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Sugar Complexation with Uranium Ion. Synthesis, Spectroscopic and Structural Analysis of UO_2–Fructose Adducts

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Abstract

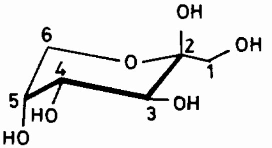
β-D-fructose interacts with hydrated uranyl salts to give adducts of the type UO_2(D-fructose)$X_2 \cdot 2H_2O$, where X = Cl^-, Br^-, NO_3^- and $0.5SO_4^{2-}$. These compounds have been characterized by means of FT-IR spectroscopy, molar conductivity and X-ray powder diffraction measurements.

The marked spectral similarities observed with those of the structurally characterized Mg(D-fructose)$X_2 \cdot 4H_2O$ (X = Cl^- or Br^-) adducts suggested that the UO_2^{2+} cation binds to two D-fructose molecules through O2, O3 of the first and O4, O5 of the second sugar moiety, resulting into a six-coordination geometry around the uranium ion. There is no direct interaction between UO_2^{2+} ion and the inorganic anions associated with the metal cation.

On complex formation the strong sugar intermolecular hydrogen bonding network is rearranged to that of the sugar-OH:..H_2O...anion ligand. The sugar moiety has β-anomer configuration in these uranyl–sugar adducts and the binding of the uranium ion is through both the β-D-fructopyranose and the β-fructofuranose isomers.

Introduction

In recent reports from this laboratory [1, 2], the interaction of uranium ion with sugar moieties such as the D-glucuronic acid and the L-arabinose have been investigated. On the basis of proton-NMR spectroscopy, it was concluded that the uranium ion prefers the β-anomer configuration of D-glucuronic acid [1], whereas the α-anomer configuration of L-arabinose is favored upon complexation [2]. Therefore, it is interesting to study the interaction of β-D-fructose with the uranium cation and the effect of the metal coordination on the sugar anomeric changes. In the present work, we describe the synthesis and characterization by means of FT-IR spectroscopy, X-ray powder diffraction and molar conductivity of several uranyl–fructose adducts that have not been previously reported. On the other hand, the spectroscopic properties of the uranyl–fructose compounds synthesized here are compared with those of the structurally identified Ca(II)–fructose [3–5] and Mg–fructose adducts [6], in order to detect the characteristic features of each structural type of the adduct prepared for uranium ion and to establish a correlation between the spectral changes and the coordination sites used by D-fructose molecule. Furthermore, the effect of metal ion binding on the sugar isomeric changes and the assignments of the sugar vibrational modes are discussed here. The chemical structure of β-D-fructose with the numbering of the atoms is shown below.



D-fructose

Experimental

Crystalline D-fructose was from BDH and used as supplied. Hydrated uranyl nitrate and uranyl sulphate, purchased from BDH, were reagent grade and used without further purification. Uranyl halides were prepared according to our previous report [7] by metathesis of $UO_2(SO_4)_2$ with $BaCl_2$ or $BaBr_2$ in aqueous solution and filtering off the insoluble $BaSO_4$ salt. All the other chemicals were reagent grade and used as purchased.

Preparation of the Uranyl–Sugar Complexes

Hydrated uranyl salt (1 mmol) was added to a hot solution of D-fructose (1 mmol) in methanol (20 ml), except for uranyl sulphate salt which was dissolved in water–methanol mixture. After heating the solution for 20 min at 80 °C, the solution was left at room

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temperature for 2 days; acetone was then used to precipitate the compounds. The pale yellow crystalline adducts were filtered off, washed with acetone several times and dried over $CaCl_2$. The analytical results showed the composition of UO_2(D-fructose)-$X_2 \cdot 2H_2O$, where X = Cl^-, Br^-, NO_3^- and $0.5SO_4^{2-}$. The uranium–fructose compounds are very soluble in water and hot alcohol, but not soluble in any other common organic solvents. The uranyl–sugar adducts are very hygroscopic and should be kept in a desiccator.

