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INTERACTION OF D-GLUCOSE WITH ALKALINE-EARTH METAL IONS. SYNTHESIS, SPECTROSCOPIC, AND STRUCTURAL CHARACTERIZATION OF Mg(II)– AND Ca(II)–D-GLUCOSE ADDUCTS AND THE EFFECT OF METAL-ION BINDING ON ANOMERIC CONFIGURATION OF THE SUGAR

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ABSTRACT

The interaction of D-glucose with the hydrated alkaline-earth metal halides has been studied in solution, and adducts of the type Mg(D-glucose)$X_2 \cdot 4$ H_2O, Ca(D-glucose)$X_2 \cdot 4$ H_2O, and Ca(D-glucose)$_2X_2 \cdot 4$ H_2O, where $X = Cl^-$ and Br^-, have been isolated, and characterized by means of F.t.-i.r. and ^{1}H-n.m.r. spectroscopy, X-ray powder diffraction, and molar conductivity measurements. Spectroscopic and other evidence suggested that the Mg(II) ion in the Mg(D-glucose)$X_2 \cdot 4$ H_2O adducts six-coordinate, binding to a D-glucose molecule (possibly *via* O-1 and O-2 atoms) and to four H_2O molecules, whereas, in the corresponding 1:1 Ca–D-glucose adduct, the Ca(II) ion is possibly seven-coordinate, binding to a sugar moiety (through the O-1, O-2, and other sugar donor atoms) and to four H_2O molecules. In 1:2 Ca(D-glucose)$_2X_2 \cdot 4$ H_2O, the calcium ion may be eight-coordinate, binding to two D-glucose molecules (possibly *via* the O-1 and O-2 atoms of each sugar moiety) and to four H_2O molecules. The strong, sugar H-bonding network is rearranged upon D-glucose adduct-formation, and the α-anomeric configuration is favored by these metal cation coordinations.

INTRODUCTION

Recent findings by Templeton and Sarkar[1] on the formation of metal–carbohydrate complexes in human kidney demonstrate the biological importance of metal–sugar complexes. The Ni(II) ion was found[1] to form complexes with several sugar moieties, including D-glucose and D-glucosamine derivatives. Calcium ions and sugars appear to participate in a variety of biological adhesion and agglutination processes, including those occurring at the cell surfaces[2]. The stabilizing effects of the alkaline-earth metal ions on the double helix structure of DNA are well known[3]. The interaction of magnesium and calcium ions with the sugar residue of nucleic acids and their components has been demonstrated through X-ray diffraction and spectroscopic measurements, and the effect of binding of these metal

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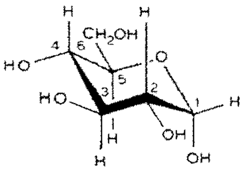
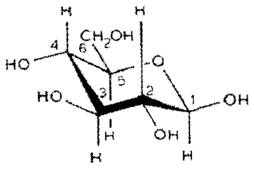
cations on the sugar conformational transitions have been studied[4–6]. The interaction of the calcium ion with D-glucose has been studied by ^{1}H-n.m.r. spectroscopy[7], and the effects of interaction of alkali, alkaline-earth, and other metal cations on the anomeric configurations of this sugar have been reported[8]. The synthesis and characterization of several metal–sugar complexes of the alkali, alkaline-earth, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}, UO_2^{2+}, $[Co(NH_3)_4Cl_2]^+$, $[Co(NH_3)_5Cl]^{2+}$, *cis*-$Pt(NH_3)_2Cl_2$ (antitumor), and *trans*-$Pt(NH_3)_2Cl_2$ containing the D-glucuronate anion[9], the D-gluconate anion[10], L-arabinose[11], D-fructose[12], D-glucurono-1,4-lactone[13], D-glucurono-1,5-lactone[14], vitamin C[15], and sucrose[16] have been reported.

