Carbohydrate–Silver Complexes. Interaction of β-D-Glucurono-γ-lactone with Ag(I) Ion and the Effect of Metal Ion Binding on Sugar Hydrolysis

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Abstract

The interaction of β-D-glucurono-γ-lactone (D-glucurone) with $AgNO_3$, $AgClO_4$, $AgCH_3COO$ and Ag_2CO_3 has been studied in aqueous solutions and solid compounds of the type Ag(D-glucurone)$NO_3 \cdot H_2O$, Ag(D-glucurone)$ClO_4 \cdot H_2O$ and Ag(D-glucuronate) have been synthesized and characterized by means of FT-IR spectroscopy, X-ray powder diffraction and molar conductivity.

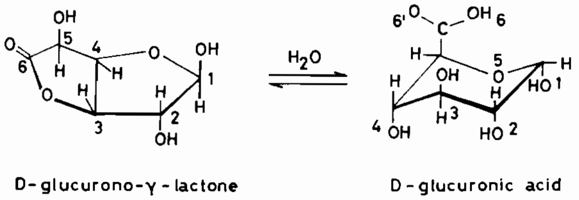
Spectroscopic and other evidence showed that in the Ag(D-glucurone)$X \cdot H_2O$ ($X = NO_3^-$ or ClO_4^-) complexes the silver(I) ion is two-coordinate, binding to a lactone carbonyl oxygen atom (O6) and to a nitrate or perchlorate oxygen atom, whereas the Ag(D-glucuronate) salt is dimeric with each Ag(I) ion bonded to two sugar anions via O6 and O6′ carboxyl oxygen atoms, resulting in a linear two-coordinate geometry around each silver ion.

Silver nitrate and silver perchlorate stabilized the lactone domination, while silver acetate or silver carbonate facilitated the sugar-to-acid conversion and the ionization of the sugar moiety in aqueous solutions.

Introduction

Interactions of Ag(I) ion with D-glucuronic acid [1] and D-glucono-δ-lactone [2] in aqueous solution and in the solid state have been reported earlier. With silver nitrate the lactone and acid coordination was preferred, while with silver acetate and silver perchlorate sugar hydrolysis and acid ionization occurred in aqueous solutions [1, 2]. Silver nitrate has carcinogenic properties [3] and therefore interactions of Ag(I) ion with nucleic acids and their constituents have been the subject of several recent studies [4–7]. Carbohydrates are part of the nucleic acids and the sugar–silver interaction is of biochemical importance.

β-D-Glucurono-γ-lactone (D-glucurone) has biological properties. It is converted to L-ascorbic acid in the human body [8] and animals [9] and has been shown to have an antihypnotic action against sodium 5,5-diethylbarbiturate [10]. Among several possible stereoisomers that can be formed for this sugar molecule, the one shown in Scheme 1 is the one found in the crystal structure of β-D-glucurono-γ-lactone [11] and it is readily hydrolysed to D-glucuronic acid in aqueous solution (Scheme 1).



Scheme 1.

Recently, we have demonstrated that the alkaline earth metal ions prefer a lactone coordination in ethanolic solution, while the hydrolysis of β-D-glucurono-γ-lactone was facilitated by the presence of these metal cations in aqueous solutions [12]. In the present work we describe the interaction of Ag(I) ion with β-D-glucurono-γ-lactone in aqueous solution and the isolation and characterization of several silver–lactone compounds, using FT-IR spectroscopy, X-ray powder diffraction and molar conductivity measurements that have not been reported so far. On the other hand, the spectroscopic properties of these silver–sugar compounds are compared with those of the structurally characterized metal–glucuronate [1] and metal–gluconate compounds [2]. This comparison allowed us to detect the characteristic features of each structural type of the compound synthesized here for the Ag(I) ion and to establish a correlation between the sugar binding sites and the spectral changes observed. Furthermore, the effect of each silver salt interaction on the free lactone hydrolysis is reported.

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Experimental

Materials and Methods

β-D-Glucurono-γ-lactone was from the Aldrich Chemical Company and used as supplied. All other chemicals were reagent grade and used without further purification.

