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INFRARED SPECTRA OF CRYSTALLINE L-ARABINOSE AND TWO OF ITS CALCIUM COMPLEXES

HEIDAR-ALI TAJMIR-RIAHI*
Department of Physics, Nuclear Research Center "Demokritos", Aghia Paraskevi, Attica (Greece)

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ABSTRACT

L-Arabinose reacts with hydrated calcium salts to give complexes of the type Ca(α-L-arabinose)$X_2 \cdot 4\ H_2O$, where $X = Cl^-$ or Br^-. In the known structure Ca(α-L-arabinose)$Cl_2 \cdot 4\ H_2O$, the Ca(II) ion is 8-coordinated, binding through two symmetry-related L-arabinose molecules (*via* O-3 and O-4 in the first, and O-1 and O-5 in the second), as well as to four water molecules. The eight oxygen atoms form a slightly distorted, square-antiprism geometry around the Ca(II) ion, with no direct, calcium chloride interaction. All of the sugar hydroxyl groups and water molecules, as well as the Cl^- anions, are involved in a strong, hydrogen-bonded network.

Spectroscopic and other evidence indicates that the two calcium–sugar complexes are isostructural, in terms of octacoordination and the common coordination sites involved. The strong, intermolecular, hydrogen-bonding system of the free sugar is preserved upon metalation, and the sugar moiety crystallizes as the α anomer in these calcium–sugar complexes.

INTRODUCTION

Although the vibrational spectra of carbohydrates have been reported in detail[1-3], characterization of the metal–sugar complexes has been limited to X-ray[4] and n.m.r. spectroscopy[5-8]. Recently, a correlation between the spectral changes and the coordination sites used by the sugar moiety in a series of metal–sugar complexes has been demonstrated[9]. Evidence for this came through comparison of the infrared spectra of the structurally known[10] Ca(D-glucuronate)$Br \cdot 2\ H_2O$ with those of the corresponding free acid and other Ca glucuronate complexes.

In the present work, having at our disposal the structurally known[11] Ca(α-L-arabinose)$Cl_2 \cdot 4\ H_2O$ compound, we decided to examine the F.t.-i.r. spectrum of this compound, in order to ascertain characteristic features of each of the structural types of complex of the Ca(II) ion examined here, and to establish a correlation be-

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*Present address: Departement de Chimie, Université de Montréal, Case postale 6210, Succ. A, Montreal, Que., H3C 3V1, Canada.

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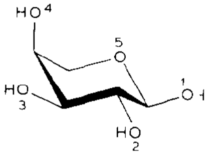
tween the spectral changes and the coordination sites used by the α-L-arabinose molecule (**1**), which had not previously been reported.

It should be noted that this discussion is largely based on the assignments and the normal coordinate analyses conducted by Hineno[1] and Vasko *et al.*[2], and that it is in good agreement with their observations.



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EXPERIMENTAL

All of the chemicals were reagent grade and were used as supplied. L-arabinose was obtained from BDH, and was recrystallized from water by slow evaporation.

Preparation of the complexes. — Calcium–sugar complexes were prepared by addition of a solution of L-arabinose (1 mmol) in water (20 mL) to a solution of the hydrated calcium halide (1 mmol) in water (20 mL). The solution was decolorized by means of activated charcoal, and then 95% ethanol was added, to afford colorless crystals[11]. These were filtered off, washed several times with cold alcohol, dried, and analyzed. The compounds have the composition Ca(α-L-arabinose)$X_2 \cdot 4\ H_2O$, $X = Cl^-$ and Br^-, are hygroscopic, and are very soluble in water and in hot alcohol.

Physical measurements. — The F.t.-i.r. spectra were recorded for KBr pellets with a Digi-Lab FTS 15/C Fourier-transform, Michelson infrared interferometer equipped with a high-sensitivity, HgCdTe detector and a KBr beam splitter having spectral resolution of 4 cm^{-1}. X-Ray powder photographs were taken for comparative purposes, using a powder camera (Philips, Debye–Scherrer) with CuKα radiation and nickel filters.

Conductance measurements were performed at room temperature, for mM solutions in H_2O, with a conductivity meter, type CDM2c (Radiometer, Copenhagen).

RESULTS AND DISCUSSION

Structural analysis had shown[11] that, in the Ca(α-L-arabinose)$Cl_2 \cdot 4\ H_2O$ compound, the Ca(II) ion binds to two molecules of α-L-arabinose through O-1 and O-5 in one molecule and through O-3 and O-4 in the other, as well as to four water molecules. All of the sugar OH groups and all of the water molecules, as well as the Cl^- ions, are involved in a strong, inter- and intra-molecular, hydrogen-bonding network[11].