The aim of the present work was the synthesis and characterization of several Mg(II) and Ca(II) adducts containing a D-glucose molecule, in both the solid and in solution, by using F.t.-i.r. and ^{1}H-n.m.r. spectroscopy, X-ray powder diffraction, and molar conductivity measurements that have not previously been reported. Comparisons have been made between the i.r. spectra of the alkaline-earth metal–D-glucose adducts and free α- and β-D-glucose and their equilibrated solution and the effects of binding of these metal ions on the sugar anomeric configurations. Furthermore, assignments of the sugar OH-stretching frequencies have been made, based on neutron diffraction measurements, hydrogen-bonding energies, and the geometrical parameters reported in the literature[17–21]. The chemical structure of D-glucopyranose, with the numbering of the atoms, is shown.



α-D-glucopyranose



β-D-glucopyranose

EXPERIMENTAL

Materials and methods. — Anhydrous D-glucose was purchased from Aldrich Chemical Company, and recrystallized from water–methanol. The α- and β-D-glucose were from Kodak, and were used as supplied. D_2O (99.8%) and Me_2SO-d_6 (99.8%) were obtained Cambridge Isotope Laboratories. Other chemical compounds were reagent grade and were used as supplied.

Synthesis of calcium halide–D-glucose adducts. — Calcium halide (1 mmol) in H_2O (10 mL) was added to a hot solution of D-glucose (1 mmol) in H_2O (20 mL), and the mixture were heated for 30 min at 80°. The solution was then kept for 48 h at room temperature, and 7:3 acetone–ethanol was added to precipitate the compound. This was filtered off, washed several times with acetone, and dried ($CaCl_2$). In another experiment, a solution of D-glucose (2 mmol) in H_2O (20 mL) was mixed with a solution of the calcium halide (1 mmol) in H_2O (10 mL), and the mixtures were heated for 40 min at 80°, cooled to room temperature, and 7:3 acetone–ethanol added to afford a precipitate; this was filtered off, washed several times with acetone, and dried ($CaCl_2$). The analytical data showed the composition of $Ca(\text{D-glucose})Cl_2 \cdot 4\ H_2O$ and $Ca(\text{D-glucose})_2X_2 \cdot 4\ H_2O$, where $X = Cl^-$ or Br^-. Several attempts made to prepare the 1:1 Ca–Br–D-glucose adduct were unsuccessful. The calcium–sugar compounds are very soluble in water and in hot alcohol, but insoluble in any other common organic solvents, and were recrystallized from water–ethanol.

*Synthesis of magnesium halide–*D*-glucose adducts.* — A solution of D-glucose (1 mmol) in methanol (30 mL) was added to a hot solution of the magnesium halide (1 mmol) in methanol (20 mL), and the mixtures were heated to boiling until all of the D-glucose had dissolved. This solution was cooled to room temperature and 3:7 acetone–ether was added to precipitate the adduct; this was washed several times with ether, and dried ($CaCl_2$). The analytical results showed the composition of $Mg(\text{D-glucose})X_2 \cdot 4\ H_2O$, where $X = Cl^-$ or Br^-. The Mg–D-glucose adducts are very hygroscopic, and should be kept in a desiccator over $CaCl_2$. The compounds are very soluble in water, alcohol, and hot acetone, but insoluble in other common organic solvents, and were recrystallized from water–methanol.

Physical measurements. — The F.t.-i.r. spectra were recorded with a Digilab FTS 15/C and Nicolet 5XDB Fourier-transform infrared interferometer, equipped with a high-sensitivity HgCdTe or DTGS detector and a KBr beam-splitter. The spectra were recorder with a spectral resolution of 2 to 4 cm^{-1} for KCl pellets. The film of D-glucose solution was prepared by spreading an aqueous solution of the sugar (10%) on a AgCl plate, followed by evaporation and respreading as needed, to obtain a uniform thickness. ^{1}H-N.m.r. spectra were recorded with a Bruker WH 90-MHz instrument, with D_2O or Me_2SO-d_6 solutions containing sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) or Me_4Si as reference. Molar conductance measurements were carried out at room temperature in H_2O solution (mM) with a conductivity meter of the CDM2e type (Radiometer, Copenhagen). The X-ray powder diagrams were taken for comparative purposes, using a powder camera (Philips, Debye-Scherre) with CuKα radiation.