Preparation of Silver–Lactone Adducts

Silver nitrate or silver perchlorate 0.01 mol in H_2O (20 ml) was added to a solution of β-D-glucurono-γ-lactone 0.01 mol in H_2O (20 ml). The solution was heated up to 60 °C for 10 min and then cooled down to room temperature. After a period of one week (under slow evaporation in the dark), colorless crystals were deposited. These were washed with ethanol several times and dried over $CaCl_2$. The analytical data showed the composition of $Ag(D\text{-glucurone})X \cdot H_2O$ ($X = NO_3^-$ or ClO_4^-).

Preparation of Silver–Sugar Salts

Silver acetate or silver carbonate (freshly prepared from reaction of $AgNO_3$ and Na_2CO_3 in H_2O) 1 mmol in H_2O (20 ml) was added to a hot solution of β-D-glucurono-γ-lactone 1 mmol in H_2O (20 ml). The solution was heated up to 80 °C for a period of 10 min and then was cooled down to room temperature. It was decolorized by activated charcoal, and ethanol (50 ml) was used to bring down the precipitate. The white precipitate was filtered off and washed with ethanol several times and dried over $CaCl_2$. The analytical results showed the composition of Ag(D-glucuronate). The silver–sugar compounds are very hygroscopic and light-sensitive and should be kept in a desiccator in the dark. The compounds are very soluble in water but not in other common organic solvents.

Physical Measurements

The infrared spectra were recorded on a Nicolet Fourier Transform infrared 5DXB instrument with DTGS detector. The spectra were taken as KBr pellets with a resolution of 4 to 2 cm^{-1}. X-ray powder diagrams were taken for comparative purposes, using a camera (Philips, Debye-Scherre) with copper Kα radiation and nickel filters. Conductance measurements were carried out at room temperature in aqueous solution (10^{-3} M) with a conductivity meter type CDM2e (Radiometer, Copenhagen).

Results and Discussion

FT-IR Spectra

The infrared spectra of the free β-D-glucorono-γ-lactone 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 characterized alkaline earth metal–glucuronate, $Ag(D\text{-glucuronic})NO_3$ and $Ag(D\text{-gluconolactone})NO_3 \cdot H_2O$ compounds [1, 2, 13]; the results of the spectral analyses are discussed below.

Sugar OH and CH stretching vibrations in sugars

Structural information showed that in the crystal structure of β-D-glucurono-γ-lactone [11], the free lactones are associated by a simple intermolecular hydrogen bonding network. According to the hydrogen bonding structure, the O(1)–H is a hydrogen bond donor to the O(6) carbonyl group and a hydrogen bond acceptor from the O(2)–H group. The O(2)–H group participates as a donor to O(1)–H only and the O(5)–H group is not involved in the hydrogen bonding network [11]. Therefore, based on the intermolecular O···O distances [11], the three strong, broad absorption bands observed in the IR spectrum of the free lactone are assigned to the strongly H-bonded O(1)–H (O···O = 2.730 Å) at 3297 cm^{-1}, to O(2)–H (O···O = 2.839 Å) at 3433 cm^{-1} and to an unperturbed O(5)–H stretching vibration at 3504 cm^{-1} [12].

The OH stretching vibrations of the free lactone showed no significant changes on silver interaction. The slight changes of the sugar OH stretching in the spectra of the silver compounds studied here is indicative of the non-participation of the sugar OH groups in metal–ligand bondings. It is worth mentioning that the participation of the sugar OH groups in metal–ligand bondings caused drastic intensity changes and shifting of the OH stretching vibrations towards lower frequencies in the infrared spectra of several structurally characterized metal–glucuronate [13, 14] and metal–glucurone complexes [12].

The free sugar C–H stretching vibrations appeared as several sharp absorption bands in the region of 3000–2800 cm^{-1} and exhibited no major changes on silver ion interaction.

