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D-Glucose Interaction with Uranium Ion. Synthesis, Spectroscopic and Structural Characterization of Uranyl–Glucose Adducts and the Effect of Metal Cation Binding on the Sugar Anomeric Structures

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Abstract

The interaction of D-glucose with hydrated uranyl salts has been investigated in solution and solid adducts of the type $UO_2(D\text{-glucose})X_2 \cdot 2H_2O$, where $X = Cl^-$, Br^-, NO_3^- and $0.5\ SO_4^{2-}$ have been isolated. These adducts are characterized by means of FT-IR, ^1H NMR and molar conductivity measurements.

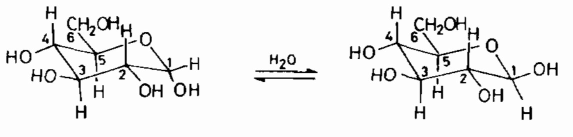
Spectroscopic evidence suggested that the UO_2^{2+} cation could be bonded to one D-glucose molecule (possibly through O(1)–H and O(2)–H hydroxyl groups) and to two H_2O, resulting in six-coordination around the uranium ion.

The strong sugar H-bonding network is perturbed, on metal ion interaction and the D-glucose α-anomeric structure is favoured, upon uranyl cation coordination.

Introduction

Carbohydrate–metal complexes show biological importance. The nickel(II) ion was found to complex with D-glucose derivatives in human kidneys [1], whereas calcium–sugar complexes appear to participate in a variety of biological adhesion and agglutination processes such as calcium storage, calcification and calcium-dependent cell–cell adhesion [2–4]. On the other hand, the solution of simple reducing carbohydrates contains two or more isomeric species [5] and the composition of the equilibrium mixtures would be effected by the metal ion interaction [6, 7]. ^1H NMR [6] and Raman spectroscopy [7] have been used to demonstrate the effects of the metal ion interaction on the anomeric mixtures of D-glucose and other monosaccharides. Recently, I have reported the interaction of D-glucose with the alkaline earth metal ions (Mg^{2+} and Ca^{2+}) and the effects of these metal cation bindings on the sugar anomeric mixtures [8]. The uranyl cation coordination with several sugar moieties such as D-glucuronic acid [9], D-fructose [10] and L-arabinose [11] has been recently reported by us.

The aim of this work is the synthesis and characterization of several adducts formed of uranyl salts and the D-glucose molecule both in solid and solution, using FT-IR, ^1H NMR and molar conductivity measurements that have not been previously reported. Furthermore, the effect of uranyl cation binding on D-glucose anomeric structures (Scheme 1) is discussed.



α - D - glucopyranose β - D - glucopyranose

Scheme 1.

Experimental

Materials and Methods

The anhydrous dextrose was from Aldrich Chemical Company and used as supplied. The α- and β-D-glucose were from Kodak and were used without further purification. The hydrated uranyl nitrate and uranyl sulphate were purchased from BDH (as reagent grade) and used as supplied. The uranyl halides were prepared according to our previous report [12], by the reaction of UO_2SO_4 with $BaCl_2$ or $BaBr_2$ in aqueous solution and filtering off the insoluble $BaSO_4$ salt. All other chemicals were reagent grade and used as supplied.

Synthesis of Uranyl–Glucose Adducts

Hydrated uranyl salt (2 mmol) in methanol (20 ml) was added to a hot solution of D-glucose (1 mmol) in methanol (30 ml), except for UO_2SO_4 which was dissolved in water–methanol mixtures. After heating the solution mixtures for 30 min at 80 °C, the solution was left at room temperature for a week (under slow evaporation) and acetone was used to bring down the pale yellow precipitate. This was filtered off and washed with acetone several times and dried over $CaCl_2$. The analytical data

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showed the composition of UO_2(D-glucose)$X_2 \cdot 2H_2O$, where $X = Cl^-$, Br^-, NO_3^- and $0.5\ SO_4^{2-}$. The uranyl–glucose adducts are soluble in water and hot alcohol but not soluble in any other common organic solvents. These metal–sugar adducts are very hygroscopic and should be kept in a desiccator over $CaCl_2$.

Physical Measurements

The infrared 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. The spectra were taken as KBr pellets with a resolution of 2 to 4 cm^{-1}. The solution spectra (film cast) were prepared by spreading an aqueous solution of D-glucose (10%) on a AgCl plate, followed by evaporation and respreading as needed, to obtain a uniform thickness. ^1H NMR spectra were recorded on a Bruker WH-90 MHz instrument with D_2O and DMSO-d_6 solutions containing DSS or TMS as reference. The molar 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 the α- and β-D-glucose and their equilibrated mixtures as well as uranyl–glucose adducts have been recorded in the region of 3700–500 cm^{-1} and a comparison was made with those of the alkaline earth metal–glucose adducts [8]. The results of the spectral analysis will be discussed below.