Physical Measurements

The FT-IR spectra were recorded on a DIGILAB FTS 15/C Fourier Transform Michelson Infrared Interferometer, equipped with a high sensitivity HgCdTe detector and a KBr beam splitter, with a spectral resolution of 2 to 4 cm^{-1} and KCl pellets. X-ray powder photographs were taken for comparative purposes, using a camera (Philips, Debye–Scherre) with copper Kα radiation. Molar conductance measurements were carried out on a conductivity meter type CDM2e (Radiometer, Copenhagen).

Results and Discussion

Spectroscopic properties and X-ray structural analysis have shown that the Mg(II) ion in the Mg(D-fructose)$X_2 \cdot 4H_2O$ (X = Cl^- or Br^-) compounds is six-coordinate, binding to two sugar molecules via O2, O3 of the first and O4, O5 of the second sugar moiety and to two H_2O molecules [6]. On the other hand, the Ca(II) ion in the Ca(D-fructose)$X_2 \cdot 2H_2O$ (X = Cl^- or Br^-) adducts was found to be seven-coordinate, binding to three sugar moieties through O2, O3 of the first, O4, O5 of the second and O1 of the third molecules, as well as to two H_2O [3–4]. In the 2:1 Ca(D-fructose)$_2Cl_2 \cdot 3H_2O$ the calcium ion is eight-coordinate, bonding to four sugar moieties via O1 of the two and O4, O5 of the other two sugar molecules and to two H_2O [5]. The intermolecular sugar hydrogen bonding network is rearranged to that of the sugar-OH... H_2O... halide system upon fructose metalation [3–5]. The FT-IR spectra of the uranyl–fructose adducts together with the free D-fructose have been recorded in the region of 4000–400 cm^{-1} and a comparison made with those of the structurally known Ca(II) and Mg(II)–fructose complexes. The results of the spectral analysis are described below.

D-fructose OH Stretching Vibrations and Binding Modes

In our previous studies [6, 8] the assignments of the infrared vibrational frequencies of β-D-fructose were reported. The OH stretching vibrations of the free D-fructose were assigned based on the intermolecular O...O distances of the hydrogen bonding structure obtained from neutron [9] and X-ray diffraction measurements [10].

On the basis of the intermolecular O...O distances obtained from neutron diffraction measurements [9], the following relationships are present between the hydrogen bonding structures and the hydrogen bond strengths: O(2)–H > O(5)–H > O(1)–H > O(3)–H > O(4)–H

Hydrogen bond neutron diffraction	O–H (Å)	H...O (Å)	O...O (Å)	ν(OH) (cm^{-1})
O(4)–H...O(2′)	0.948	2.063	2.972	3526s
O(3)–H...O(5′)	0.964	1.977	2.930	3422bs
O(1)–H...O(3′)	0.972	1.965	2.859	3406s
O(5)–H...O(2′)	0.963	1.869	2.805	3366s
O(2)–H...O(1″)	0.979	1.750	2.668	3180m

Therefore, the five strong absorption bands observed in the infrared spectrum of the free D-fructose are assigned to the hydrogen bonded OH groups as summarized as follows: an absorption band with medium intensity at 3526 cm^{-1} to the unperturbed O(4)–H; a strong band at 3422 cm^{-1} to O(3)–H; a broad absorption band at 3406 cm^{-1} to O(1)–H; a strong absorption band at 3366 cm^{-1} to O(5)–H stretching; the band at 3180 cm^{-1} is related to the strongly hydrogen bonded O(2)–H stretching frequency.

The OH stretching vibrations of the free D-fructose showed major intensity changes and shifted towards lower frequencies upon uranium interaction (Table I). The spectral changes observed are due to the participation of the sugar hydroxyl groups in the metal complex formation [6, 8]. Similar trends were observed in the IR spectra of the structurally-known Mg(II)–fructose adducts, where the magnesium ion was found to be coordinated to two sugar moieties via O2, O3 of the first and O4, O5 of the second molecule as well as to two H_2O [6], which is indicative of the similar binding arrangements around the UO_2^{2+} cation.

