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Sugar Interaction with Uranium Ion. Synthesis, Spectroscopic and Structural Analysis of UO_2–Sugar Complexes Containing D-Glucuronate Moiety

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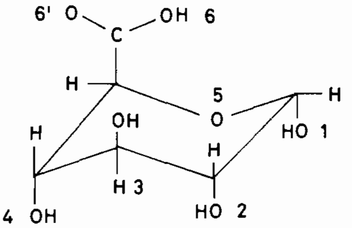
Abstract

Interaction between D-glucuronic acid and hydrated uranyl salts has been studied in aqueous solution and solid complexes of the type UO_2(D-glucuronate)X·$2H_2O$ and UO_2(D-glucuronate)$_2$·$2H_2O$, where X = Cl^-, Br^- or NO_3^-, are isolated and characterized by means of FT-IR and proton-NMR spectroscopy.

On comparison with the structurally identified Ca(D-glucuronate)Br·$3H_2O$ compound, it is concluded that the UO_2^{2+} cation binds to two D-glucuronate moieties in uranyl–sugar complexes via O6, O5 oxygen atoms (ionized carboxyl group) of the first and O6′, O4 (non-ionized carboxyl group) of the second sugar moiety, whereas in the UO_2(D-glucuronate)$_2$·$2H_2O$ salt the uranyl ion is bonded to two sugar anions through O6, O6′ oxygen atoms of the ionized carboxyl group, resulting in a six-coordination geometry around the uranium ion. The strong intermolecular hydrogen bonding network of the free acid is rearranged upon sugar metalation and the sugar moiety showed β-anomer conformation both in the free acid and in these uranyl–sugar complexes.

Introduction

The biological importance of D-glucuronic acid is related to the presence of this acid in the complex molecules of specific bacterial polysaccharides [1]. Glucuronide formation may play an important part in the detoxification and in the absorption of various substances [2]. Remarkable differences have been observed in the behaviour of the uronic acids and the corresponding aldohexoses, such as in the rate of hydrolysis of the glycosides and in the epimerization reactions [3]. It has also been indicated that the inductive effect of the carboxyl group has a significant stabilizing effect on the glycosidic linkage [3]. On the other hand D-glucuronic acid shows great affinity towards complexation with alkali, alkaline earth and heavy metal ions such as Hg(II), Cd(II) ions [4–7]. In the present work, we describe the synthesis and characterization of several uranium–glucuronate complexes by means of FT-IR, ^1H NMR spectroscopy, molar conductivity and X-ray powder diffraction measurements, that has not been reported so far. The spectroscopic properties of the UO_2–glucuronate compounds have been compared with those of the structurally known Ca(D-glucuronate)Br·$3H_2O$ compound [8], in order to detect the characteristic features of each structural type of the uranyl–sugar complexes synthesized here and to establish a correlation between the spectral changes and the binding sites, used by the sugar moiety. Furthermore, the effect of uranium interaction on the sugar conformational transitions has been discussed and the sugar vibrational frequencies with the possible band assignments are reported here. The chemical structure of D-glucuronic acid with the numbering of the atoms is given below.



D - glucuronic acid

Experimental

Materials and Methods

D-glucuronic acid was obtained from Sigma Chemical Co., and was recrystallized from water by slow evaporation. Hydrated $UO_2(NO_3)_2$, UO_2Cl_2 and $UO_2(CH_3COO)_2$ salts were BDH reagent grade and used as supplied. Hydrated UO_2Br_2 was obtained according to our previous report [9] by metathesis of $UO_2(NO_3)_2·6H_2O$ with $BaBr_2$, and filtering off the insoluble $Ba(NO_3)_2$. All the other chemicals were reagent grade and used as supplied.

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TABLE I. FT-IR Absorption Bands (cm^{-1}) for D-glucuronic Acid and its Uranyl Compounds in the Region 3700–500 cm^{-1} with Possible Assignments[a]

