cdot 4H_2O$ and Mg(β-D-fructose)$Br_2 \cdot 4H_2O$ have been isolated and characterized. On the basis of comparisons of the spectroscopic and other chemical properties of several structurally known calcium-fructose compounds with those of the corresponding magnesium complexes, it is concluded that Mg^{2+} binds to two sugar moieties via O(2), O(3) of the first and O(4), O(5) of the second and to two water molecules, resulting in a six-coordinate geometry around the Mg^{2+}. The strong sugar hydrogen-bonding network is rearranged upon sugar metallation and the sugar moiety shows the β-anomer conformation in these magnesium-sugar complexes.

1. Introduction

Mg^{2+} plays an important role in a number of biological processes. Sugar is a component part of the nucleic acids and, therefore, the magnesium-sugar interaction bears significant biochemical importance. Calcium-sugar complexes are well known among the alkaline earth metal ions [1–3], whereas magnesium-sugar interactions are limited to our recent publications [4,5]. In our previous communications, we have demonstrated how Mg^{2+} binds to D-glucuronic acid and L-arabinose [4,5], and the way that Mg^{2+} binding influences the sugar conformation. In the present work, we describe the synthesis and characterization of several magnesium-fructose complexes by means of Fourier transform-infrared spectroscopy, X-ray powder photography and molar conductivity. These have not been previously reported. Having ambiguous structural information on several calcium-fructose complexes [6–8], we have examined and compared their infrared spectra with those of the corresponding Mg-sugar compounds. This is in order to detect the characteristic features of each structural type of the sugar compound synthesized for Mg^{2+} and to establish a correlation between the spectral changes and the binding sites used by the β-D-fructose in these series of metal-sugar complexes. Furthermore, we discuss the effects of Mg^{2+} coordination on the sugar conformation with the assignments of the sugar vibrational frequencies. The structure of β-D-fructose with the numbering of the atoms is shown below:



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2. Experimental

2.1. Materials

D-Fructose was purchased from BDH and recrystallized from water by slow evaporation. Other chemicals were reagent grade and used as supplied.

2.2. Synthesis of magnesium-sugar complexes

Magnesium-sugar complexes were prepared by the addition of hydrated magnesium halide salt (1 mmol) to a solution of D-fructose (1 mmol) in H_2O (20 ml). The solution was heated at 50°C for a period of 20 min. After cooling to room temperature, the solution was decolourized by activated charcoal, and a mixture of acetone-ether was used to precipitate the compound. This was washed with ether and recrystallized from acetone-ether. The analytical results give the composition of $Mg(\beta\text{-D-fructose})Cl_2 \cdot 4H_2O$ and $Mg(\beta\text{-D-fructose})Br_2 \cdot 4H_2O$. Magnesium-fructose compounds are very hygroscopic and deteriorate out of the desiccator. The compounds are very soluble in water and alcohol, and slightly soluble in acetone but not in other common organic solvents.

2.3. Physical measurements

The Fourier transform-infrared (FT-IR) spectra were recorded with KCl pellets on a DIGILAB FTS-15D/C Fourier transform Michelson infrared interferometer, equipped with an HgCdTe detector and a KBr beam splitter, having a spectral resolution of 4–2 cm^{-1}. X-ray powder diagrams were taken for comparative purposes using a camera (Phillips, Debye-Scherrer) with copper K_α radiation. Conductance measurements were carried out at room temperature in H_2O solution (10^{-3} M) with a type CDM2e conductivity meter (Radiometer, Copenhagen).

3. Results and discussion

Structural information has shown that the Ca^{2+} in $Ca(\beta\text{-D-fructose})Cl_2 \cdot 2H_2O$ and $Ca(\beta\text{-D-fructose})Br_2 \cdot 2H_2O$ is seven-coordinate, binding to three sugar molecules through O(2), O(3) of the first; O(4), O(5) of the second and O(1) of the third, as well as to two water molecules [6,7]. In the 2 : 1 $Ca(\beta\text{-D-fructose})_2Cl_2 \cdot 3H_2O$ compound, the Ca^{2+} binds to two fructose moieties via O(1), O(4), O(5) of each sugar, and to two H_2O molecules, resulting in an eight-coordinate geometry around Ca^{2+} [8]. The halide anions and water molecules, as well as the sugar hydroxyl groups, are involved in a strong hydrogen-bonding network. The FT-IR spectra of these complexes with the free D-fructose have been recorded in the region 4000–400 cm^{-1} with the free D-fructose having been recorded in the region 4000–400 cm^{-1} and compared with those of the corresponding 1 : 1 Mg^{2+}-fructose adducts studied here. The results of the spectral analysis are discussed below:

3.1. Sugar OH stretching vibrations and bonding modes

The assignments of the free D-fructose OH stretching frequencies have been carried out based on the intermolecular O...O distances of the hydrogen-bonding structure obtained from neutron and X-ray diffraction analyses [9,10]. On the basis of the intermolecular O...O distances listed in table 1, the order of the hydrogen-bonding strengths is as follows: O(2)H > O(5)H > O(1)H > O(3)H > O(4)H. Therefore, the five infrared absorption frequencies observed in the region 3600–3100 cm^{-1} in the spectra of the free sugar are assigned as follows: an absorption band with medium intensity at 3526 cm^{-1} to the unperturbed O(4)-H; the broad absorption band at 3422 cm^{-1} to O(3)-H; the strong bands at 3406 and 3366 cm^{-1} to O(1)-H and O(5)-H stretching vibrations, respectively, and the band at 3180 cm^{-1} is related to the strongly hydrogen-bonded O(2)-H stretching frequency (table 1).

Upon magnesium coordination, the sugar OH stretching vibrations showed considerable intensity changes and shifted towards lower frequencies (table 1). The changes observed are due to the participation of the sugar OH groups in the metal-ligand bonding [11]. Similar behaviour was observed in the infrared spectra of the 1 : 1

Table 1

Infrared absorption frequencies (cm^{-1}) of crystalline β-D-fructose and its magnesium complexes in the region 3600–400 cm^{-1} with possible assignments

s, strong; v, very; sh, shoulder; b, broad; w, weak; m, medium; ν, stretching; δ, bending; τ, internal rotation.

β-D-Fructose	Mg(β-D-fructose)Cl_2 ·$4H_2O$	Mg(β-D-fructose)Br_2 ·$4H_2O$	Ca(β-D-fructose)Cl_2 ·$2H_2O$ *	Assignments [9–15]
3526 s	3435 sh	3445 s	3483 s	νO(4)–H(O4)...O(2′)
–		3430 sh		(O...O = 2.972 Å)
3422 bs	3400 s	3410 s	3340 sh	νO(3)–H(O3)...O(5′)
				(O...O = 2.930 Å)
3406 s	3383 bs	3389 s	3330 s	νO(1)–H(O1)...O(3′)
	3365 s	3370 sh	3294 vs	(O...O = 2.859 Å)
3366 s	3315 s	3320 s	3250 s	νO(5)–H(O5)...O(2′)
				(O...O = 2.805 Å)
3180 s	3160 sh	3175 sh	3143 vs	νO(2)–H(O2)...O(1′)
				(O...O = 2.668 Å)
3013 w	3020 w	3015 vw	3000 vw	νasy(CH_2) of C-1
2990 w	2995 vw	2990 w	2970 vw	νasy(CH_2) of C-6
2959 w	2950 w	2955 vw	2940 vw	νsy(CH) of C-4
2934 m	2940 m	2944 w	–	νsy(CH) of C-5
2900 m	–	–	–	νsy(CH_2) of C-6
2835 vw	–	–	2835 vw	νsy(CH_2) of C-1
–	1651 bs	1652 bs	1634 s	δ(H_2O)
–			1605 sh	
1470 w	–	–	1460 sh	δ(COH)+ δ(OCH)+ δ(CCH)
1453 w	1452 m	1450 m	1452 m	δ(CH_2)
1429 m	1419 s	1417 s	1411 s	δ(COH)+ δ(CCH)
1398 m	1392 sh	1404 sh	1388 w	δ(OCH)+ δ(COH)+ δ(CCH)
1373 vw	1371 vw	1370 sh	1371 vw	δ(CH_2)
1337 s	1342 m	1342 s	1340 w	
–			1323 w	δ(CCH)+ δ(COH)
–			1294 m	
1275 vw	–	–	1273 m	δ(CCH)+ δ(COH)
1265 m	1254 sh	1256 m	1261 s	
1252 vw	1244 s	1242 m	1242 w	
1232 vw	–	–	–	δ(COH)+ δ(CCH)
1177 m	1180 m	1182 m	1180 s	δ(OCH)+ δ(CCH)
1150 s	1145 sh	1143 s	1126 s	ν(CO)+ ν(CC)+ δ(CCC)
1094 s	1090 sh	1091 sh	1089 s	ν(CO)+ ν(CC)
1078 vs	1063 bs	1061 bs	1064 vs	ν(CO)+ δ(CC)
1053 vs	–	–	–	ν(CO)
1025 sh	1020 sh	1015 sh	1009 m	ν(CO)+ ν(CC)
978 s	976 m	978 m	968 s	ν(CO)+ δ(CCO)
924 m	925 w	926 w	929 m	ν(CO)+ δ(CCH)
			893 m	ν(CC)+ δ(CCH)+ δ(CH)
874 m	865 m	866 m	866 m	β-anomer
817 s	818 m	820 m	827 s	δ(CH)
783 s	779 s	779 s	789 s	τ(CO)+ δ(CCO)+ δ(CCH)
	735 sh	737 m		
689 m	698 s	698 s	715 m	δ(CCO)+ τ(CO)+ δ(OCO)
–	663 m	664 m	–	
627 s	717 s	625 s	636 sh	
596 sh	590 sh	590 sh	602 s	τ(CO)
567 m	553 vw	554 vw	570 sh	ν(CO)+ δ(CCO)
536 sh	522 m	523 m	529 sh	
–			520 s	δ(CC)+ τ(CO)
469 m	478 m	475 m	449 m	δ(CCO)+ ν(CO)
–			–	
430 vw	–	–	–	δ(CCO)+ δ(CCH)