D-Glucose OH Stretching Vibration and Uranyl Cation Coordination

The assignments of the IR vibrational frequencies of the α-D-glucose have been reported earlier [8]. The assignments of the α-D-glucose OH stretching vibrations have been based on the intermolecular O···O distances, hydrogen bonding energies and the geometrical parameters [13–17]. There are five intermolecular H-bondings in the crystal structure of the α-D-glucopyranose, two of which are strong hydrogen bonds such as OH(3)···O(2) and OH(6)···O(3), two slightly weaker OH(4)···O(4) and OH(2)···O(6) and one of moderate energy OH(1)···O(5) group [14]. The energies of these hydrogen bonds ranges from 9.4 kJ mol^{-1} for the OH(1)···O(5) to 14.6 kJ mol^{-1} for the OH(3)···O(2) system [14].

The IR spectrum of the free α-D-glucose shows five absorption bands in the region of 3500–3200 cm^{-1}, which are assigned to the following frequencies: the two strong absorption bands at about 3404 and 3342 cm^{-1} can be assigned to the OH(3)···O(2) and OH(6)···O(3) respectively, and the two broad and strong bands at 3310 and 3266 cm^{-1} are related to the OH(4)···O(4) and OH(2)···O(6) respectively, and a band at 3234 cm^{-1} to the OH(1)···O(5) group stretching vibrations (Fig. 1). Our present assignments are in good agreement with the other observations, recently published [17].

The OH stretching vibrations of the free α-D-glucose exhibited considerable changes, shifting and splitting, in the IR spectra of the UO_2–glucose adducts (Fig. 1). The observed spectral changes for the sugar hydroxyl stretching vibrations are indicative of the participation of sugar OH groups in UO_2–glucose bindings. Similar trends were observed for the D-glucose OH stretching vibrations, in the spectra of the alkaline earth metal–glucose adducts, where the metal–sugar binding was suggested to be via D-glucose O(1)–H and O(2)–H hydroxyl groups [8].

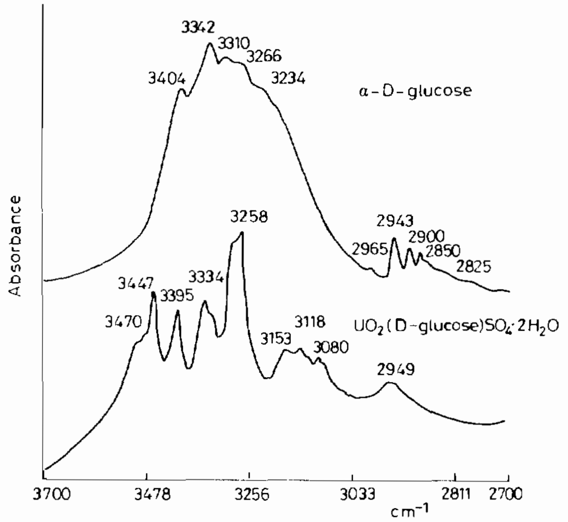

Fig. 1. FT-IR spectra of the free α-D-glucose and its uranyl cation adduct in the region of 3700–2700 cm^{-1}.

H_2O Binding

The presence of a broad and strong band at about 3250 cm^{-1}, related to the water OH stretching vibration and a band with medium intensity at about 1650 cm^{-1} related to the H_2O bending mode, which are absent in the free D-glucose spectrum are attributed to the coordinated water molecule (Figs. 1 and 2).

D-Glucose C–H Stretching Vibrations

The C–H stretching vibrations of the α- and β-D-glucose have been assigned by Longhi *et al.* [18]. The two sugar anomers contain different C–H stretching patterns [18]. The five infrared absorption