D-glucuronic acid	UO_2(glucuronate)-Cl•$2H_2O$	UO_2(glucuronate)-Br•$2H_2O$	UO_2(glucuronate)-NO_3•$2H_2O$	UO_2(glucuronate)$_2$•$2H_2O$	Assignments [4–7, 10–14]
3451s	3460sh	3465sh	3457sh		
3415bs	3425bs	3415s	3440sh	3416bs	ν OH (strongly H-bonded)
			3412vs		
3380sh	3383bs	3385s	3383vs	3384s	
3350s	3348s	3345s	3345m	3348s	
3275b	3289m	3290s	3290m	3285m	
3241sh	3255m	3257m	3250m	3255m	
3204m	3210m	3209m	3210m	3215m	
3180b					
2918m	2920vw	2925m	2925m	2920m	ν CH
2874m	2880w	2882vw	2880w	2875w	
2823m	2820vw		2825vw	2822vw	
2770w					overtone
1709vs	1777s	1775sh	1784vs		ν HOCO
	1720w	1725vs	1710		
	1612bs	1622bs	1640vs	1630bs	ν OCO antisymmetric
			1610vs	1610sh	δ H_2O
	1415vs	1417vs			
			1452s	1404vs	ν OCO symmetric
				1394vs	ν NO_3^-
1475sh				1352vs	
1460s					δ (OCH) + δ(CCH)
1350s	1365sh	1369sh			δ (CCH) + δ(COH)
1300sh	1291s	1288s	1287sh	1288s	δ(COH) + δ(OCH)
1258s	1268sh	1265m	1259s	1258sh	δ(CCH) + δ(COH)
1227s			1225s	1193vw	δ(COH) + δ(CCH)
1190sh	1192w	1191w	1201m		ν(CO) + ν(CC)
			1155vs		
1158s	1140m	1143m	1128m	1145m	ν(CC) + ν(CO)
1125m	1120sh	1086sh	1089vs	1090sh	ν(CO) + δ(COC)
1090vs	1051vs	1053vs	1053m	1054bs	ν(CO) + δ(CCC)
		1025sh	1024vs	1013s	ν(CO) + δ(CCO)
946m					ν(CO) + δ(CCH)
	922vs	926s			
900sh			932vs	920vs	ν(OUO) antisymmetric
			850m	845vw	δ(CH)
870vw	845w	842w			
			790vw	808m	δ(CO) + δ(CCO) + δ(CCH)
774m	799m	798w			
			775m	762w	
753m	769m	768m			
			712m	698w	δ(CCO) + δ(OCO)
713s	687m	688w			
			665m	667w	δ(CCO) + τ(CCO)
665m	624m	621m			
			621w	624m	δ(H_2O)
592w	588w	591w	582m	580m	
567s	561w				
545m	543vw	546m	546m	540w	δ(CO) + δ(CCO)
519m	523vw		519m		

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

Preparation of Uranyl–Sugar Complexes

Uranyl–sugar complexes were prepared by the addition of the hydrated uranyl salt 1 mmol in H_2O (20 ml) to a solution of D-glucuronic acid 1 mmol in H_2O (20 ml). The solution mixture was heated up to 60 °C for 30 min and then cooled down to room temperature. Ethanolic solution was then used to precipitate the compound and this was filtered off, washed with ethanol several times and dried over $CaCl_2$. The analytical results showed composition of UO_2(D-glucuronate)X·$2H_2O$, where X = Cl^-, Br^- and NO_3^-.

Preparation of Uranyl–Sugar Salt

A solution of hydrated uranyl acetate 1 mmol in water (20 ml) was added to a hot solution of D-glucuronic acid 2 mmol in H_2O (20 ml). The solution was cooled down to room temperature and ethanol was used to precipitate the uranyl salt. This was filtered off and washed with ethanol and recrystallized from water–ethanol mixture. The analytical data correspond to UO_2(D-glucuronate)$_2$·$2H_2O$. All uranyl–sugar compounds are very soluble in water and slightly soluble in hot ethanol, but not soluble in common organic solvents.

Physical Measurements

X-ray powder diagrams were taken for comparative purposes, using a camera (Phillips, Debye-Scherre) with Kα radiation and nickel filter. Proton NMR were recorded on a Bruker WH-90 MHz instrument in D_2O solution containing DSS as reference. Infrared spectra were recorded on a DIGILAB FTS 15/C Fourier Transform Michelson Interferometer, equipped with high sensitivity HgCdTe detector and a KBr beam splitter with spectral resolution of 4 to 2 cm^{-1} and KCl pellets. Conductance measurements were carried out at room temperature in H_2O solution (10^{-3} M) with a conductivity meter, type CDM2e (Radiometer, Copenhagen).

Results and Discussion

FT-IR Spectra

The infrared spectra of D-glucuronic acid and its uranium complexes have been recorded in the region of 4000–500 cm^{-1} and a comparison made with those of the corresponding structurally characterized eight-coordinated Ca(D-glucuronate)Br·$3H_2O$ [8] and six-coordinate Zn(D-glucuronate)Cl·$2H_2O$ [7] compound and the results of the spectral analysis are discussed in three parts: (a) sugar OH stretching vibrations and binding modes, (b) carboxyl coordination and (c) ribose ring vibrational frequencies.