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...H_2O... halide system observed in the crystal structures of the metal–fructose complexes [3–5] are also responsible for the alterations of the sugar hydroxyl group stretching vibrations. However, it is difficult to differentiate the effects of metalation and the modification of the hydrogen bonding network of the sugar OH stretching frequencies.

D-fructose C–H Stretching Vibrations

The assignments of the free D-fructose vibrational frequencies were reported by Szarek *et al.* [11] and us [6, 8]. The D-fructose has seven fundamental C–H stretching modes. However, due to the possible overlap and the inherent width of some of the vibrational frequencies, not all of these fundamental modes can be observed. There are six strong infrared bands at about 3000–2800 cm^{-1} in the spectrum of the free D-fructose at room temperature; they are attributed to the asymmetric and symmetric CH_2 and CH stretching vibrations (Table I). There were no major changes in the CH stretching vibrations of the D-fructose upon uranium ion interaction.

D-fructose Ring Vibrational Frequencies and Coordination Modes

Several absorption bands with medium intensities in the region of 1470–1200 cm^{-1} in infrared spectrum of the free D-fructose are assigned to the strongly coupled COH, CH_2, CCH and OH bending modes [12, 13]; these bands exhibited intensity changes and shifted towards higher frequencies in the spectra of the uranyl–fructose adducts (Fig. 1 and Table I). The changes observed for the bending vibrations of the COH and OH groups, together with the spectral alterations which occurred for the sugar OH stretching vibrations (3500–3200 cm^{-1}), are indicative of the participation of the sugar hydroxyl groups in metal–ligand bondings and the rearrangements of the intermolecular sugar hydrogen bonding network [6, 8], on sugar metalation.

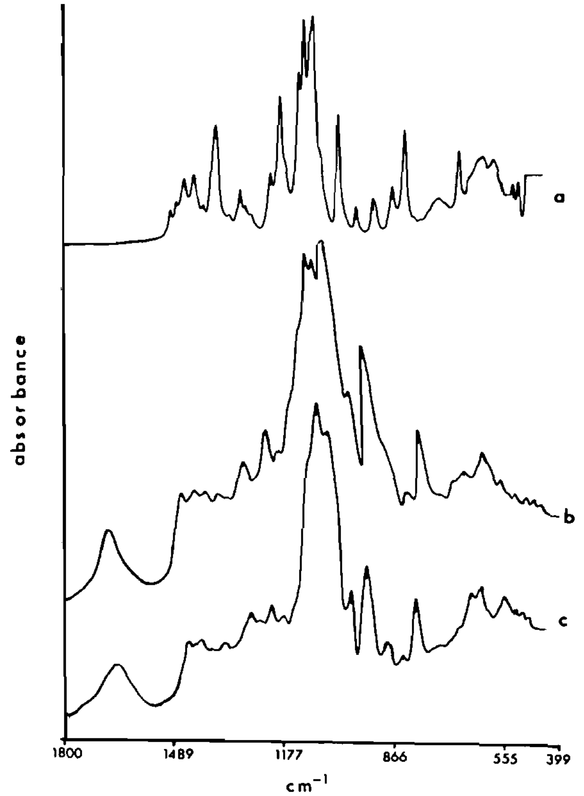


Fig. 1. FT-IR spectra of the crystalline β-D-fructose and its uranyl adducts in the region of 1800–400 cm^{-1} for: (a) crystalline β-D-fructose; (b) UO_2(D-fructose)$Cl_2 \cdot 2H_2O$; (c) UO_2(D-fructose)$Br_2 \cdot 2H_2O$.