Carbonyl stretching vibrations in sugars and silver coordination

The C=O stretching vibration of the free β-D-glucurono-γ-lactone appeared as a strong, broad absorption band at 1758 cm^{-1} (Fig. 1) and showed drastic changes (intensity and shifting) on silver interaction. The shifting of the free lactone carbonyl stretching vibration towards higher frequencies in the infrared spectra of the $Ag(D\text{-glucurone})NO_3 \cdot H_2O$ (1777 cm^{-1}) and the $Ag(D\text{-glucurone})ClO_4 \cdot H_2O$ complexes (1782 cm^{-1}) (Fig. 1 and Table I) are indicative of the silver–carbonyl interaction through the O6 oxygen atom. Similar spectral changes were observed for the sugar carbonyl group in the spectra of $Ag(D\text{-glucuronic})NO_3$ [1], $Ag(D\text{-gluconolactone})\ NO_3 \cdot H_2O$ [2] and $M(D\text{-glucurone})X_2 \cdot 4H_2O$ ($M = Mg^{2+}$ and Ca^{2+} ions and $X = Cl^-$ or Br^-) [12].

TABLE I. FT-IR Absorption Bands (cm^{-1}) for the Free β-D-glucurono-γ-lactone (D-glucurone) and its Silver Compounds in the Region of 1800–500 cm^{-1} with Possible Band assignments[a]

D-glucurone	Ag(d-glucurone)-$NO_3 \cdot H_2O$	Ag(D-glucurone)-$ClO_4 \cdot H_2O$	Ag(D-glucuronate)	Assignments [1, 2, 12, 13, 15, 16]
1758vs	1777vs	1782vs		$\nu(\mathrm{C{=}O})$
	1635mb	1630mb		$\delta(H_2O)$
			1588bs	$\nu(\mathrm{OCO}^-)_{\mathrm{antisym}}$
			1413vs	$\nu(\mathrm{OCO}^-)_{\mathrm{sym}}$
1437sh	1440m	1443m	–	$\delta(\mathrm{COH}) + \delta(\mathrm{CCH})$
1407m	1405m	–	–	$\delta(\mathrm{CCH}) + \delta(\mathrm{COH})$
	1400s		–	$\nu_3(NO_3^-)$
	1390vs	–	–	
1380m		1385m	–	$\delta(\mathrm{COH}) + \delta(\mathrm{CCH})$
1353s	1355vs	1356s	1359s	$\delta(\mathrm{COH}) + \delta(\mathrm{OCH})$
1312w	1310w	1312w	1296s	$\delta(\mathrm{CCH}) + \delta(\mathrm{COH})$
1274m	1275s	1273m	–	$\delta(\mathrm{COH}) + \delta(\mathrm{CCH})$
1252vw	1255w	1256w	1255sh	$\delta(\mathrm{CCH}) + \delta(\mathrm{OCH})$
1216w	1215m	1217w	–	$\delta(\mathrm{COH}) + \delta(\mathrm{OCH})$
1192s	1205s	1190s	1198w	$\nu(\mathrm{CO}) + \delta(\mathrm{CCO})$
1180sh	1185s	–	–	$\nu(\mathrm{CO}) + \nu(\mathrm{CC})$
1129s	1130sh	1140s	1149s	$\nu(\mathrm{CO}) + \delta(\mathrm{CCO})$
1112w	1113m	1115m	1106sh	$\nu(\mathrm{CC}) + \nu(\mathrm{CO})$
1086s	1088s	1086vs	1063s	$\nu(\mathrm{CO}) + \delta(\mathrm{CCO})$
1075w	1074w	1070m	–	$\nu(\mathrm{CO}) + \delta(\mathrm{CCC})$
1047sh	1057sh	–	1048bs	$\nu(\mathrm{CO}) + \delta(\mathrm{CCO})$
	–	1050vs	–	$\nu_1(ClO_4^-)$
1041vs	1045vs	1042sh	–	$\nu(\mathrm{CO}) + \nu(\mathrm{CC})$
1000s	1002s	1004s	990sh	$\nu(\mathrm{CO}) + \delta(\mathrm{CCH})$
945sh	960sh	952sh	946m	$\nu(\mathrm{CO}) + \delta(\mathrm{CCH})$
935m	930s	940m	910w	$\nu(\mathrm{CC}) + \nu(\mathrm{CO})$
907m	900s	910m	910w	$\nu(\mathrm{CO}) + \nu(\mathrm{CC})$
845m	835s	840m	870w	$\delta(\mathrm{CH})$
806w	805w	805sh	–	$\delta(\mathrm{CH})$
795m	794w	798w	794m	$\tau(\mathrm{CO}) + \delta(\mathrm{CCO})$
772s	778s	780s	768w	$\delta(\mathrm{CCH})$
711m	712m	710m	715w	$\delta(\mathrm{CCO}) + \delta(\mathrm{OCO})$
	700sh	700m	–	
665w	670m	668w	675m	$\delta(\mathrm{CCO}) + \delta(\mathrm{OCO})$
–	–	660w	–	$\nu_3(ClO_4^-)$
620m	640m	620m	–	
571m	575m	580m	592w	$\tau(\mathrm{CO}) + \delta(\mathrm{CCO})$
	565m	570m	547vw	
508m	510m	515m	520w	

