Sugar Complexation with Uranium Ion. Synthesis, Spectroscopic and Structural Analysis of UO₂-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.

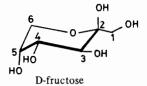
The marked spectral similarities observed with those of the structurally characterized Mg(D-fructose) $X_2 \cdot 4H_2O$ (X = Cl⁻ or Br⁻) adducts suggested that the UO₂²⁺ cation binds to two D-fructose molecules through O2, O3 of the first and O4, O5 of the second sugar moiety, resulting into a six-coordination geometry around the uranium ion. There is no direct interaction between UO₂²⁺ 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 uranylfructose 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.



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 UO₂(SO₄)₂ with BaCl₂ or BaBr₂ in aqueous solution and filtering off the insoluble BaSO₄ 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 $UO_2(D\text{-fructose})$ - $X_2 \cdot 2H_2O$, 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(Dfructose) $X_2 \cdot 4H_2O$ (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 H₂O molecules [6]. On the other hand, the Ca(II) ion in the Ca(D-fructose)X2·2H2O $(X = Cl^- \text{ or } Br^-)$ adducts was found to be sevencoordinate, 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)₂Cl₂·3H₂O 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 H₂O [5]. The intermolecular sugar hydrogen bonding network is rearranged to that of the sugar-OH... H₂O... halide system upon fructose metalation [3-5]. The FT-IR spectra of the uranyl-fructose adducts together with the free Dfructose 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)	HO (Å)	OO (Å)	ν(OH) (cm ⁻¹)
O(4)-HO(2')	0.948	2.063	2.972	3526s
O(3)-HO(5')	0.964	1.977	2.930	3422bs
O(1)-HO(3')	0.972	1.965	2.859	3406s
O(5)-HO(2')	0.963	1.869	2.805	3366s
O(2)-HO(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 H₂O [6], which is indicative of the similar binding arrangements around the UO₂²⁺ 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

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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 CH₂ 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, CH₂, 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.

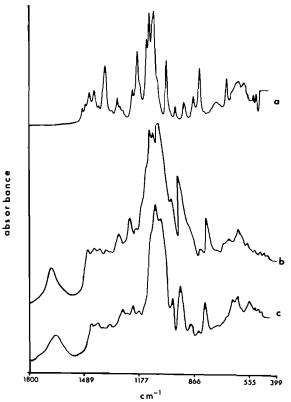


Fig. 1. FT-IR spectra of the crystalline β -D-fructose and its uranyl adducts in the region of $1800-400 \text{ cm}^{-1}$ for: (a) crystalline β -D-fructose; (b) UO₂(D-fructose)Cl₂·2H₂O; (c) UO₂(D-fructose)Br₂·2H₂O.

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 $UO_2(D\text{-fructose})(NO_3)_2 \cdot 2H_2O$ 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 -NO₃ interaction in this uranyl-sugar compound. Other ionic nitrate vibrational frequencies at $1050 \text{ cm}^{-1}(\nu_1)$, 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