The ring CO stretching vibrations [12, 13] appeared as strong absorption bands at 1150, 1094, 1078, 1053, 1025, 978 and 924 cm^{-1} in the free sugar spectrum; they showed major intensity changes (broadening) and shifted towards lower frequencies upon uranyl ion interaction (Fig. 1 and Table I). The observed spectral changes for the CO stretching vibrations are related to the participation of the CO group in uranium–sugar bondings [6, 8].

Several other absorption bands with medium intensities at about 800–400 cm^{-1} in the free D-fructose spectrum were attributed to the ring skeletal C–O–C, C–C–C deformation modes [12, 13]; they also exhibited changes on complex formation (Table I and Fig. 1). Since the ring vibrational frequencies are strongly coupled, metalation of the sugar moiety perturbs the electron distribution within the ring system where the vibrations are mostly localized and finally brings up the ring distortion [6, 8].

Nitrate Ion Vibrations

A broad and strong absorption band at 1392 cm^{-1} in the IR spectrum of the UO_2(D-fructose)$(NO_3)_2 \cdot 2H_2O$ compound which is not present in the spectra of the free sugar and the corresponding halides and sulphate complexes was assigned to the ν_3 of the nitrate ion in D_{3h} symmetry [14] (Table I). This is indicative of the ionic nature of the UO_2–NO_3 interaction in this uranyl–sugar compound. Other ionic nitrate vibrational frequencies at 1050 cm^{-1} (ν_1), 850 cm^{-1} (ν_2) and 740 cm^{-1} (ν_4) were obscured by the strong sugar absorption bands (Table I).

Sulphate Ion Vibrations

A broad and strong absorption band centered at about 1103 cm^{-1} in the spectrum of the UO_2(D-fructose)$SO_4 \cdot 2H_2O$, which was overlapping other sugar vibrational frequencies, was assigned to the ν_3 of the ionic sulphate in *Td* symmetry [16]. Similarly, a band with medium intensity at 598 cm^{-1} in the spectrum of the uranyl–sulphate sugar adduct was related to the ν_2 of the ionic sulphate anion [16] (Table I). These bands suggest that there is no direct uranyl–sulphate interaction in this uranium–sugar adduct.

A strong absorption band observed at about 940 cm^{-1} in the spectra of all the uranyl–fructose compounds and which is absent in the free sugar spectrum was assigned to the antisymmetric stretching of OUO group [7]. The absorption band at about 900–800 cm^{-1} related to the OUO symmetric stretching vibration [7] was obscured by the sugar vibrational frequencies (Table I and Fig. 1).

D-fructose Isomeric Changes

It is well known that the crystalline D-fructose has β-D-fructopyranose configuration [9, 10, 17], whereas in aqueous solution an equilibrium exists

TABLE I. FT-IR Absorption Bands (cm^{-1}) of the Crystalline β-D-fructose and its Uranium Adducts in the Region of 3700–400 cm^{-1} with Possible Band Assignments[a]

