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Sugar Interaction with Silver Ion. Synthesis, Spectroscopic and Structural Analysis of Silver–Glucuronate Compounds

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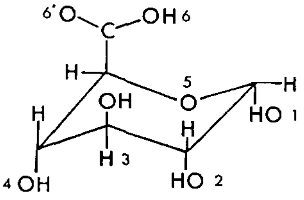
Abstract

Interaction between the D-glucuronic acid and the Ag(I) ion has been studied, in aqueous solution and solid compounds of the type Ag(D-glucuronic)NO_3 and Ag(D-glucuronate) have been isolated and characterized, by means of ^1H NMR and FT–IR spectroscopy.

Spectroscopic and other evidence indicated that the Ag(I) ion in Ag(D-glucuronic)NO_3 compound binds to two sugar moieties via non-ionized carboxyl O6′ atoms, resulting into a linear coordination around silver ion with no direct interaction between the nitrate anion and the Ag(I) ion. On the other hand, the Ag(D-glucuronate) salt is a dimeric with each silver ion binding to two sugar anions through O6 and O6′ carboxyl oxygen atoms with a linear binding around each Ag(I) ion. The strong sugar hydrogen bonding network is rearranged upon metalation and the β-anomer sugar conformation is dominating both in the free acid and in these silver–sugar compounds.

Introduction

In recent years, the interaction of silver ion with nucleic acids and their components has been the subject of extensive investigations [1–4]. The interest in this area of research is based on the carcinogenic properties of $AgNO_3$ compound, which is believed to decrease the fidelity of the DNA transcription [5] and also the use of the Ag(I) ions to probe the structure of DNA in filamentous viruses [6]. Sugar is a constituent part of the nucleic acids and the sugar interaction with the silver ion bears significant biological importance. Sugar complexes of the alkali and alkaline earth metal ions have been known for many years [7], meanwhile the sugar interaction with the silver ion has not been reported, so far. Recently, we have studied several sugar complexes of the alkali, alkaline earth and zinc group metal cations [8–12] and the effects of metal coordination on the sugar conformational transitions. The alkali and zinc group metal ions preferred the β-anomer conformation of D-glucuronic acid [8, 12], whereas the α-anomer conformation was favoured by the alkaline earth metal ions, in D-glucuronic acid and L-arabinose metal complexes [9–11]. In the present work, we describe the synthesis and characterization of several Ag–glucuronate compounds by means of FT–IR, ^1H NMR spectroscopy and molar conductivity that have not been reported so far. Furthermore, the effect of the silver ion coordination on the sugar conformations has been discussed and a correlation between the spectral changes and the binding sites used by the sugar moiety has been established here. The structure of D-glucuronic acid with the numbering of the atoms is shown below:



D-glucuronic acid

Experimental

Materials

D-glucuronic acid was purchased from Sigma Chemical Co., and was recrystallized from water. Other chemicals were reagent grade and used as supplied.

Synthesis of Silver–Sugar Compound

Silver glucuronate compound was prepared by the addition of D-glucuronic acid 1 mmol in H_2O (10 ml) to a solution of silver nitrate 1 mmol in water (10 ml). The solution was kept for 48 h and ethanolic solution was then used to precipitate the compound. This was filtered off, washed with ethanol several times and dried over $CaCl_2$. The analytical data

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showed the composition of Ag(D-glucuronate)NO_3. This compound is light sensitive and goes dark by exposure to light.

Preparation of Silver–Sugar Salt

Silver carbonate (freshly prepared) 1 mmol was dissolved in the hot solution of the free D-glucuronic acid 1 mmol in water (10 ml). The solution cooled down at room temperature and ethanol was used to precipitate the compound. This was filtered off and washed with hot ethanol and dried over $CaCl_2$. The analytical data showed composition of Ag(D-glucuronate). The silver–glucuronate compounds are very soluble in water, but not soluble in other common organic solvents.

Physical Measurements

^1H NMR spectra were taken on a Bruker-WH-90 MHz in D_2O solution containing DSS as reference. The infrared spectra were recorded on a DIGILAB FTS 15/C Fourier Transform Infrared 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 conductivity meter, type CDM2e (Radiometer, Copenhagen).

Results and Discussion

FT–IR Spectra

Infrared spectra of D-glucuronic acid and its silver compounds have been recorded in the region of 4000–500 cm^{-1} and a comparison was made with those of the structurally identified metal–glucuronate compounds. The results of the spectral analyses are discussed below.