RESULTS AND DISCUSSION

F.t.-i.r. spectra. — The infrared spectra of free D-glucose and its alkaline-earth metal halide adducts were recorded in the region of 4000–500 cm^{-1}, and the results of the spectral analysis are described.

D*-Glucose OH stretching vibrations and metal ion coordination.* — The assignment of the D-glucose OH stretching frequencies presented here is based on the intermolecular O···O distances, the H-bonding energies, and the geometrical parameters reported in the literature[17–21]. In the crystal structure of α-D-glucopyranose, there are five intermolecular H-bondings[18], two of which are relatively

TABLE I

F.T.-I.R. ABSORPTION BANDS[a] (CM^{-1}) FOR D-GLUCOSE AND ITS ALKALINE-EARTH METAL IONS ADDUCTS IN THE REGION OF 3600–500 CM^{-1}, WITH POSSIBLE ASSIGNMENTS[a]

α-D-Glucose	*Ca(D-glucose)Cl_2· 4 H_2O*	*Ca(D-glucose)$_2Cl_2$· 4 H_2O*	*Ca(D-glucose)$_2Br_2$· 4 H_2O*	*Mg(D-glucose)Cl_2· 4 H_2O*	*Mg(D-glucose)Br_2· 4 H_2O*	*Assignments*[17–25]
3404 s	3389 s	3419 s	3414 s	3380 s	3390 s	ν O(3)H···O(2)
3342 vs	3337 vs	3335 vs	3338 vs	3337 vs	3340 vs	ν O(6)H···O(3)
3310 bs	3309 m	3300 m	3300 vs	3300 s	3305 vs	ν O(4)H···O(4)
3266 bs	3235 s	3245 s	3240 s	3250 vs	3255 s	ν O(2)H···O(6)
3234 s	3216 vs	3220 vs	3224 s	3220 mb	3225 bs	ν O(1)H···O(5)
3203 sh	3200 b	3200 b	3200 b	3200 b	3210 b	$\nu\, H_2O$
2965 w	2966 w	2968 w	2965 w	2960 w	2960 w	ν C4-H
2943 m	2940 m	2940 m	2939 m	2940 w	2940 m	ν C6-H + ν C1-H
2900 m	2905 w					ν C3-H
2890 sh	2895 w	2890 sh	2895 vw	2880 m	2890 m	ν C2-H
2860 vw						ν C5-H + ν C3-H
2760 w						overtone
	1645 mb	1640 mb	1644 mb	1640 vs	1645 vs	$\delta\, H_2O$
1460 m	1470 m					δ(OCH) + $\delta(CH_2)$ + δ(CCH)
1445 m	1442 m	1450 m	1445 sh	1445 m	1440 m	δ(OCH) + δ(CCH)
1409 m	1420 m	1410 s	1420 mb	1422 m	1420 m	δ(CCH) + δ(OCH) + $\delta(CH_2)$
	1403 m					δ(OCH) + δ(CCH)
1382 m	1362 s		1375 m			
				1372 m	1375 m	δ(CCH) + δ(OCH) + δ(COH)
1340 m	1345 sh	1344 mb	1335 vw			
1297 w	1313 s		1280 vw			δ(OCH) + δ(CCH)
1282 m				1289 w	1290 vw	δ(CCH) + δ(OCH)
1275 sh	1283 m	1244 mb	1248 m			
				1253 m	1250 m	δ(COH) + δ(CCH) + δ(CC)
1250 vw	1243 m	1241 m	1233 m			
				1233 m	1230 w	δ(CCH) + δ(OCH) + δ(COH)
1225 m	1230 sh		1210 sh	1216 m	1215 m	δ(OCH) + δ(COH) + δ(CCH)
1204 m	1193 s	1180 m	1150 sh			ν(CO) + ν(CC) + δ(COH)
	1172 s					ν(CO) + ν(CC)