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

The silver ion binding to the C=O group of several nucleobases has been demonstrated by spectroscopic and X-ray diffraction measurements [4–7].

On comparing the infrared spectra of the Ag–glucurone adducts with those of the Ag(D-glucuronate) salt, the carbonyl stretching vibration of the free sugar is shown to split into two components and to shift towards lower frequencies on silver salt formation (Fig. 1 and Table I). The two strong, broad absorption bands observed at about 1600 and 1400 cm^{-1} in the spectra of the Ag–glucuronate salt are related to the antisymmetric and symmetric stretching of the carboxylate OCO^- vibrations, respectively [12]. The shift of the carbonyl stretching vibration towards higher frequencies in the spectra of the Ag(D-glucurone)$NO_3 \cdot H_2O$ and the Ag(D-glucurone)$ClO_4 \cdot H_2O$ adducts is indicative of free lactone coordination to the Ag(I) ion, whereas the splitting and the shift of the carboxyl group vibration towards lower frequencies are related to the hydrolysis of the lactone and the ionization of the produced acid in the silver–sugar salt (Fig. 1 and Table I). Similar observations were made in the spectra of free D-glucono-δ-lactone [2] and β-D-

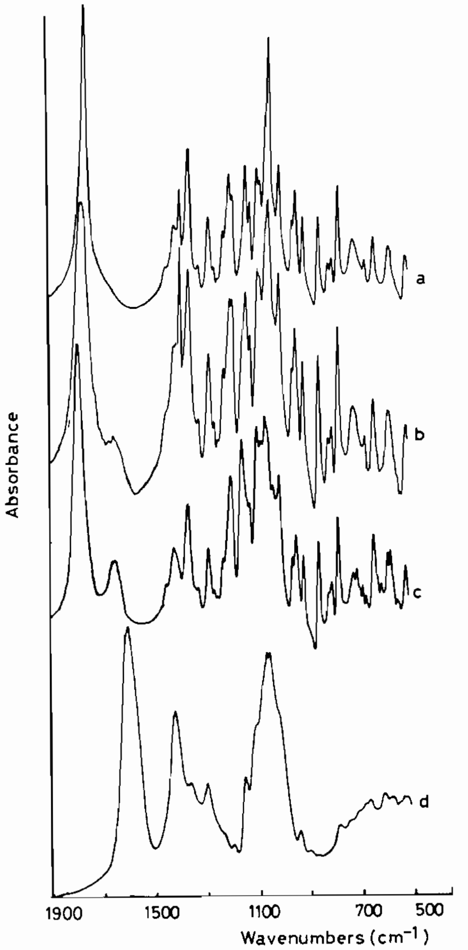


Fig. 1. FT-IR Spectra of the free β-D-glucurono-γ-lactone and its silver ion compounds in the region of 1900–500 cm^{-1} for (a) free β-D-glucurono-γ-lactone; (b) Ag(D-glucurone)-$NO_3 \cdot H_2O$; (c) Ag(D-glucurone)$ClO_4 \cdot H_2O$; and (d) Ag(D-glucuronate).

glucurono-γ-lactone [12] on interaction with silver and alkaline earth metal ions.