In the present work, the X-ray powder pattern of the chloride complex shows features isomorphic with those of the corresponding calcium bromide complex. The molar conductivity (180–200 $\Omega^{-1}.cm^2.mol^{-1}$) obtained exhibits 2:1 electrolytes for these two complexes. The F.t.-i.r. spectra of these sugar complexes and of the free L-arabinose molecule have been recorded in the region 4000–400 cm^{-1}, and the results in two different regions, (*a*) 3600–2700 cm^{-1} and (*b*) 1800–400 cm^{-1}, are discussed.

(a) 3600–2700 cm^{-1}. — In this region, the free L-arabinose shows four groups of absorption bands centered at ~3530, 3350, 3200, and 2950 cm^{-1}. The first three (strong and broad) absorption bands are assigned to the hydrogen-bonded OH groups[1,2,12] of the free sugar molecule; these shift to lower frequencies in the spectra of the metal complexes (see Fig. 1). The shift of the OH-stretching vibrations towards lower frequencies indicates retention of the strong, hydrogen-bonding network of the free sugar on metalation. The crystal structure of free β-L-

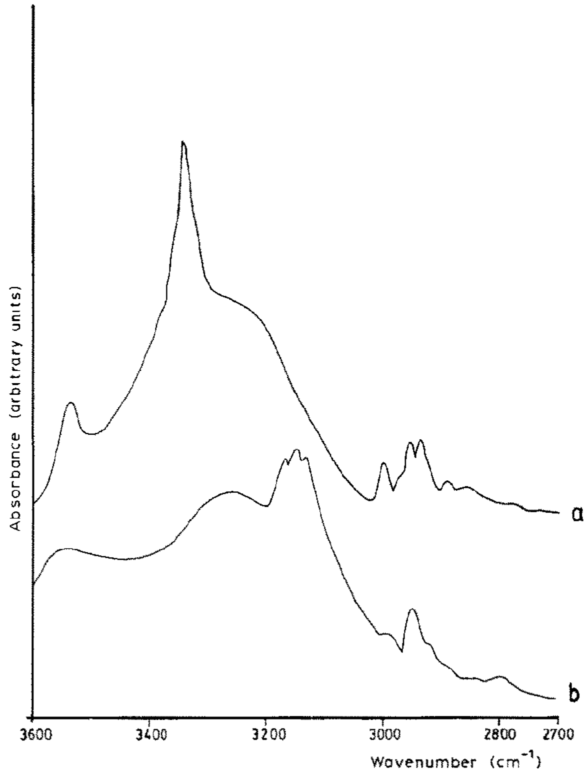

Fig. 1. F.t.-i.r. spectra of L-arabinose and a calcium complex thereof in the region 3600–2700 cm^{-1}. [a, L-Arabinose, and b, Ca(α-L-arabinose)$Cl_2 \cdot 4 H_2O$. These spectra, and those in Fig. 2, have been reduced by 65%.]

TABLE I

F.T.-I.R. ABSORPTION BANDS[a] (cm^{-1}) OF CRYSTALLINE α-L-ARABINOSE AND RELATED METAL COMPLEXES

α-L-Arabinose	*Ca(arabinose)Cl_2 · 4 H_2O*	*Ca(arabinose)Br_2 · 4 H_2O*	*Possible assignments*
3539 s	3528 s	3529 s	νOH[1,2,12]
3348 s	3270 b	3290 b	
	3163 sh	3160 sh	
3250 b	3147 bs	3150 s	
	3134 sh	3120 sh	
2997 w	2980 w	2980 w	νCH_2[1,2]
2954 w	2950 w	2955 w	
2940 w	2942 w	2943 w	νCH[1,2]
2890 w	2880 w	2885 w	
2850 vw	2840 w	2845 w	
—	1631 s	1629 s	$\delta(H_2O)$[15]
1473 m	1460 w	1459 w	δ(OCH) + δ(CCH)[1] + δ(CH)[2]
1425 w	1430 w	1425 m	δ(OCH) + δ(CCH)[1,2]
1402 vw	1400 vw	1405 vw	δ(OCH) + δ(COH) + δ(CCH)[1,2]
1371 s	1384 w	1383 m	δ(OCH) + δ(CCH) + δCH_2[1,2]
1354 m	1352 s	1345 s	δ(CCH) + δ(COH)[1]
1317 s	1315 sh	1320 w	δ(CCH) + δ(COH) + δ(OCH)[1]
1257 m	1286 m	1285 m	δ(CCH) + δ(COH)[1]
	1254 s	1252 m	
1232 m	1231 s	1220 s	δ(COH) + δ(CCH)[1]
1134 vs	1160 sh	1155 sh	ν(CO) + ν(CC) + δ(CCO)[1]
	1137 s	1134 s	
1100 sh	—	—	ν(CO) + ν(CC)[1]
1092 s	1096 m	1099 s	
1069 sh	1074 s	—	ν(CC) + ν(CO)[1]
1053 vs	1063 vs	1066 vs	ν(CO)[1]
1001 vs	1013 vs	1026 vs	ν(CO) + δ(CCO) +δ(CC)[1]
—	—	1010 vs	
943 m	940 w	947 w	ν(CO) + δ(CCH)[1]
893 s	900 m	891 m	ν(CC) + δ(CCH) + δ(CO)[1]
842 s	844 m	845 m	δ(CH)[2] + α anomer[3]
785 vs	800 s	796 vs	τ(CO) +δ(CCO) + δ(CCH)[1] + ring-breathing mode[3]
713 m	700 m	705 m	δ(CCO) + δ(OCO) + τ(CO)[1]
677 s	670 m	670 w	δ(CCO) + τ(CO)[1]
627 w	620 m	620 m	τ(CO)[1]
602 m	601 m	602 m	
590 m	590 m	566 w	τ(CO) + δ(CCO)[2]
520 vw	525 w	556 w	τ(CO) + δ(CCO)[1]
501 m	—	520 m	
428 vw	460 m	460 m	δ(CCO) + δ(CCC)[1]
400 vw	400 m	400 w	δ(CCO) + δ(CCC)[1]