1149 s	1148 m	1143 s		1147 s	1145 vs	ν(CO) + ν(CC) + δ(COH)
1112 s	1124 m	1100 sh	1106 s	1137 sh	1140 m	ν(CO) + ν(CC) + δ(CCC)
1100 sh	1105 s	1080 s	1074 s	1116 s	1115 vs	ν(CO) + ν(CC) + δ(CCO)
1078 m	1074 s		1074 s	1075 s	1070 vs	ν(CO) + ν(CC)
1051 vs	1048 s		1046 vs	1045 vs	1045 vs	ν(CO) + ν(CC) + δ(CCO)
1025 s			1020 vs	1020 vs	1018 s	ν(CO) + ν(CC) + δ(CCO)
1014 s 995 s	984 vs	976 m	980 sh	982 sh	980 m	ν (CO) + ν (CC) + δ (COC)
915 m	914 m	920 m	920 m	914 m	916 m	δ(CH) + ν(CC) + δ(CCH)
						ν(CO) + ν(CC) + δ(CCH)
838 m	839 m	842 m	842 m	840 m	840 m	δ(CH) + ν(CC) + δ(CCH)
776 m	770 w	779 s	770 m	770 m	770 m	δ(CH) + ν(CC) + δ(CCH)
731 s	735 m			738 sh	735 w	δ(CCO) + δ(CCH)
701 w	703 m	702 m	706 w	705 m	706 m	τ(CO) + δ(CCH)
670 sh	665 sh		660 m	672 sh	670 w	δ(CCO) + δ(OCO) + τ(CO)
648 m	628 s	629 mb	638 m	626 bs	625 vs	δ(CCO) + δ(CCH)
621 mb	615 sh		606 s	603 sh	600 w	τ(CO) + δ(CCO)
585 m	589 w	596 m	590 s	568 m	565 m	τ(CO) + δ(CCO)
561 w	570 w	551 w				δ(CCC) + δ(CCO)
555 w	535 m	520 m	525 m			τ(CO) + δ(CCC)
				525 m	520 m	
545 m						
536 m						

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

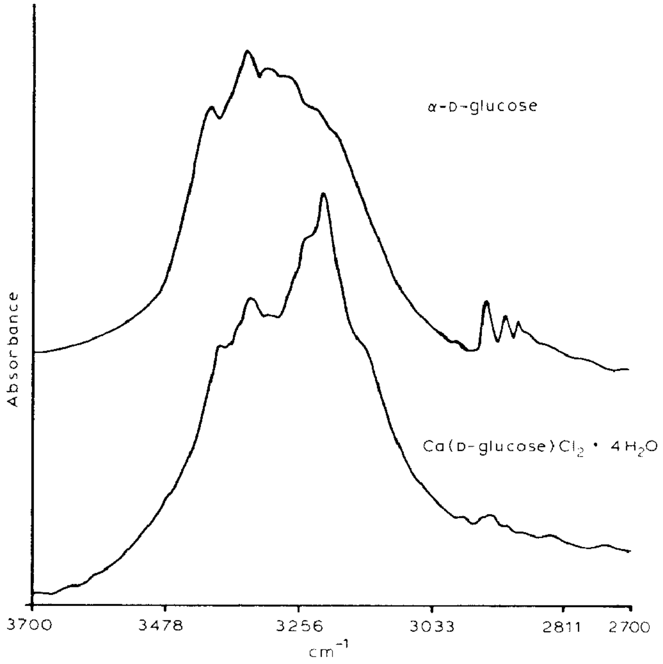


Fig. 1. F.t.-i.r. spectra of D-glucose and its alkaline-earth metal ions in the region of 3700–2700 cm^{-1}.

strong hydrogen-bonds, such as OH-3···O-2 and OH-6···O-3, two slightly weaker, namely, OH-4···O-4 and OH-2···O-6, and one of moderate energy, OH-1···O-5. The energies of these hydrogen bonds range[18] from 9.4 kJ.mol^{-1} for OH-1···O-5 to 14.6 kJ.mol^{-1} for OH-3···O-2.