(a) Sugar OH stretching vibrations and binding modes

The free acid OH stretching vibrations [4, 5] appeared in the region of 3500–3280 cm^{-1} and showed major intensity changes and shifted towards lower frequencies upon acid ionization (Table I). The changes observed are due to the participation of the sugar OH groups in metal–ligand bondings and the rearrangements of the sugar intermolecular hydrogen bonding network to that of the sugar OH···H_2O··· halide system found in the crystal structure of the Ca(D-glucuronate)Br·$3H_2O$ compound [8]. Similar spectral changes were observed in the spectra of the Zn(II) and Cd(II) sugar complexes containing D-glucuronate anion [7]. It should be noted that a broad absorption band at 3180 cm^{-1}, in the spectra of the free acid, is related to the strongly hydrogen bonded carboxyl group, and disappeared upon sugar ionization (Table I). The CH stretching vibrations of the free acid [4, 5] observed at about 3000–2800 cm^{-1}, showed no major changes upon sugar metalation (Table I).

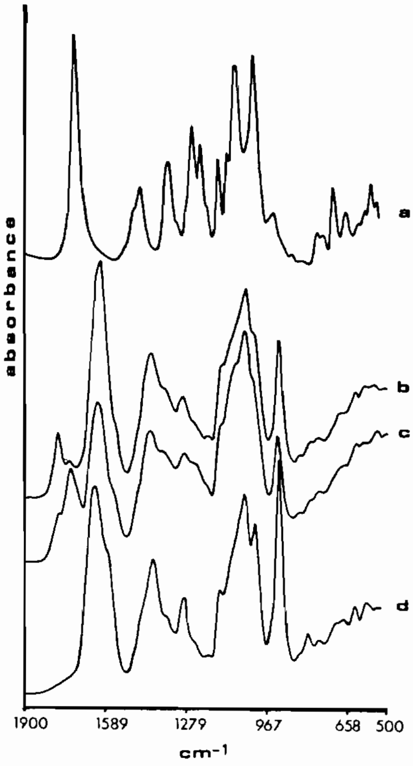


Fig. 1. FT-IR spectra of D-glucuronic acid and its uranyl compounds in the region of 1900–500 cm^{-1} for: (a) D-glucuronic acid; (b) UO_2(D-glucuronate)Cl·$2H_2O$; (c) UO_2(D-glucuronate)Br·$2H_2O$ and (d) UO_2(D-glucuronate)$_2$·$2H_2O$.

(b) Carboxyl group coordination

The free acid carboxyl group stretching vibration [10], observed as a strong absorption band at 1709 cm^{-1}, exhibited considerable changes upon uranyl interaction (Table I and Fig. 1). The changes observed for the carboxyl group are summarized below.

1. Two sets of the carbonyl stretching vibrations have been observed for all the uranyl halide and nitrate sugar complexes. One appeared at about 1770–1720 cm^{-1} (at higher frequencies), which is related to the unionized carboxyl group binding through O6′ and O4 oxygen atoms (Fig. 1 and

Table I). The other two strong absorption bands, observed at about 1600 and 1400 cm^{-1} in the spectra of these uranyl–sugar complexes, are assigned to the antisymmetric and symmetric stretching vibrations of the ionized OCO^- group [4, 5] coordinating via O6 and O5 oxygen atoms (Fig. 1 and Table I), resulting in the binding of the uranyl cation to two sugar moieties. Similar behaviours were observed [7] in the spectra of the Zn(II) and Cd(II) glucuronate complexes, where each metal ion was found to be bonded to two D-glucuronate moieties, through O6′, O4 oxygen atoms of the first (unionized) and O6, O5 of the second anion (ionized).