A broad absorption band with medium intensity at about 1635 cm^{-1} in the spectra of the Ag–glucurone adducts, which is absent in the spectrum of the free sugar, is related to the presence of hydration water molecules in these metal–sugar complexes (Fig. 1).

Several absorption bands with medium intensities in the region of 1440–1200 cm^{-1} in the free lactone spectrum, related to the strongly coupled sugar ring COH and CCH bending modes [15, 16], shifted towards higher frequencies on sugar metalation or ionization (Fig. 1 and Table I). The small shifts of the COH and CCH bendings are due to the rearrangements of the lactone hydrogen bonding network on sugar–metal complex formation. The sugar ring C–O stretching vibrations of the free lactone appeared as several strong absorption bands at 1180, 1129, 1086, 1075, 1047, 1041, 1000, 945, 935 and 907 cm^{-1} and shifted towards higher frequencies in the spectra of the silver–glucurone adducts (Fig. 1 and Table I). The shift of the C–O stretching vibrations towards higher frequencies is indicative of the non-participation of the C–O groups, in the silver–sugar bondings [2].

The lactone ring skeletal deformations C–O–C and C–C–C are observed as several absorption bands at about 800–500 cm^{-1} in the free sugar spectrum and showed some alterations on sugar complexation (Fig. 1 and Table I). Since the sugar ring vibrational frequencies are strongly coupled, metalation or ionization of the lactone moiety largely perturbs the electron distributions within the ring system, where the vibrations are mostly localized and finally causes ring distortion [1, 2].

Nitrate and perchlorate anion binding modes

The X-ray structural data and spectroscopic properties of the silver nitrate compound showed the presence of a bridging nitrate group (Ag–NO_3–Ag) [17, 18]. The strong, broad absorption band at about 1400 cm^{-1} related to the ionic NO_3^- in D_{3h} symmetry [19] appeared as two strong absorption bands at 1400 and 1385 cm^{-1} in the spectrum of the Ag(D-glucurone)$NO_3 \cdot H_2O$ adduct (Fig. 1 and Table I). The splitting of the ν_3 mode of the ionic nitrate here is related to the lowering of the nitrate group symmetry and is indicative of the participation of the nitrate anion in the metal–ligand bonding. Therefore, the possibility of the formation of a [sugar–Ag–NO_3–Ag–sugar]NO_3 complex with the presence of both ionic and bridging nitrate groups can be proposed here. Similar structural arrangements were observed for the Ag(D-gluconolactone)$NO_3 \cdot H_2O$ adduct [2]. Other nitrate anion vibrational frequencies [19] at about 1050, 840 and 750 cm^{-1} were obscured by the strong sugar vibrational frequencies. It should be noted that, although we have suggested that there is no direct interaction between the Ag(I) ion and the nitrate anion in the Ag(D-glucuronic)NO_3 adduct reported earlier [1], the possibility of a similar structure arrangement [acid–Ag–NO_3–Ag–acid]NO_3 cannot be excluded.

The perchlorate anion vibrational frequencies [20] in the region of 1200–600 cm^{-1} were overlapped by the strong lactone absorption frequencies (Fig. 1 and Table I) and this makes it difficult to draw conclusions on the nature of the silver perchlorate interaction. However, the presence of the strong absorption bands at 1050 and 660 cm^{-1} (Fig. 1), which are different from those of the free lactone and the nitrate spectra, are due to the ClO_4^- anion in low symmetry and the participation of the perchlorate group in silver–ligand bonding [20]. Thus, similar structural arrangements to that of the silver nitrate adduct [sugar–Ag–ClO$_4$–Ag–sugar] ClO$_4$ could be proposed for the Ag(D-glucurone)ClO$_4$ compound. It is interesting to note that the silver perchlorate interaction with D-gluconolactone has led to hydrolysis of the free lactone and ionization of D-gluconic acid in aqueous solutions [2], while similar interaction with D-glucurone here resulted in silver perchlorate coordination with the free lactone. The reason for this could be related to the stability of D-glucurone with respect to D-gluconolactone in aqueous solutions.