The five infrared absorption bands observed in the region of 3500–3200 cm^{-1} in the spectrum of free α-D-glucose were assigned as follows. The two strong absorption bands at ~3404 and 3342 cm^{-1} were respectively assigned to OH-3···O-2 and OH-6···O-3, and the two broad, strong bands at ~310 and 3266 cm^{-1} are related to OH-4···O-4 and OH-2···O-6, respectively, and a band at 3234 cm^{-1} to OH-1···O-5 group-stretching frequency (see Table I). The present assignments are in good agreement with the observations[21] made by Mathlouthi and co-workers.

The free α-D-glucose OH stretching vibrations showed considerable changes on metal-adduct formation. In the spectra of the 1:1 metal–D-glucose complexes, the absorption bands related to OH-2 at 3342, and OH-1 at 3234 cm^{-1} showed major intensity changes and shifted towards lower frequencies (see Table I and Fig. 1). On the other hand, in the spectra of the 1:2 metal–D-glucose adducts, the OH-3-H stretching vibration at 3404 cm^{-1} shifted towards higher frequency, whereas the other sugar OH stretching vibrations shifted towards lower frequencies (see Fig. 1 and Table I). The shifts of the D-glucose OH-1 and OH-2 stretching vibrations towards lower frequencies in the spectra of the 1:1 metal–sugar adducts are indicative of the Mg(II) and Ca(II) binding *via* the 1- and 2-hydroxyl groups of the sugar. The shifts of the OH-3 stretching vibration towards higher frequency in the spectra of the 1:2 metal–D-glucose adducts is due to rearrangements of the sugar hydrogen-bonding system and not to participation of the sugar OH-3 in metal–ligand bonding. The participation of the sugar OH-1 in metal–D-glucose binding is supported by the major downfield shifts of the anomeric OH groups in Me_2SO solution on sugar-adduct formation; the ^{1}H-n.m.r. spectra will be discussed later. It is worth noting that the minor spectral changes observed for the other D-glucose OH stretching vibrations may be related to rearrangements of the sugar H-bonding system on complex formation.

D-*Glucose C–H stretching vibrations.* — Recently, the C–H stretching vibrations of solid α- and β-D-glucose have been assigned by Longhi *et al.*[22] by