3450vs 3455vs 3480vs 3460vs 3460vs 3460vs 3460vs 3478s 3478s 3478s 3478s 3478s 3478s 3100vs 3000w	β-D-fructose	UO ₂ (D-fructose)Cl ₂ ·2H ₂ O	UO ₂ (D-fructose)Br ₂ ·2H ₂ O	$UO_2(D\text{-fructose})(NO_3)_2 \cdot 2H_2O$	$\mathrm{UO}_2(\mathrm{D}\text{-fructose})\mathrm{SO}_4 \cdot 2\mathrm{H}_2\mathrm{O}$	Assignments [6-16]
3426bs 3425bs 3427bs 3400xs 340xs 340xs 340xs <td>3526s</td> <td>3450vs</td> <td>3455vs</td> <td>3480vs</td> <td>3460vs</td> <td>ν(O(4)–HO(2'))</td>	3526s	3450vs	3455vs	3480vs	3460vs	ν(O(4)–HO(2'))
3310s 3315s 3320vs 3310s 310w 315ws 3150ws 3100vs 310w 310ws 3100ws 3100ws 310w 310ws 3100ws 3100ws 2990w 2995w 2990w 2990w 2990m 2995w 2990w 2990w 2990m 2995m 2935m 2990w 2990m 2995m 2995m 2995m 2990m 2995m 2995m 2995m 2990m 2995m 2995m 2995m 290m 2995m 2995m 2995m 1464m 1640mb 1645mb 1645mb 145m 1450m 1450m 1450m 1403w 1397m 1380m 1375w 1380m 1337w 1340m 1375w 1264s 126s 1270m 1275m 1264s 1169h 1169h 1169h 1153h 1070ws 106ws 1085w 104s <t< td=""><td>3422bs</td><td>3426bs</td><td>3425bs</td><td>34238</td><td>3427bs</td><td>v(O(3)-HO(5'))</td></t<>	3422bs	3426bs	3425bs	34238	3427bs	v(O(3)-HO(5'))
3290vs 3392vs 3290vs 3100vs 3100vs 310vs 3100vs 3100vs 310vs 310vs 3100vs 301vm 310vs 3100vs 301vm 310vs 3100vs 301vm 310vs 3100vs 301vm 295vm 2990w 2990w 2950m 295vm 2990w 2990w 2930m 2935m 2990w 2990w 2930m 2930m 2990m 2990w 144m 1445m 145m 145m 1445m 1445m 145m 145m 1445m 1450m 137sm 137sm 1380w 137m 137sm 137sm 1154s 1130s 1130s 1130s	3406s	3310s	3315s	3320vs	3310s	$\nu(O(1)-HO(3'))$
3150s 3100s 3150s 3100s 3010w 3100s 3100s 3100s 2995xw 2995xw 2995xw 2996w 2995xw 2995xw 2996w 2996w 2995xw 2995xw 2996w 2996w 2995xw 2995xw 2996w 2996w 2996m 2995xw 2996w 2996w 1445m 1445m 1450m 1450m 1445m 1444m 1450m 1450m 1445m 1445m 1450m 1450m 1445m 1450m 1450m 1450m 1445m 1392bs 1450m 1450m 1345m 1337w 1340m 125xm 1345m 1337w 1340m 125xm 1158m 1158m 1156xm 1156xm 1158m 115xm 115xm 115xm 115xm 115xm 115xm 115xm 105xm 105xm 105xm 105xm 95xm	3366s	3290vs	3295vs	3300vs	3292vs	$\nu(O(5)-HO(2'))$
3010w 3000w 3000w 2990w 2990w 2990w 2955w 2956w 2990w 2950w 2955w 2950w 2950m 2955w 2950w 2950m 2955w 2950w 2900m 2955w 2950w 2900m 2956w 2950m 144cm 144fm 145m 1645mb 144cm 1445m 145m 145m 1402w 1408m 137m 145m 1402w 137m 1380m 137w 1380w 137w 137w 137w 1380w 137w 137w 135m 1380m 137w 135w 135w 1380m 137w 135w 135w 1380m 137w 135w 135w 1158m 116m 116m 116m 115sh 116m 116m 116m 115sh 116m 116m 116m 105ss	3180s	3150vs	3100s	3150s	3100vs	$\nu(O(2)-HO(1'))$