Solution Studies

The infrared spectra recorded in D_2O solution for the free lactone and its silver compounds, in the region 1900–1400 cm^{-1}, exhibited marked similarities to those of the solid compounds. The carbonyl stretching vibration of the free sugar appeared as a broad, strong band at about 1750 cm^{-1} and showed a shift towards higher frequencies in the infrared spectra of the Ag(D-glucurone)NO$_3$·H$_2$O and Ag(D-glucurone)ClO$_4$·H$_2$O adducts, whereas in the spectra of the Ag(D-glucuronate) salt, this absorption band split into two components and shifted towards lower frequencies. The shift of the carbonyl stretching band towards higher frequency in the spectra of the silver–glucurone adducts is indicative of retention of the sugar lactone form and binding of the Ag(I) ion via the sugar $C_6{=}O$ group in aqueous solution. On the other hand, the shift of the lactone carbonyl stretching vibration towards lower frequency in the presence of silver acetate or silver carbonate is related to sugar hydrolysis and ionization of D-glucuronic acid in aqueous solution.

X-ray Powder Diffraction Measurements and Molar Conductivity

The X-ray powder diagrams of the Ag(D-glucurone)NO$_3$·H$_2$O and Ag(D-glucuronate) compounds showed marked similarities with those of the corresponding Ag(D-gluconolactone)NO$_3$·H$_2$O, the Ag(D-gluconate) salt [2] and the Ag(D-glucuronic)NO$_3$ adduct [1]. This is indicative of similar coordination number and binding arrangements for the Ag(I) ion in these sugar compounds. On the other hand, the X-ray powder photographs of the silver–sugar compounds studied here exhibited no marked similarities with those of the structurally characterized Ca(D-glucuronate)Br·3H$_2$O [14] and Mn(D-gluconate)$_2$·2H$_2$O [21] compounds. The dissimilarities observed are due to the eight- or six-coordination numbers found for the Ca(II) and Mn(II) ions with respect to the linear two-coordination numbers suggested for the Ag(I) ion in these metal–sugar compounds.

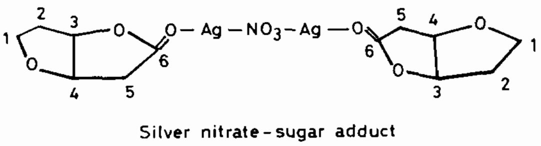
The molar conductivities observed (90–110 Ω^{-1} cm^2 mol^{-1}) in aqueous solution for these silver–sugar compounds are indicative of partial dissociation of these metal–sugar compounds in aqueous solution.

Conclusion

On the basis of the spectroscopic properties of the Ag–glucurone compounds synthesized here and the comparisons made with those of the structurally known metal–glucuronate compounds, the following points can be emphasized:

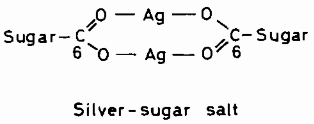
(a) Hydrolysis of β-D-glucurono-γ-lactone is facilitated in aqueous solution by the presence of silver acetate and silver carbonate, while silver nitrate and silver perchlorate cause lactone coordination.

(b) The silver ion binding in the Ag(D-glucurone)NO$_3$·H$_2$O and the Ag(D-glucurone)ClO$_4$·H$_2$O adducts is through the lactone carbonyl ($C_6{=}O$) oxygen atom and to a bridging nitrate or perchlorate group (Scheme 2).



Scheme 2.

(c) In the fully ionized Ag(D-glucuronate) salt, the silver ion binds to two sugar anions (in a dimeric fashion) via O6 of the one and O6′ of the other, resulting in two-coordination geometry around the silver ion (Scheme 3).



Scheme 3.

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