β-D-fructose	UO_2(D-fructose)$Cl_2 \cdot 2H_2O$	UO_2(D-fructose)$Br_2 \cdot 2H_2O$	UO_2(D-fructose)$(NO_3)_2 \cdot 2H_2O$	UO_2(D-fructose)$SO_4 \cdot 2H_2O$	Assignments [6–16]
3526s	3450vs	3455vs	3480vs	3460vs	ν(O(4)–H...O(2'))
3422bs	3426bs	3425bs	3423s	3427bs	ν(O(3)–H...O(5'))
3406s	3310s	3315s	3320vs	3310s	ν(O(1)–H...O(3'))
3366s	3290vs	3295vs	3300vs	3292vs	ν(O(5)–H...O(2'))
3180s	3150vs	3100s	3150s	3100vs	ν(O(2)–H...O(1'))
3013w	3010w	3010w	3000w	3000w	$\nu_{asy}(CH_2)$ of C-1
2990w	2990vw	2995vw	2990w	2990w	$\nu_{asy}(CH_2)$ of C-6
2959w	2955w	2950w	2955w	2950w	ν_{sy}(CH) of C-4
2934m	2930m	2935m	2930m	2935m	ν_{sy}(CH) of C-5
2900m	2900m	2890m	2895m	2900m	$\nu_{sy}(CH_2)$ of C-6
2835vw					$\nu_{sy}(CH_2)$ of C-1
	1645mb	1640mb	1645mb	1645mb	$\delta(H_2O)$
1470w					$\delta(CH_2) + \delta(COH) + \delta(CCH)$
1451w	1446m	1444m	1450m	1450m	$\delta(OCH) + \delta(CCH)$
1428m	1422m		1425sh	1430m	$\delta(OCH) + \delta(COH) + \delta(CCH)$
1399m	1403w	1408m			$\delta(OCH) + \delta(CCH) + \delta(CH_2)$
			1392bs		$\nu_3(NO_3^-)$
1372vw	1380w	1377m	1380m	1375w	$\delta(CCH) + \delta(COH)$
1336s	1342m	1338m	1337vw	1340m	
1320vw					$\delta(COH) + \delta(CCH)$
1265m	1264s	1266s	1270m	1275m	
1250sh	1234vw		1252vw	1255w	$\delta(COH) + \delta(CCH)$
1235sh	1203m	1199s	1219w	1220w	$\delta(COH) + \delta(CCH)$
1176m	1168m	1181m	1160sh	1160sh	$\delta(COH) + \delta(CCH)$
1150s	1125sh	1130sh	1125sh	1130sh	$\nu(CO) + \delta(CCC) + \nu(CC)$
				1103bs	$\nu_3(SO_4^{2-})$
1100sh	1076vs	1074vs	1070vs		
1094s	1045s	1055vs	1060vs	1085bs	$\nu(CO) + \nu(CC)$
1079vs					$\nu(CO) + \nu(CC)$
1053vs		1025bs	1030sh	1030vs	$\nu(CO)$
1000sh					$\nu(CO) + \nu(CC)$
978s	969m	974s	973s		$\nu(CO) + \delta(CCO)$
	926s	927s	936vs	943vs	ν(OUO) antisym.
924m				861m	$\nu(CC) + \delta(CCH) + \delta(CH)$
874m	864m	865sh	880m	819m	$\delta(CH)$
818m	818w	820w	817m	780vw	$\tau(CO) + \delta(CCO) + \delta(CCH)$
783s	781s	777s	779m	690vw	
686m	707vw	685w	699w	644m	$\tau(CO) + \delta(CCO) + \delta(OCO)$
665sh	660sh	655m	665vw	610sh	$\tau(CO)$
628s	622m	620sh	616m		
596sh	593m	596m	600m		

(continued)

TABLE I. *(continued)*

β-D-fructose	UO_2(D-fructose)$Cl_2 \cdot 2H_2O$	UO_2(D-fructose)$Br_2 \cdot 2H_2O$	UO_2(D-fructose)$(NO_3)_2 \cdot 2H_2O$	UO_2(D-fructose)$SO_4 \cdot 2H_2O$	Assignments [6–16]
				597s	$\nu_2(SO_4{}^{2-})$
560m	555sh	549w	550vw	530vw	$\delta(CO) + \delta(CCO)$
528m	526m	510w	524w	500vw	$\delta(CCO) + \tau(CO)$
488sh	486w	485m	504w		$\delta(CCO) + \delta(CCH)$
470w	470w	465w	470w		
454w	450w	450w	450w		