Sugar OH stretching vibrations

The OH stretching vibrations of the D-glucuronic acid [8, 9] appeared as strong and broad absorption bands in the region of 3450–3180 cm^{-1} and shifted towards higher frequencies, upon sugar metalation. The shifts of the OH stretching vibrations towards higher frequencies are indicative of the general weakening of the strong sugar hydrogen bonding network on complex formation. It should be noted, that the participation of the sugar hydroxyl groups in the metal–ligand bonding causes the shift of the OH stretchings towards lower frequencies [9]. Therefore, the changes observed for the OH stretching vibrations, in the spectra of the Ag–glucuronate compounds, are due to the rearrangements of the sugar hydrogen bonding system and are not related to the Ag–sugar OH group interaction. The CH stretching vibrations of the free acid [9] at about 3000–2800 cm^{-1} exhibited no significant changes, upon sugar metalation.

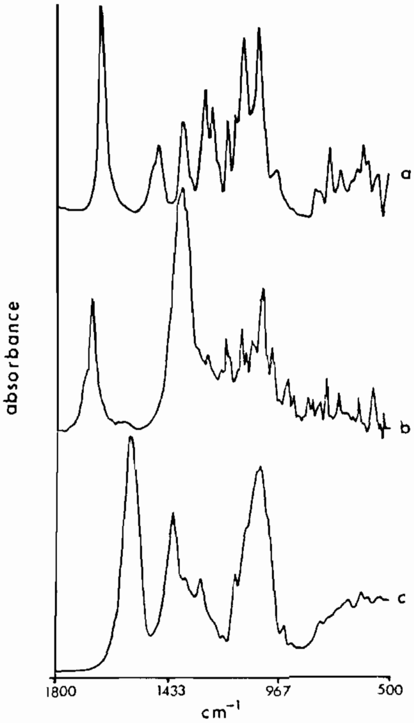


Fig. 1. FT–IR spectra of D-glucuronic acid and its silver compounds in the region of 1900–500 cm^{-1} for: (a) D-glucuronic acid; (b) Ag(D-glucuronic)NO_3; (c) Ag(D-glucuronate).

Carboxyl group coordination modes

The carbonyl stretching vibration of the free acid [9, 13] appeared as a strong absorption at 1709 cm^{-1} and showed considerable changes, upon silver binding (Fig. 1 and Table I). The changes observed for the carbonyl group are different for the Ag(D-glucuronic)-NO_3 compound and the Ag(D-glucuronate) salt and they shall be dealt with separately.

(a) The carbonyl stretching vibration of the free acid at 1709 cm^{-1} showed shifting and splitting, in the spectrum of the Ag(D-glucuronate) salt (Fig. 1). The two broad and strong absorption bands that appeared at 1588 and 1413 cm^{-1}, in the spectrum of this sugar salt are assigned to the antisymmetric and symmetric stretching vibrations of the OCO^- group, respectively (Table I). Similar spectral changes were observed for the carboxyl group, in the spectra of the alkali and alkaline earth metal-glucuronate salts, where the metal sugar interaction was found to be through the carboxyl oxygen atoms [8, 9]. Therefore, the Ag–sugar binding in the Ag(D-glucuronate) salt would be *via* O6 and O6′ of the one carboxyl group (chelation) or in a dimeric compound formed, the two Ag(I) cations bind to two sugar anions through the O6 of the first and O6′ of the second sugar moiety, yielding a linear two coordination environment around each silver ion.

(b) In the spectrum of the Ag(D-glucuronic)NO_3 compound the carbonyl stretching vibration of the free acid at 1709 cm^{-1} shifted towards higher frequencies and appeared as a doublet at 1775 and

TABLE I. FT–IR Absorption Bands (cm^{-1}) for D-Glucuronic Acid and its Silver Compounds in the Region of 1900–500 cm^{-1} with Possible Assignments