2990w 2990w 2990w 2955w 2995w 2996w 2930m 2956w 2956w 2930m 2956w 2995w 2930m 2956w 2956w 2930m 2956w 2956w 2930m 2956w 2956w 2930m 2956w 2956w 1645mb 1645mb 1645mb 1446m 1446m 1450m 1450m 1403w 1408m 1337m 1450m 1380w 1377m 1380m 1376m 11342m 1338m 1337w 1340m 1234vw 1338m 1337w 1340m 11234vw 1180m 1155m 1256w 103m 1166h 1166h 1166h 115sh 1166h 1103bs 1030s 1076s 1070s 1030s 1030s 1045s 1030sh 1030s 819m 864m 865sh 880m 819m 884m </td <td>3013w</td> <td>3010w</td> <td>3010w</td> <td>3000w</td> <td>3000w</td> <td>$\nu_{\rm asv}({\rm CH_2})$ of C-1</td>	3013w	3010w	3010w	3000w	3000w	$\nu_{\rm asv}({\rm CH_2})$ of C-1
2955w 2956w 2955w 2956w 2930m 2935m 2936m 2935m 2930m 2895m 2936m 2935m 2900m 2895m 2936m 2935m 1645mb 1640mb 1645mb 1645mb 1446m 1444m 1458m 1645mb 1422m 1408m 137m 1458m 1380w 1377m 1390m 1375w 1380w 1377m 1390m 1375w 11264s 1266s 1270m 1250w 11264s 1199s 1219w 1250w 1128m 1181m 1160sh 1160sh 1160sh 1125h 1150sh 1160sh 1160sh 1160sh 1125h 1076ss 1076ss 1030sh 1030sh 1045s 105ss 1030sh 1030sh 819m 864m 865sh 865sh 861m 861m 818w 650sh 616m 616m	2990w	2990vw	2995vw	2990w	2990w	v _{asv} (CH ₂) of C-6
2930m 2935m 2935m 2935m 2900m 2890m 2895m 2900m 1645mb 1645mb 1645mb 1645mb 1446m 1444m 1450m 1450m 1445m 1448m 1450m 1450m 1403w 1408m 1395s 1378w 1380w 1377m 1380m 1378w 1234w 1380m 1337w 1340m 1234w 125sw 125w 125w 1234w 125sw 125w 125w 1234w 1337m 1337w 125w 1234w 125w 125w 125w 1234w 125w 125w 125w 1234w 1130sh 1160sh 1160sh 1158m 1130sh 1160sh 1103sh 1076s 1076s 1080s 1080s 1045s 105ss 1030sh 1030sh 1045s 927s 936s 943s 108s 880m<	2959w	2955w	2950w	2955w	2950w	v _{sv} (CH) of C-4
2900m 2895m 2900m 1645mb 1646mb 1645mb 1645mb 1422m 144m 1450m 1450m 1422m 144m 1450m 1450m 1422m 1403m 1430m 1430m 1430m 1392bs 1370m 1392bs 1380w 1377m 1392bs 1375w 1380w 1377m 1392bs 1375w 1254s 125cw 1375m 1258w 1254w 1393m 125cw 1258w 1168m 1181m 1160sh 1100sh 1168m 1130sh 1100sh 1100sh 1168m 1130sh 1100sh 1100sh 1168m 1105ss 106os 1085bs 1076ss 105ss 106os 1030ss 1045s 105ss 943ss 943ss 96m 881m 810m 810m 818w 820w 880m 644m 652m 620sh	2934m	2930m	2935m	2930m	2935m	v _{sy} (CH) of C-5
1645mb 1640mb 1645mb 165m 1425m 1450m 1450m 1450m 1450m 1450m 1450m 1450m 1370m 1392bs 1370m 1370m 1375w 1470w 1470w 1470w 1470w <td>2900m</td> <td>2900m</td> <td>2890m</td> <td>2895m</td> <td>2900m</td> <td>ν_{sy}(CH₂) of C-6</td>	2900m	2900m	2890m	2895m	2900m	ν _{sy} (CH ₂) of C-6
1645mb 165mm 1420mm 1420mm 1450mm 1275mm 1103sh 1103sh </td <td>2835vw</td> <td></td> <td></td> <td></td> <td></td> <td>$\nu_{\mathbf{S}\mathbf{y}}(\mathrm{CH}_2)$ of C-1</td>	2835vw					$\nu_{\mathbf{S}\mathbf{y}}(\mathrm{CH}_2)$ of C-1
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1422m 1425h 1430m 1403w 1408m 1392bs 1375w 1380w 1377m 1380m 1375w 124s 126s 1275m 1340m 1234w 1199s 1250w 1250w 1234w 1199s 1250w 1250w 1203m 1181m 1160sh 1160sh 1105m 1135sh 1105sh 1103bs 1076s 1070s 1085bs 1075s 1070s 1085bs 1075s 1030sh 1030sh 1025bs 1030sh 1030sh 969m 974s 936vs 86fm 96s 927s 936vs 86fm 864m 820w 817m 780vw 781s 777s 779m 669vw 660sh 665vw 610sh 610sh 622m 650sw 610sh 610sh	1451w	1446m	1444m	1450m	1450m	$\delta(OCH) + \delta(CCH)$