2. On comparison of the infrared spectra of these uranyl–sugar complexes with those of the fully ionized UO_2(D-glucuronate)$_2\cdot 2H_2O$ salt, in the region of 1800–1400 cm^{-1}, two absorption bands at 1600 and 1400 cm^{-1} related to the antisymmetric and symmetric stretching vibrations of the carboxyl group are observed (Fig. 1), indicating the presence of the two fully ionized sugar anions in this uranium–sugar salt. It is interesting to note that similar observations were made in the infrared spectra of several peach-gum polysaccharides, containing D-glucuronic acid and its derivatives [11]. It was suggested [11] that the absorption band at about 1750 cm^{-1} is due to the presence of the unionized sugar moiety, while the other absorption band at about 1650 cm^{-1} was assigned to the ionized carboxyl group [11]. It is worth mentioning that since the separation of the polysaccharides was carried out in the presence of several mono-, bi- and trivalent metal ions (ionic exchange process) and these metal cations were still present after multiple deionization of the polysaccharides, the presence of the two absorption bands at about 1750 and 1650 cm^{-1} in the spectra of these polysaccharides must therefore be attributed to the binding of the unionized and ionized sugar carboxyl groups to these metal ions [11].

(c) Ribose ring vibrational frequencies

The bending vibrations of the COH and CCH groups of the ribose ring [12, 13] appeared as sharp and fine absorption bands at about 1475, 1460, 1350, 1300, 1258, 1227 and 1190 cm^{-1} in the spectrum of the free acid and showed considerable intensity changes and shifting, upon sugar metalation (Fig. 1 and Table I). The changes observed for the COH bending vibrations are due to the participation of the sugar hydroxyl groups in metal–ligand bondings [4, 5].

The CO stretching vibrations of the ribose ring [12, 13] occurred as several sharp and strong bands at 1125, 1090, 1023 and 946 cm^{-1} in the free acid spectrum and exhibited major alteration (intensity changes and shifting towards lower frequencies), in the spectra of all the uranyl–sugar complexes (Fig. 1 and Table I). The changes observed for the CO stretching vibrations are related to the involvement of the ribose CO group in metal complex formation [4].

The skeletal deformation modes of the C–C–C and C–O–C groups [12, 13] of the ribose ring, centered around 800–500 cm^{-1} showed major alterations, in the spectra of the uranyl–glucuronate compounds (Table I). It should be noted that since the sugar ring vibrational frequencies are strongly coupled, metalation or ionization of the free sugar would change the electron distribution in the ring system, where the vibrations are mostly localized, causing the ring distortion and finally the alteration of the ring vibrational frequencies [4].

The infrared spectra of the fully ionized UO_2(D-glucuronate)$_2\cdot 2H_2O$ salt are substantially different from those of the UO_2–sugar complexes (Fig. 1). In the spectrum of the metal–sugar salt there is no absorption band at about 1770 cm^{-1}, related to the presence of the unionized sugar moiety, and the two strong and broad absorption bands observed at 1630 and 1404 cm^{-1} in the salt spectrum are related to the antisymmetric and symmetric stretching vibrations of the fully ionized carboxyl groups (Fig. 1 and Table I). The spectral dissimilarities observed for this uranyl–sugar salt are due to the different coordination environments around the UO_2^{2+} cation. The binding involves two sugar anions coordinating via the carboxyl O6 and O6′ oxygen atoms, resulting in a six-coordination geometry around the uranium ion.

Nitrate ion and uranyl cation vibrational frequencies

The two strong and broad absorption bands at 1394 and 1352 cm^{-1} in the infrared spectrum of the UO_2(D-glucuronate)$NO_3\cdot 2H_2O$ are assigned to the presence of the nitrate ion in D_{3h} symmetry [14] (Table I). This is indicative of no direct uranyl–NO_3 binding. Other vibrational frequencies at about 1050, 850 and 740 cm^{-1}, related to the ionic nitrate vibrations [14], were masked by the strong sugar vibrational frequencies.

A strong absorption band at 930–920 cm^{-1}, in the spectra of all the uranyl–sugar compounds, which is absent in the spectrum of the free acid (Fig. 1), is assigned to the antisymmetric stretching of the OUO group [14]. The symmetric stretching vibration of the UO_2^{2+} group [14] in the region of 900–800 cm^{-1} was overlapped by the strong sugar vibrational frequencies.