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

arabinose shows[13] the presence of strong, intermolecular hydrogen-bonding through the hydrogen and the oxygen atoms of the hydroxyl groups of the sugar molecules, whereas, in the crystal structure of Ca(α-L-arabinose)$Cl_2 \cdot 4\ H_2O$, strong inter- and intra-molecular hydrogen-bonding exists between all of the OH groups and H_2O molecules, as well as the Cl^- anions[11]. The rearrangement of the hydrogen-bonding system of the free sugar in the crystal structure of the calcium complexes causes the lowering of the OH-stretching frequencies[14]. Other weak absorption bands at 2900 cm^{-1}, mainly related to the C–H stretching vibrations[1,2] of the free sugar, appear in almost the same position in the spectra of the metal complexes (see Fig. 1). The main features of the spectra relevant to this region, together with possible assignments, are given in Fig. 1 and Table I.

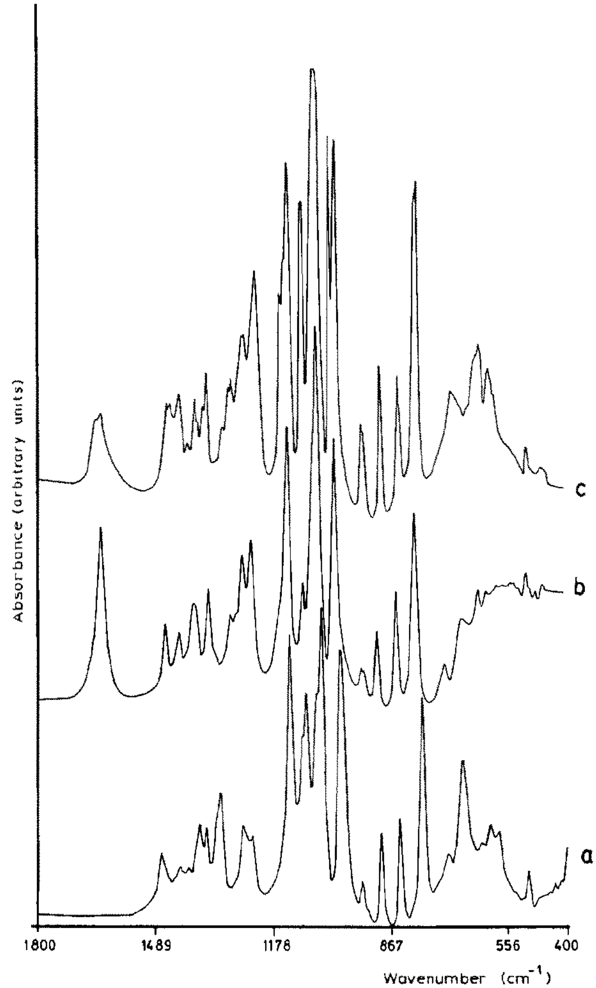

Fig. 2. F.t.-i.r. spectra of L-arabinose and two calcium complexes thereof in the region 1800–400 cm^{-1}. [a, L-Arabinose; b, Ca(α-L-arabinose)$Cl_2 \cdot 4\ H_2O$; and c, Ca(α-L-arabinose)$Br_2 \cdot 4\ H_2O$.]

(b) 1800–400 cm^{-1}. — A strong absorption band at 1633 cm^{-1} in the spectra of the calcium complexes that is absent from the spectrum of the free arabinose is assigned to the bending motion of the coordinated water molecules[15] (see Fig. 2). It should be noted that the OH stretching of the bonded water molecules at 3400 cm^{-1} in the spectra of the metal complexes is overlapped by the strong hydrogen-bonding system of the sugar moiety (see Fig. 1).