D-glucuronic acid	Ag(D-glucuronic)NO$_3$	Ag(D-glucuronate)	Assignments [8, 9, 16, 17]
1709vs	1775sh 1758vs		νHOCO
		1588bs	νOCO$^-$ antisym.
		1413s	νOCO$^-$ sym.
1475sh	–	–	δ(COH) + δ(CCH)
1460s	–	–	δ(CCH) + δ(COH)
–	1379bs	–	νNO$_3^-$
1350s	1364s	1359s	δ(CCH) + δ(COH)
1300sh	1313sh	1296s	δ(COH) + δ(OCH)
1258s	1269m	1255sh	δ(CCH) + δ(COH)
1227s	1213w	–	δ(COH) + δ(CCH)
1190sh	1193s	1198w	ν(CO) + δ(CCO)
1158s	1179sh 1145sh	1149s –	ν(CC) + ν(CO)
1125m	1128s	1106sh	ν(CO) + δ(CCO)
1090vs	1109m 1084s	1063s –	ν(CO) + δ(CCC)
1023vs	1038vs	1048bs	ν(CO) + δ(CCO)
960sh	991s	990sh	ν(CO) + δ(CCH)
946m	968vw	946m	ν(CO) + δ(CCH)
900sh	933m	910w	ν(CC) + ν(CO)
870vw	875vw	870vw	δ(CH)
	844m		νNO$_3^-$
773m	792m	794m	τ(CO) + δ(CCO)
753m	770m	768w	δ(CCH)
713s	716m	715w	δ(CCO) + δ(OCO)
665m	670w	675m	δ(CCO) + τ(OCO)
592w	595vw	592w	τ(CO) + δ(CCO)
567s	572s	–	
545m	550w	547vw	
519m	521w	520w	

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

1758 cm^{-1} (Fig. 1 and Table I). The changes observed are due to the non-ionization of the carboxyl group, in this Ag–sugar nitrate compound. Thus, the Ag(I) binding is through the O6′ of the non-ionized carboxyl groups of the two sugar moieties, forming a two coordination geometry around the silver ion, in the Ag(D-glucuronic)NO$_3$ compound. It is interesting to note, that the coordination of the Ag(I) ion to the C=O oxygen atom of several nucleobases has been demonstrated through the proton-NMR spectroscopy and the X-ray diffraction measurements [2–4]. The metal-coordination via the non-ionized carboxyl oxygen atom of the D-glucuronic acid produced similar spectral changes, in a series of metal–glucuronate complexes, reported earlier [12, 14].

(c) By comparing the spectra of the fully ionized Ag–glucuronate salt with that of the non-ionized Ag(D-glucuronic)NO$_3$ compound, it is evident the way that the ionization of the free acid causes the splitting and the shifting of the carbonyl stretching towards lower frequencies, while the metal-binding to the non-ionized carboxyl group brings shifting of the carbonyl stretching vibration, towards higher frequencies (Fig. 1).

The strong and broad absorption band centered at about 1380 cm^{-1}, in the spectrum of the Ag(D-glucuronic)NO$_3$ compound, is assigned to the ν_3 of the ionic nitrate of D_{3h} symmetry [15] (Fig. 1 and Table I). This is indicative of no direct interaction between the Ag(I) and the nitrate anion and also confirms the presence of the non-ionized acid moiety in this compound. The other absorption band at about 840 cm^{-1} is also related to the ν_2 of the ionic nitrate absorptions, whereas the ν_1 at 1050 and the ν_4 at 750 cm^{-1} of the ionic nitrate absorption bands are masked by the sugar vibrational frequencies (Table I).

The COH bending vibrations [16, 17] of the free sugar, in the region of 1470–1258 cm^{-1}, exhibited major changes and shifted towards higher frequencies (Table I). The changes observed for the COH bendings together with those of the OH stretching vibrations at 3500–3200 cm^{-1} are consistent with the weakening and the rearrangements of the sugar hydrogen bonding network upon acid metalation. Similarly, the ribose ring CO stretchings [16, 17] centered at 1190–950 cm^{-1} shifted towards higher frequencies on complex formation (Table I). The shifts of the CO stretchings towards higher frequencies are related to the weakening of the H-bonding system around the CO group.

The skeletal deformations C–O–C and C–C–C of the free sugar [16, 17] observed at 1000–500 cm^{-1} showed changes, in the spectra of the silver–glucuronate compounds (Table I). The alterations are due to the ionization or metalation of the carboxyl group, which cause a large perturbation to the electronic distribution of the ring system, where the vibrations are mostly localized and finally bring up the ring distortion [8, 9].