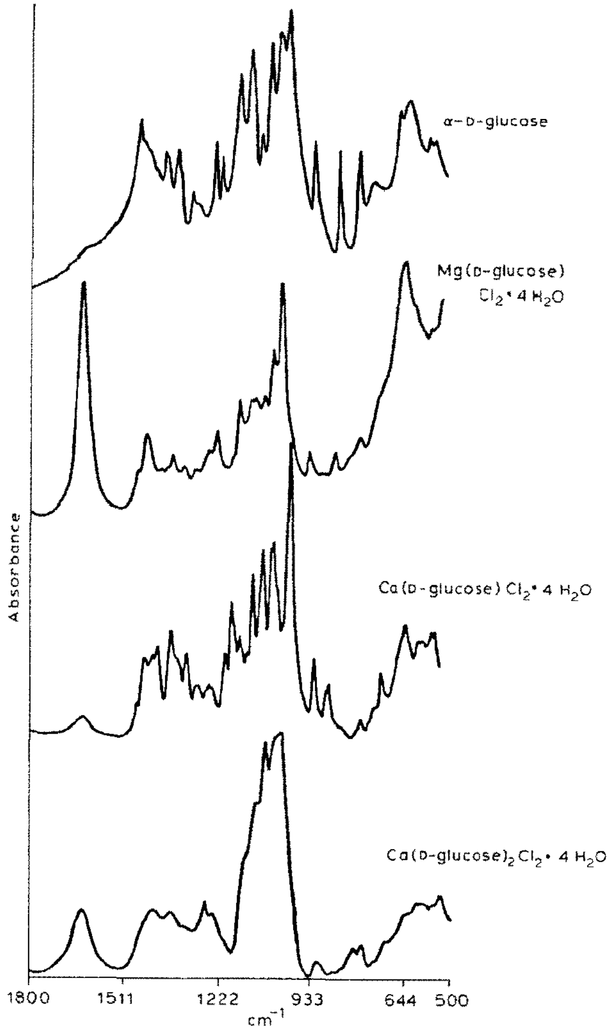


Fig. 2. F.t.-i.r. spectra of D-glucose and its alkaline-earth metal ions in the region of 1800–500 cm^{-1}.

using isotopic substitutions. The α- and β-D-glucose have different C–H stretching features[22]. The five i.r. absorption bands observed in the spectrum of α-D-glucose and studied here are assigned to the C-4–H (2965), C-6–H (2943), C-3–H (2900), C-2–H (2850), and C-5–H (2825 cm^{-1}) stretching vibrations (see Fig. 1 and Table I). Our observations are in good agreement with those that Longhi *et al.*[22] made for α-D-glucose. The C–H stretching vibrations of α-D-glucose exhibited no major changes on sugar adduct-formation (see Fig. 1).

H_2O binding. — The presence of a broad absorption band at ~3200 cm^{-1} (related to the water OH stetching vibration) and a medium band at ~1640 cm^{-1} (due to the water bending mode), which are absent from the spectrum of the free sugar, are assigned to the bonded H_2O molecules (see Fig. 2 and Table I).

D-*Glucose ring vibrational frequencies.* — The strongly coupled COH, CH_2, and CCH bending modes of free D-glucose[23–25] appeared as several absorption bands, having medium intensities, in the region of 1460–1200 cm^{-1}, exhibited major intensity changes, and shifted towards higher frequencies (see Fig. 2 and Table I). The shifts of the sugar OH bending modes towards higher frequencies, together with the shifts of the sugar OH stretching vibrations towards lower frequencies (see Fig. 1), are consistent with the participation of the sugar OH groups in metal–ligand bonding[9,11].

The D-glucose C–O stretching vibrations[23–25] were observed as several absorption bands, at 1149, 1112, 1100, 1078, 1051, 1025, and 997 cm^{-1}, and showed alterations upon sugar-adduct formation (see Fig. 2 and Table I). The spectral changes observed for the sugar ring C–O stretching vibrations are related to metal–hydroxyl group coordination and the rearrangements of the sugar H-bonding network, on metal complexation[9,11].

The free sugar skeletal deformation modes of C–O–C–O and C–C–C groups[23–25] appeared as several absorption bands in the region of 1000–500 cm^{-1} and showed some changes on sugar-adduct formation (see Fig. 2 and Table I). Because the sugar ring vibrational frequencies are strongly coupled, metal ion binding could change the electron distribution within the ring system (where the vibrations are mostly localized), resulting in ring distortion which finally causes alterations of the ring vibrational frequencies[9,11].