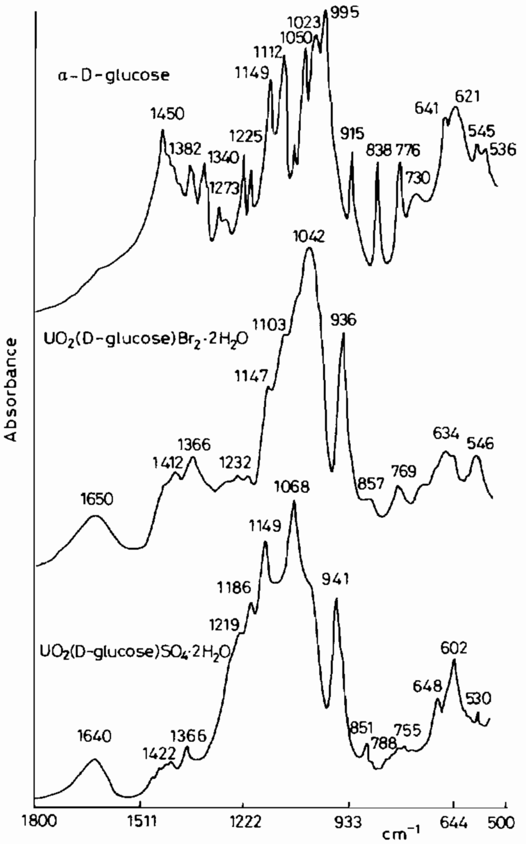

Fig. 2. FT-IR spectra of the free α-D-glucose and its uranyl cation adducts in the region of 1800–500 cm^{-1}.

bands observed in the region of 3000–2800 cm^{-1}, in the spectrum of the free α-D-glucose studied here are assigned to the C4–H (2965 cm^{-1}), C6–H (2943 cm^{-1}), C3–H (2900 cm^{-1}), C2–H (2850 cm^{-1}) and C5–H (2825 cm^{-1}) stretching vibrations (Fig. 1). Our assignments are in a good agreement with those of Longhi *et al.* [18] for the α-D-glucose molecule. The D-glucose C–H stretching vibrations exhibited no major changes on uranyl cation interaction.

D-Glucose Ring Vibrational Frequencies and Metal Cation Binding

The free D-glucose COH, CH_2 and CCH bending vibrations [19–21] appeared as several bands with medium intensities in the region of 1460–1200 cm^{-1} and showed major intensity changes and shifted towards higher frequencies, on sugar adduct formation (Fig. 2). The shifts of the sugar OH bending modes towards higher frequencies, together with the observed spectral changes for the sugar OH stretching vibrations (3500–3200 cm^{-1}), are consistent with the involvement of the sugar hydroxyl groups in uranyl–glucose bondings. Several other sharp and strong absorption bands at about 1150–950 cm^{-1}, in the spectrum of the free D-glucose related to the ring C–O stretching vibration bands [19–21], also exhibited major intensity changes and shiftings, upon uranyl cation coordination (Fig. 2). The spectral changes observed for the ring C–O stretching vibrations are due to the metal–sugar OH group coordination and possibly the rearrangements of the sugar H-bonding network, on adduct formation.

Nitrate and Sulphate Anions Vibrational Frequencies

A strong and broad absorption band at about 1380 cm^{-1} in the spectrum of UO_2(D-glucose)-$(NO_3)_2 \cdot 2H_2O$ (absent in the free sugar) is related to the ν_3 of the nitrate ion in D_{3h} symmetry [22] and it is indicative of the ionic nature of uranyl–nitrate interaction. Other nitrate ion vibrations [22], in the region of 1300–700 cm^{-1} were masked by the strong sugar vibrational frequencies. Similarly, the presence of a broad and strong absorption band centered at about 1100 cm^{-1}, in the spectrum of the UO_2(D-glucose)SO_4 adduct, is related to the ν_3 of the sulphate ion in T_d symmetry [23] and it is indicative of the ionic interaction of UO_2–SO_4, in this metal–glucose adduct. Other sulphate ion vibrations in the region of 1000–500 cm^{-1} were obscured by the sugar vibrational frequencies (Fig. 2). The ionic nature of the uranyl anions (NO_3^-, SO_4^{2-}, Cl^- or Br^-) interactions, is evident by the high molar conductivities observed (180–200 Ω^{-1} cm^2 mol^{-1}) in aqueous solution for these uranyl–glucose adducts.

A strong absorption band observed at about 935 cm^{-1} in the IR spectra of these UO_2–glucose adducts, which is absent in the free sugar spectrum, is attributed to the antisymmetric O–U–O stretching vibration [22]. The O–U–O symmetric stretching vibration in the region of 900–800 cm^{-1} was overlapped by the sugar vibrational frequencies (Fig. 2).