^1H NMR Spectra and Sugar Conformation

On the basis of infrared and proton NMR spectroscopy, we have shown that the alkaline earth metal ions [4, 6] favored the α-anomer conformation of D-glucuronic acid, while the β-anomer con-

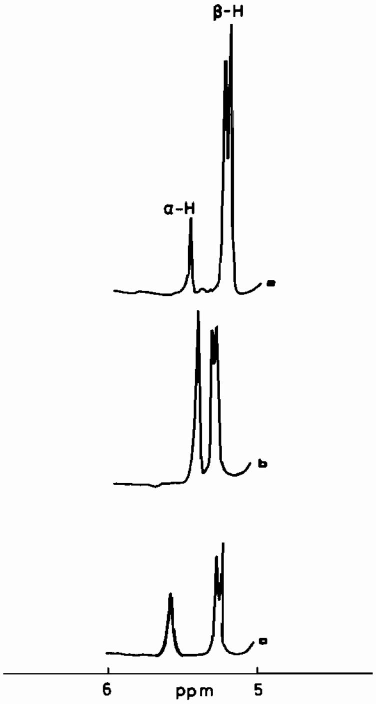


Fig. 2. Proton NMR spectra of the anomeric proton (H_1) chemical shifts in D_2O solution for: (a) D-glucuronic acid; (b) structurally known Ca(D-glucuronate)Br$\cdot$3H_2O and (c) UO_2(D-glucuronate)$NO_3\cdot$2H_2O.

formation was preferred by the alkali [5] and the zinc group metal ions [6]. In this work, the α-anomer and the β-anomer chemical shifts (H_1) of the free glucuronic acid in D_2O solution were observed at 5.56 and 5.28 ppm, respectively and exhibited downfield shifts at 5.68 and 5.38 ppm, upon uranyl interaction (Fig. 2). The anomeric ratio of $\alpha = 15\%$ and $\beta = 85\%$ was found for the free acid and this changed to $\alpha = 52\%$ and $\beta = 48\%$ in the NMR spectra of Ca(D-glucuronate)Br$\cdot$3H_2O compound (Fig. 2) with α-anomer domination, which is consistent with the structural information reported earlier [8]. On the other hand the anomeric ratio changed to $\alpha = 20\%$ and $\beta = 80\%$ in the spectra of the uranyl nitrate, halides and uranyl–glucuronate salt synthesised here (Fig. 2). Similar trends were observed in the spectra of the Zn(II), Cd(II) and Hg(II)–glucuronate complexes where the β-anomer conformation was predominant [7].

Molar Conductivity and X-ray Powder Diffraction Measurements

The high molar conductivities (150–170 Ω^{-1} cm^2 mol^{-1}) observed in aqueous solutions for all the UO_2–sugar compounds are indicative of the presence of no direct metal–halide or metal–nitrate interaction for these uranyl–sugar complexes. This is consistent with the infrared results observed for UO_2(D-glucuronate)$NO_3\cdot$2H_2O (discussed before) and the structural analysis of the Ca(D-glucuronate)Br$\cdot$3H_2O compound [8], which showed ionic character for Ca–Br interaction.

X-ray powder patterns of the UO_2–sugar complexes studied here exhibited no marked similarities with those of the structurally known eight-coordinated Ca(D-glucuronate)Br$\cdot$3H_2O compound, indicating different binding environments for the uranyl ion in these metal–sugar complexes. On the other hand, there were distinct similarities between the X-ray powder patterns of the uranyl–glucuronate complexes with those of the corresponding Zn(II) and Cd(II) complexes reported earlier [7], which is indicative of the similar binding geometry around these metal–sugar complexes. The coordination numbers found for Zn(II) and Cd(II) were six and therefore the uranium ion could be six-coordinate, in these series of metal–glucuronate compounds.

Conclusion

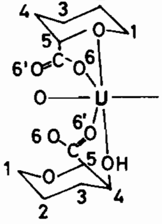
On the basis of comparisons made for the spectroscopic properties of the UO_2–glucuronate compounds synthesized here with those of the corresponding structurally identified Ca(II), Zn(II) and Cd(II)–sugar complexes, the following points can be emphasized:

(a) The strong intermolecular sugar hydrogen bonding network is rearranged upon acid ionization or metalation;

(b) The uranyl cation in UO_2–halide or nitrate sugar complexes binds to two sugar moieties via O6, O5 of the first (ionized) and O6′, O4 of the second molecule (unionized), resulting in a six-coordination around uranium ion (**1**), whereas in the UO_2(D-glucuronate)$_2\cdot$2H_2O salt, the uranium cation is six-coordinated, binding to two fully ionized acid anions through O6 and O6′ oxygen atoms of the carboxyl group (**2**);

(c) The halides and the nitrate anions are bonded ionically, and

(d) The β-anomer sugar conformation is predominant both in the free acid and in these uranyl-sugar compounds.



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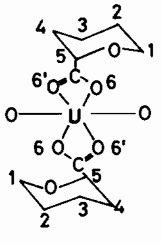
Uranyl–sugar complex



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Uranyl–sugar salt

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