* Structurally known.

calcium-fructose complexes (table 1), where Ca^{2+} was bonded to the O(2), O(3), O(4), O(5) and O(1) of the three sugar moieties [6–8], which is indicative of the similar binding arrangements around Mg^{2+} in these sugar complexes.

It should be noted that the rearrangements of the strong intermolecular hydrogen-bonding network of the free D-fructose to that of the sugar $OH \ldots H_2O \ldots$ halide system found in the crystal structures of the metal-fructose complexes [6–8] are also responsible for the modifications of the sugar OH stretching vibrations. However, it is rather difficult to separate the effects of metallation and the alteration of the hydrogen-bonding network of the sugar OH stretching vibrations.

3.2. Sugar C-H stretching vibrations

The infrared and Raman spectra of D-fructose have been reported and possible assignments have been made [11–13]. D-Fructose has seven fundamental C-H stretching vibrations. However, due to the inherent width of some bands and the possible overlap, not all of these fundamental modes can be observed. In the infrared spectrum of D-fructose studied here, the six strong absorption bands observed in the region 3000–2800 cm^{-1} are assigned to the antisymmetric and symmetric stretching vibrations of CH_2 and CH groups. No major alterations for these vibrational frequencies occurred upon sugar metallation (table 1).

3.3. Water binding

A broad and strong absorption band at about 1650 cm^{-1}, in the spectra of magnesium-fructose complexes, which is absent in the free sugar spectrum (fig. 1), is assigned to the bending vibration of the coordinated H_2O molecule [4,11]. It should be noted that the OH stretching vibration of the bonded water molecule in the region 3500–3300 cm^{-1} was overlapped by the sugar OH stretching vibrations. This made it difficult to draw definite conclusions on the nature of the magnesium-water bonding.

3.4. Sugar ring vibrational frequencies

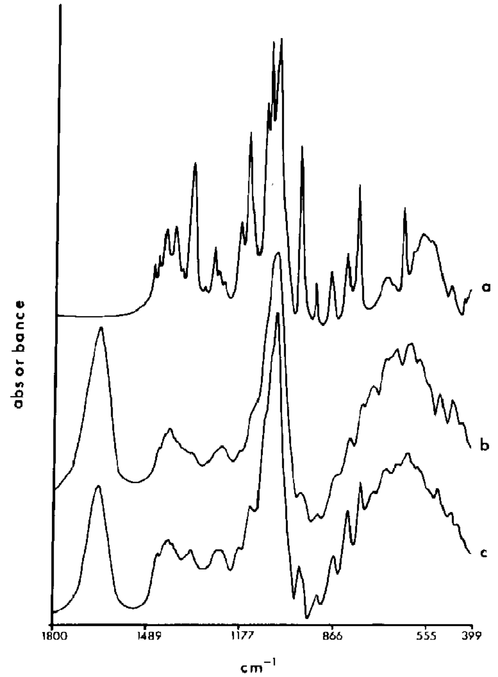


Fig. 1. FT-IR spectra for free D-fructose and its magnesium complexes in the region 1800–400 cm^{-1} for (a) D-fructose, (b) $Mg(\beta\text{-D-fructose})Cl_2 \cdot 4H_2O$ and (c) $Mg(\beta\text{-D-fructose})Br_2 \cdot 4H_2O$.