1403w 1408m 1392bs 1375w 1380w 1377m 1380m 1375w 1342m 1338m 1337w 1340m 1264s 1266s 1270m 1255w 1234vw 1199s 1275m 1275m 1234vw 1199s 1252vw 1220w 1234vw 1199s 1255v 1220w 1234vw 1190s 1255w 1220w 1103m 1168m 1160sh 1160sh 1125sh 1160sh 1160sh 1103bs 1076vs 1070vs 1060vs 1085bs 1075ss 1050vs 1030sh 1030ss 969m 974s 974s 974s 969m 974s 936vs 861m 864m 865sh 880m 819m 818w 820w 877m 690vw 707vw 685w 665vw 616m 622m 620sh 616m 616m	1428m	1422m		1425sh	1430m	$\delta(OCH) + \delta(COH) + \delta(CCH)$
1380w 1377m 1392bs 1380w 1377m 1380m 1375w 1264s 1266s 1270m 1240m 1234vw 1196s 1275w 1255w 1234vw 1199s 1275w 1255w 1203m 1199s 1255w 1250w 1168m 1181m 1160sh 1160sh 115sh 1160sh 1130sh 1130sh 1076vs 1070vs 1070vs 1085bs 1045s 1055vs 1060vs 1030sh 969m 974s 974s 973s 966m 974s 974s 936vs 864m 865sh 880m 819m 818w 820w 817m 780vw 777s 779m 669vw 644m 660sh 655m 665vw 616m 622m 665w 616m 616m	1399m	1403w	1408m			8(OCH) + 8(CCH) + 8(CH ₂)
1380w 1377m 1380m 1375w 1342m 1340m 1377w 1340m 1264s 1266s 1270m 1275m 1234vw 1266s 1270m 1255w 1234vw 1199s 1270m 1255w 1234vw 1199s 1270m 1255w 1168m 1181m 1160sh 120w 1125sh 1130sh 1103sh 1103sh 1125sh 1074vs 1070vs 103bs 1045s 1075s 1060vs 1030sh 1045s 1055vs 1060vs 1030vs 969m 974s 973s 943vs 96m 861m 861m 861m 864m 880m 819m 819m 818w 870w 817m 690w 644m 660sh 655m 665w 616m 616m				1392bs		v3(NO3)
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1076vs 1074vs 1070vs 1045s 1055vs 1060vs 1085bs 1045s 1055vs 1060vs 1085bs 1025bs 1030sh 1030vs 969m 974s 973s 943vs 926s 927s 936vs 861m 864m 865sh 880m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 669w 644m 660sh 655m 616m	1150s	1125sh	1130sh	1125sh	1130sh	$\nu(CO) + \delta(CCC) + \nu(CC)$
1076vs 1070vs 1045s 1055vs 1060vs 1085bs 1025bs 1030sh 1030vs 969m 974s 973s 943vs 926s 975 936vs 861m 864m 865sh 880m 819m 818w 820w 817m 780vw 707vw 685w 699w 644m 660sh 655m 665vw 616m					1103bs	$\nu_3(\mathrm{SO_4}^2)$
1045s 1055vs 1060vs 1085bs 1025bs 1030sh 1030vs 969m 974s 973s 943vs 926s 927s 936vs 861m 864m 865sh 880m 819m 818w 820w 817m 780vw 707vw 685w 699w 644m 660sh 655m 665vw 616m	1100sh	1076vs	1074vs	1070vs		
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969m 973s 1030sh 1030vs 969m 974s 973s 943vs 926s 927s 936vs 861m 864m 865sh 880m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 665w 644m 660sh 655m 616m 616m	1079vs					$\nu(CO) + \nu(CC)$
969m 974s 973s 926s 927s 936vs 943vs 926s 943vs 861m 864m 865sh 880m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 669w 644m 660sh 655m 665vw 616m 622m 650sh 616m	1053vs		1025bs	1030sh	1030vs	v(CO)