*A comparison between sugar anomeric forms and the alkaline-earth metal–*D-*glucose adducts.* — The i.r. spectra of α- and β-D-glucose are markedly different from each other and from the spectrum of their equilibrium solution mixture (see Fig. 3), as are their ^{1}H-n.m.r.[26], ^{13}C-n.m.r.[27], and Raman spectra[8]. The main spectral differences are in the region of 950–500 cm^{-1} (called the anomeric region), shown in Fig. 4. The infrared spectrum of the α anomer shows three sharp absorption bands, at 915, 838, and 776 cm^{-1}, and a broad band having medium intensity at 621 cm^{-1}, which are absent from the spectrum of the β anomer (see Fig. 4). The β anomer shows 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}, and these are not present in the spectrum of the α anomer (see Fig. 4). The

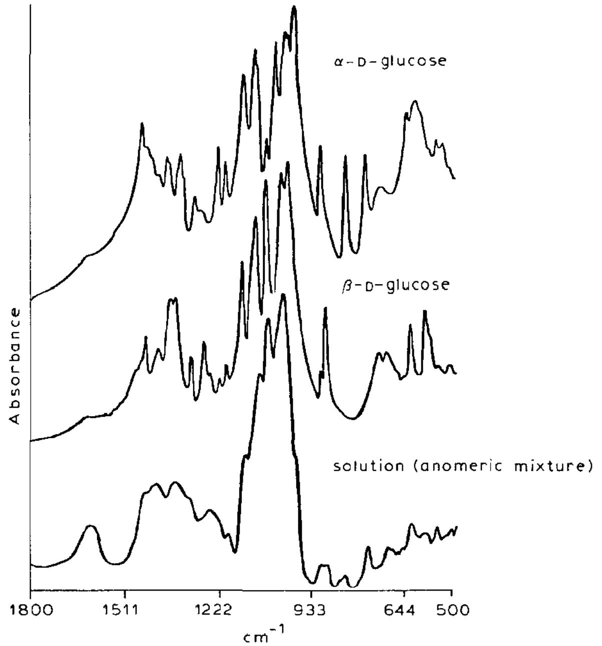


Fig. 3. F.t.-i.r. spectra of α- and β-D-glucose and their equilibrium mixture (in aqueous solution) in the region of 1800–500 cm^{-1}.

spectrum of the equilibrium solution mixture, which is composed[29] of $\alpha:\beta = \sim 2:3$ (based on the ^{1}H-n.m.r. spectrum), shows the presence of several bands related to both anomers (see Fig. 4). Several absorption bands occur, at 917 (α anomer), 903 (β anomer), 857 (β anomer), 847 (α anomer), 772 (α anomer), 725 (α and β anomer), 708 (β anomer), 668 (α and β anomer), 638 (β anomer), 602 (possibly β anomer), 559 (β anomer), and 515 cm^{-1} (β anomer) (see Fig. 4). On comparing the i.r. spectra of the alkaline-earth metal–D-glucose adducts with those of the two anomers in this region (950–500 cm^{-1}) (see Figs. 1 and 4), the presence is seen, in the spectra of these metal–sugar adducts, of several absorption bands, at ~914–920, 839–842, and 770–780 cm^{-1}, which are marker bands for the α-anomeric form, and this is indicative of the binding of D-glucose to these metal cations through its α-anomeric configuration. This is consistent with the results of Raman spectroscopic studies[8], which showed the great tendency of Ca(II) ions towards complexation with the α anomer of the D-glucose molecule. The binding of the calcium ion to the α anomer of other sugars was also reported[29].

^{1}H-N.m.r. spectra. — The anomeric proton (H-1) chemical-shifts of free D-glucose in D_2O solution were observed[26] at 5.26 (α anomer) and 4.68 p.p.m. (β anomer) and exhibited no changes in the presence of Mg(II) and Ca(II) halides, and this is mainly related to the presence of no major interaction between these metal cations and D-glucose molecules in aqueous solutions. Similar observations were made earlier by Angyal and Davies[7] for the D-glucose molecule in the

presence of the Ca(II) ion in aqueous solution. On the other hand, the β- and α-anomeric O-1-H chemical shifts of free D-glucose were observed[28] at 6.57 and 6.20 p.p.m. (in Me_2SO), respectively, and they exhibited major downfield shifts upon interaction with Mg(II) and Ca(II) ion. The changes observed are indicative of strong interaction between these metal ions and D-glucose in non-aqueous solution, in particular with the anomeric O-1-H group.