The CH_2 bending vibrations at 1453 and 1373 cm^{-1} in the free carbohydrate spectrum showed no changes upon sugar complexation, whereas the COH bending modes [14,15] of the free sugar at 1470, 1429, 1398, 1337, 1275, 1265, 1252, 1232 and 1177 cm^{-1} exhibited considerable intensity changes and shifted in the spectra of the metal-sugar complexes (table 1 and fig. 1). The changes observed for the COH bending modes together with the shifting of the OH stretching vibrations at about 3500–3200 cm^{-1} are indicative of the involvement of the sugar OH in the metal-ligand bonding [2,3]. Similar spectral changes were observed for the structurally known 1 : 1 calcium-fructose complexes (table 1), where the participation of the sugar hydroxyl groups in the Ca-sugar coordination was demonstrated [6,7]. Several other strong and sharp absorption bands at 1150, 1094, 1078, 1053, 1025, 978 and 924 cm^{-1} in the free D-fructose spectrum, mainly related to the ring C-O stretching vibrations [14,15], exhibited major intensity changes and shifted towards lower frequencies in the spectra of the Mg-fructose compounds studied here and the corresponding Ca-sugar complexes (table 1 and fig. 1). The changes observed for the CO stretching vibrations are due to the coordination of these metal ions through the sugar oxygen atoms.

The ring skeletal deformations C-O-C and C-C-C of the free sugar [14,15] in the region 1000–400 cm^{-1} showed major alterations on complex formation (table 1). The observed spectral changes for these vibrational frequencies are attributed to the participation of the sugar OH groups in the metal-ligand bondings, which cause a large perturbation to the ring electron distribution, where the vibrations are mostly localized and bring about distortion of the ring.

3.5. Sugar conformation

Recently, we have reported the separation of the α- and β-anomers of several sugars and their metal complexes, using infrared and ^{1}H-NMR spectroscopy [1,2,4,5]. The two absorption bands found at about 870 and 840 cm^{-1} in the sugar spectra were assigned to the presence of the β- and α-anomers, respectively [1,2]. The alkaline earth metal ions showed affinity for the α-anomer conformation [1,2], while alkali metal ions and Zn^{2+} preferred the β-anomer conformation [16,17]. The presence of a strong absorption band at about 870 cm^{-1} in the spectra of free D-fructose and its magnesium adducts and the absence of any absorption bands at 840 cm^{-1} are indicative of the presence of the sugar moiety in the β-conformation in these metal complexes. A similar absorption band was found in the spectra of the calcium-fructose complexes (table 1), where the presence of the β-anomer conformation was determined through X-ray structural analysis [6–8].

3.6. X-ray powder diffraction and molar conductivity

The high molar conductivities (160–180 Ω^{-1} cm^2 mol^{-1}) observed for the Mg-fructose compounds are indicative of no direct metal-halide interaction in these magnesium-sugar complexes. This is consistent with the structural information reported on calcium halide fructose compounds which showed [6–8] no direct Ca-halide bonding.

X-ray powder diagrams of the Mg-fructose compounds showed marked similarities (except for a few lines) with those of the structurally identified 1 : 1 Ca-fructose compounds [6–8]. The small dissimilarities observed are due to the lower coordination number of Mg^{2+} [18] with respect to those of seven or eight found for Ca^{2+} in the Ca-fructose complexes [6–8]. Similar observations were made for the six-coordinate Mg(L-arabinose)$Cl_2 \cdot 4H_2O$ and eight-coordinate Ca(L-arabinose)$Cl_2 \cdot 4H_2O$ compounds reported earlier [4].

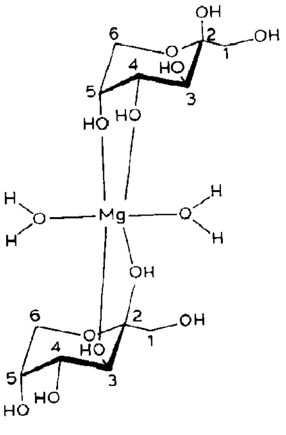
4. Conclusion

On the basis of X-ray powder diffraction and infrared spectroscopy of the Mg-fructose compounds and by comparison with those of the corresponding structurally characterized Ca-fructose adducts the following remarks can be made:

(i) The rearrangements of the strong sugar hydrogen-bonding network of the free D-fructose occurred upon sugar metallation;

(ii) Ca^{2+} forms 1 : 1 and 2 : 1 adducts with D-fructose, whereas Mg^{2+} forms only 1 : 1 sugar complexes;

(iii) Due to the ability of Ca^{2+} to exhibit higher coordination numbers (8) than Mg^{2+} (6), Ca^{2+} binds to two or three sugar molecules, while Mg^{2+} binds to two sugar molecules (in a similar fashion



Scheme 1. Mg-fructose compound.

to Ca^{2+} via O(2), O(3) of the first and O(4), O(5) of the second as well as to two water molecules, resulting in a six-coordinate geometry around Mg^{2+} (scheme 1) and

(iv) The sugar moiety shows the β-anomer conformation in these magnesium complexes.

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