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

between both α- and β-D-fructopyranose and α- and β-D-fructofuranose configurations [18]. It has been shown that the IR spectrum of the crystalline solid is rather different from that of the D-fructose in H_2O solution [19]. The solid spectrum of the free D-fructose shown in Fig. 1 showed marked similarities to those of the Ca–fructose adducts [8], while the solution spectra [19] exhibited distinct similarities to those of the Mg–fructose adducts reported earlier [6] and to the uranyl–fructose compounds studied here (Fig. 1). The observed spectral similarities of the Ca–fructose compounds to that of the free D-fructose solution spectra are due to the coordination of the sugar moiety in its β-D-fructopyranose form [8], which is consistent with the X-ray structural information reported for the calcium–fructose compounds [3–5, 9]. On the other hand, the similarities observed for the D-fructose solution spectrum with the Mg(II) and UO_2–fructose complexes are due to the presence in these metal–sugar adducts of the sugar moiety in both its β-D-fructopyranose and β-D-fructofuranose isomers.

Recently, on the basis of the IR spectroscopy, we have concluded that the D-fructose has β-anomer configuration in its free crystalline form and in the magnesium and calcium–fructose complexes [6, 8]. The evidence for this comes from the presence of an absorption band with medium intensity at 875 cm^{-1} in the infrared spectra of the free D-fructose and its calcium and magnesium compounds which was tentatively assigned to the β-anomer sugar configuration [6, 8]. In this work, the presence of the same absorption band at about 870 cm^{-1} in the spectra of the uranyl–fructose compounds and the absence of any absorption band at about 840 cm^{-1} (related to the α-anomer form) is indicative of the presence of D-fructose in its β-anomer form in these uranyl–sugar complexes (Fig. 1 and Table I).

X-ray Powder Diffraction and Molar Conductivity

The X-ray powder diagrams of the uranyl–fructose compounds exhibited no marked similarities with those of the structurally known Ca–fructose adducts. This is due to the higher coordination numbers found for Ca(II) ion (7 or 8) with respect to the uranium ion (6) in these series of metal–fructose complexes. On the other hand, the X-ray powder photographs of the uranyl–sugar adducts showed distinct similarities with those of the six-coordinated Mg–fructose adducts [6], which is indicative of the similar coordination numbers and binding arrangements for these uranyl–fructose compounds.

The high molar conductivities observed (180–200 Ω^{-1} cm^2 mol^{-1}) for the uranyl–fructose compounds in aqueous solutions are indicative of the dissociation of these metal–sugar adducts and the ionic nature of the UO_2–X_2 bonds ($X = Cl^-, Br^-, NO_3{}^-$ or $0.5SO_4{}^{2-}$). The results are consistent with the infrared spectroscopy (discussed before) and the structural information on the Ca–fructose compounds [3–5] which showed no direct Ca–halide interaction.

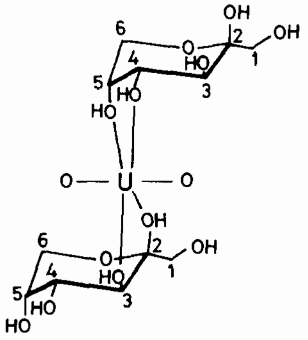
Conclusions

On the basis of the FT-IR spectroscopy and X-ray powder diffraction measurements of the uranyl–fructose adducts studied here and the comparisons made with those of the corresponding structurally identified Mg(II) and Ca(II)–fructose compounds, the following remarks can be made:

(a) The strong intermolecular hydrogen bonding network of the free D-fructose is rearranged to that of the sugar-OH...H_2O...anion system, upon UO_2^{2+} cation interaction.

(2) The uranyl cation binds to two sugar moieties via O2, O3 of the first and O4, O5 of the second molecule, resulting in a six-coordination around the uranium ion (Scheme 1).

(3) There is no direct interaction between the uranyl cation and the halide, nitrate or sulphate anions.



Scheme 1. Uranyl–fructose adduct.

(4) The sugar moiety has β-anomer configuration in these uranyl–sugar compounds and binds in its β-D-fructopyranose form to the Ca(II) ion, whereas coordination of the Mg(II) and the UO_2^{2+} cations is through both the β-D-fructopyranose and β-D-fructofuranose sugar isomers.

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