Sugar-ring vibrational frequencies and CO and OH bonding modes. — In this region, drastic spectral changes occurred upon sugar metalation. The atomic motions of the sugar ring are strongly coupled, and the vibrations are spread over the entire molecule, so that it is difficult to make an individual assignment for each absorption band. Metalation of the sugar moiety also modifies the electron distribution within the ring system, and causes further difficulties as regards the vibrational problem; however, the most common and meaningful spectral changes observed are summarized.

Seven absorption bands having medium intensities, at ~1473, 1425, 1371, 1354, 1317, 1257. and 1232 cm^{-1}, in the spectrum of the free L-arabinose, assignable mainly to the C–OH and C–CH bending vibrations[1], showed considerable changes (shifting and splitting) in the spectra of the calcium–arabinose complexes (see Fig. 2 and Table I). The changes observed for the C–OH bending frequencies, together with the shift of the OH-stretching vibrations to lower frequencies, are indicative of the participation of the sugar hydroxyl groups in metal–ligand bondings[15]. Other absorption bands, at ~1134, 1092, 1053, 1001, and 943 cm^{-1}, in the spectrum of the free carbohydrate that are related to the C–O and C–C stretching frequencies[1,2] exhibited shifting and splitting in the spectra of the metal complexes (see Table I). Such splitting and shifting of the C–O stretching vibrations towards higher frequencies is due to involvement of the sugar C–O groups in the Ca–sugar bonding[15].

It may be noted that the skeletal vibrations C–C–C and C–O–C of the sugar ring in the range 1200–700 cm^{-1}, together with the deformation modes of these absorption frequencies at 700–400 cm^{-1}, in the spectrum of the free ligand showed considerable changes upon metalation (see Table I). These observed spectral changes are mainly due to rearrangement of the strong hydrogen-bonding system of the sugar, and to participation of the sugar oxygen-atoms in the metal–ligand bonding on complex formation. A sharp absorption band at 785 cm^{-1} in the spectrum of free L-arabinose, attributed to the sugar-ring breathing-mode[3], was shifted to a higher frequency ($\Delta\nu$ 10-15 cm^{-1}) in the spectra of the calcium–sugar complexes (see Fig. 2 and Table I). The shift of this absorption band to a higher frequency is also related to the metalation of the sugar moiety, which causes a large pertubation of the ring system, where the vibrations are mostly localized, and finally causes distortion of the ring system.

It has been suggested[6] that calcium ions have different affinities for β and α anomers of certain sugars in aqueous solution. It has also been found[10] that the D-glucuronate anion crystallizes as the α anomer in the crystal structure of Ca(D-glucuronate)Cl · 3 H_2O, whereas the β anomer preponderates in solution and in the crystal structures of K^+ and Rb^+ glucuronates[16]. Therefore, it is possible that the interaction with calcium affects the favored anomeric form of L-arabinose[11]. In a previous report[9], the β and α anomers of the calcium–glucuronate complexes were separated on the basis of infrared spectroscopy. All of the calcium–glucuronate complexes showed a sharp absorption band at 830 cm^{-1}, related to the α anomer[3] of the sugar molecule (absent from the spectrum of the free acid) which was consistent with the structural analysis reported earlier[10].

In the present work, it was found difficult to distinguish between the β and α anomers of L-arabinose in the solid-state complexes examined here, because the two sharp absorption bands at 893 and 842 cm^{-1}, assignable to the β and α anomer, respectively[3], are present both in the spectrum of free L-arabinose and in those of its calcium complexes (see Fig. 2). Because the solution (H_2O) spectra of the free L-arabinose showed no sharp absorption band at 842 cm^{-1}, it may be concluded that the L-arabinose molecule exists as the β anomer in aqueous solution, whereas the α anomer preponderates in the crystal structures[11] of these calcium–sugar complexes.

The Ca–oxygen stretching vibration[17] of the sugar moiety would occur at a lower frequency (400–200 cm^{-1}) than those studied here.

CONCLUSIONS

Raman and infrared techniques have been widely used in order to characterize the sugar vibrational frequencies, but any reliable correlation between structural properties and spectral information for carbohydrates was still missing. Metalation of the sugar moieties can provide a useful probe in developing our understanding of the vibrational spectroscopy of the carbohydrates.

Using the spectroscopic and structural properties of L-arabinose and its calcium complexes studied here, the following conclusions may be drawn. (*a*) The strong, hydrogen-bonding network of the free sugar is preserved upon metalation; (*b*) the sugar OH and C–O groups, as well as the water molecules, participate in metal–sugar bondings; (*c*) the sugar molecule crystallizes as the α anomer in these calcium complexes; and (*d*) the two Ca–arabinose complexes are isomorphous, in terms of octa-coordination and the common binding-sites involved.

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