969m 974s 973s 926s 927s 936vs 943vs 926s 927s 936vs 861m 861m 880m 819m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 665w 644m 660sh 655m 665w 616m	1000sh					$\nu(CO) + \nu(CC)$
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861m 864m 865sh 880m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 699w 644m 660sh 655m 665vw 616m 622m 616m 616m		926s	927s	936vs	943vs	$\nu(OUO)$ antisym.
864m 865sh 880m 819m 818w 820w 817m 780vw 781s 777s 779m 690vw 707vw 685w 699w 644m 660sh 655m 665vw 610sh 622m 616m 616m	924m				861m	$\nu(CC) + \delta(CCH) + \delta(CH)$
818w 820w 817m 780w 781s 777s 779m 690w 707vw 685w 699w 644m 660sh 655m 665vw 616m 622m 616m 616m	874m	864m	865sh	880m	819m	8(CH)
781s 777s 779m 690vw 707vw 685w 699w 644m 660sh 655m 665vw 610sh 622m 616m 616m	818m	818w	820w	817m	780vw	
707vw 685w 699w 644m 660sh 655m 665vw 610sh 622m 616m 616m	7838	7818	7778	779m	m^069	$\tau(CO) + \delta(CCO) + \delta(CCH)$
622m 620sh 616m 610sh	686m	707vw	685w	m669	644m	$\tau(CO) + \delta(CCO) + \delta(OCO)$
622m 620sh 616m	665sh	660sh	655m	665vw	610sh	r(CO)
	628c	m269	620sh	616m		,
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β-D-fructose	-D-fructose UO ₂ (D-fructose)Cl ₂ ·2H ₂ O	UO ₂ (D-fructose)Br ₂ ·2H ₂ O	$ \text{UO}_2(\text{D-fructose}) \text{Br}_2 \cdot 2 \text{H}_2 \text{O} \\ \text{UO}_2(\text{D-fructose}) (\text{NO}_3)_2 \cdot 2 \text{H}_2 \text{O} \\ \text{UO}_2(\text{D-fructose}) \text{SO}_4 \cdot 2 \text{H}_2 \text{O} \\ \text{Assignments} \ [6-16] $	UO ₂ (D-fructose)SO ₄ ·2H ₂ O	Assignments [6-16]
				597s	$\nu_2({\rm SO_4}^{2-})$
260m	555sh	549w	550vw	530vw	8(CO) + 8(CCO)
528m	526m	510w	524w	500vw	$\delta(CCO) + \tau(CO)$
488sh	486w	485m	504w		8(CCO) + 8(CCH)
470w	470w	465w	470w		
454w	450w	450w	450w		

as, 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 H₂O solution [19]. The solid spectrum of the free Dfructose 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 Dfructose 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 UO₂-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 Dfructose 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 sixcoordinated 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} cm² 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 = CI^- , Br^- , NO_3^- or $0.5SO_4^{-2-}$). The results are consistent with the infrared spectro-

scopy (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 uranylfructose 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...H₂O...anion system, upon UO₂²⁺ 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 UO₂²⁺ cations is through both the β -D-fructopyranose and β -D-fructofuranose sugar isomers.

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