D-Glucose Anomeric Structures and Metal Cation Binding

In our previous report, the infrared spectra of crystalline D-glucose and its anomeric structures in solid and aqueous solution were reported [8]. In Fig. 3, the marker bands for the pure α- and β-D-glucose and the equilibrated mixture are shown. The α-D-glucose exhibited three sharp absorption bands at 915, 838, 776 cm^{-1} and a broad band with medium intensity at 621 cm^{-1}, which are not present in the IR spectrum of the β-D-glucose (Fig. 3). The β-anomer showed a weak band at 912 cm^{-1}, a sharp band at 900 cm^{-1}, a weak band at 860 cm^{-1}, a strong band at 711 cm^{-1} and a strong band at 592 cm^{-1}, which are absent in the α-anomer spectrum (Fig. 3). The spectrum of the equilibrated mixture composed of $\alpha/\beta = 40/60\%$ [24], showed the presence of several marker bands related to both anomers

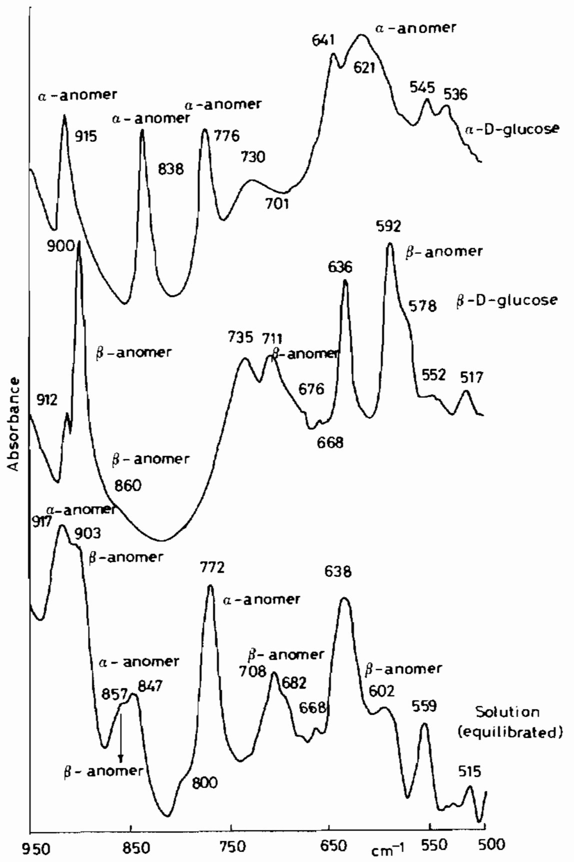

Fig. 3. FT-IR spectra of α-D-glucose, β-D-glucose and their solution mixture (equilibrated) in the region of 950–500 cm^{-1} (anomeric region).

(Fig. 3). On comparing the IR spectra of the UO_2–glucose adducts synthesized here, with those of the corresponding D-glucose anomeric structures both in solid and solution, in the region of 950–500 cm^{-1} (anomeric region), the presence of the bands at about 850, 780 and 600 cm^{-1}, in the spectra of the uranyl–sugar adducts, are indicative of the D-glucose binding via its α-anomeric form, in these uranium–sugar complexes (Figs. 2 and 3). It should be noted that the other band at 915 cm^{-1}, characteristic of the α-anomer was overlapped by the strong antisymmetric OUO stretching band at 935 cm^{-1} (Fig. 2). Similar marker bands were observed in the IR spectra of the alkaline earth metal–glucose adducts, where the sugar coordination was suggested to be through the α-anomeric structure [8].

^1H NMR Spectra

The D-glucose anomeric proton (H_1) chemical shifts appeared at 5.26 ppm for α-H and 4.68 ppm for β-H in D_2O solution [25] and showed no changes in the presence of the uranyl cation salts. This is mainly due to the presence of non-considerable interaction between the uranyl cation and the D-glucose molecule in aqueous solution. The only interaction between these metal cation salts and the D-glucose moiety could be via intermediated H_2O molecules. On the other hand, in DMSO solution, the β- and α-anomeric O(1)H chemical shifts of the free D-glucose were observed at 6.57 and 6.20 ppm, respectively [24] and exhibited major downfield shifts, on uranyl cation interaction. The observed downfield shift of the O(1)H chemical shift (0.3 ppm) is related to the strong interaction between the UO_2^{2+} cation and the D-glucose molecule in non-aqueous solution and possibly to the direct metal–sugar binding, through the O(1)H hydroxyl group. Similar behaviours were observed for the alkaline earth metal ions (Mg^{2+} or Ca^{2+}) and the D-glucose molecule, in DMSO solution, where the metal ion binding was suggested to be through the sugar O(1)H and O(2)H groups [8].

Conclusions

On the basis of the spectroscopic properties of D-glucose and its uranyl cation adducts both in solid and solution, the following points can be emphasized:

(a) The D-glucose interaction with uranyl cation salts is negligible in H_2O solution, while in non-aqueous solution, such interaction is of great importance.

(b) The uranyl–glucose interaction alters the sugar H-bonding network.

(c) In these metal–sugar adducts, the uranyl cation binds to the O(1)H, O(2)H hydroxyl groups of a D-glucose molecule and to two H_2O, resulting in a six-coordination geometry around the uranium ion.

(d) The D-glucose binding is through its α-anomeric structure.

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