^{1}H NMR Spectra and Sugar Conformation

Recently, on the basis of the infrared and proton-NMR spectroscopy, we have demonstrated how the alkaline earth metal ions [9, 14] favoured the α-anomer complexation, whereas the β-anomer conformation of D-glucuronic acid was preferred by the alkali and zinc group metal cations [8, 12]. In this work, the α- and β-anomers proton chemical shifts of D-glucuronic acid in D_2O solution were observed at 5.58 and 5.28 ppm respectively, and showed considerable changes upon silver ion interaction (Fig. 2). The integration of the anomeric proton signals showed that the ratio of $\alpha/\beta = 20/80\%$ for the free acid and this ratio changed to $\alpha/\beta = 15/85\%$, in the spectra of the silver–glucuronate compounds (Fig. 2), which is indicative of the β-anomer domination in these metal-compounds. This is in marked contrast with the anomeric ratio of $\alpha/\beta = 52/48\%$ found for the calcium–glucuronate complexes [14] with the α-anomer domination (Fig. 2). The dissimilarities observed are in fact due to the complexation of the Ca(II) ion with the sugar OH groups, which is structurally identified [18] and required β- to α-anomer conformational transition, whereas the Ag(I) ion coordination is only through the carboxyl oxygen atoms and does not require such conformational transition.

X-ray Powder Patterns and Molar Conductivity

The molar conductivities of 100–120 Ω^{-1} cm^2 mol^{-1}, observed for the Ag–glucuronate compounds, are indicative of the ionic nature of these metal–sugar compounds and the presence of no direct bonding between the Ag(I) ion and the nitrate anion, in the $Ag(glucuronic)NO_3$ compound. This is consistent with the infrared results obtained for the nitrate group vibrational frequencies (see the discussion for the infrared spectra).

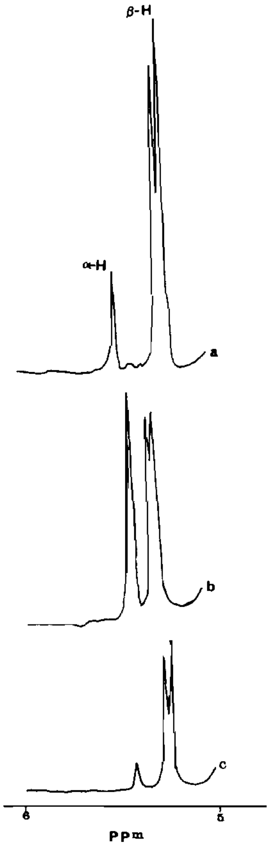


Fig. 2. ^{1}H NMR spectra of the anomeric proton (H_1) chemical shifts (D_2O) of the free D-glucuronic acid and its metal compounds for: (a) free D-glucuronic acid; (b) Ca(D-glucuronate)-Br·$3H_2O$; (c) Ag(D-glucuronic)NO_3.

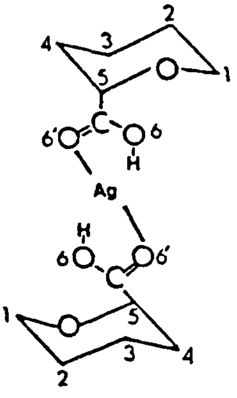
The X-ray powder diagrams of the silver–sugar compounds showed no marked similarities with those of the structurally known alkali and alkaline earth metal–glucuronate compounds [8, 9]. This is not surprising, since the high coordination numbers (6 or 8) found for these metal cations [8, 9] require different binding arrangements, with respect to the linear two coordination numbers around the silver ion.

Conclusions

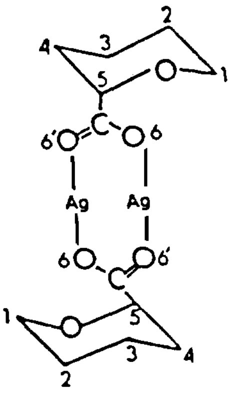
On the basis of infrared, proton-NMR and other evidence studied here, for the Ag–glucuronate compounds and comparisons made with the other structurally known metal–glucuronate complexes, the following remarks can be made:

(a) The strong hydrogen bonding network of the free acid is weakened, upon sugar metalation.

(b) The Ag(I) ion is bound to two sugar moieties via the O6′ of the non-ionized carboxyl groups, in the



Type A



Type B

Ag(D-glucuronic)NO_3 compound (Type A), whereas in the Ag(D-glucuronate) salt, the binding is through the O6 and O6′ of the ionized carboxyl group (chelation) or in a dimeric fashion, the two silver ions could join the two acid anions via O6 and O6′ of each carboxyl group (Type B), resulting into a linear two coordination geometry around each Ag(I) ion.

(c) The β-anomer conformation is predominant both in the free acid and in these silver–sugar compounds.

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