X-Ray powder diffraction and molar conductivity measurements. — The X-ray powder patterns of the Mg(II)–D-glucose adducts were similar. The X-ray powder diagrams of the 1:1 Ca halide–sugar adducts were almost identical, but were different from those of the 1:2 metal–sugar adducts, and this is mainly due to the different coordination numbers of the Ca(II) ion in these two Ca(II)-complexes (possibly 7 in the 1:1 and 8 for the 1:2 metal–sugar adduct). It should be noted that the coordination numbers of the Ca(II) ion were found not the same in the

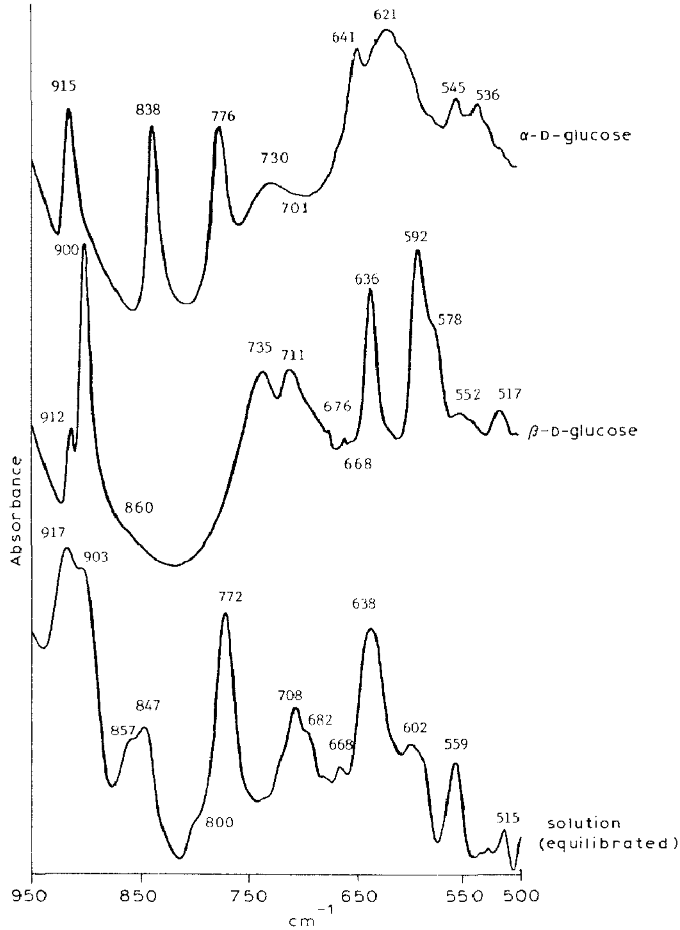


Fig. 4. The F.t.-i.r. spectra of α- and β-D-glucose and their equilibrium mixture (in aqueous solution) in the region of 950–500 cm^{-1} (anomeric region).

structurally known[30,31] 1:1 and 1:2 Ca halide–D-fructose adducts (that in the 1:1 was found to be 7, and that in the 1:2 was 8). The X-ray powder patterns of the Mg(II)–D-glucose adducts were not similar to those of the corresponding Ca(II) complexes, and this is also related to the smaller coordination numbers of the Mg(II) ion (possibly 6) with respect to the calcium ion (possibly 7 or 8).

The high molar conductivities (170–200 $\Omega^{-1}.cm^2.mol^{-1}$) observed for the alkaline-earth metal–D-glucose adducts in H_2O solution are indicative of major dissociation of these metal–carbohydrate complexes in aqueous solution, which is consistent with the ^{1}H-n.m.r.-spectral observations in D_2O solutions already discussed. Similar behavior was observed for several Ca halide–D-fructose adducts in aqueous solution, where their crystal structures (solid) showed direct metal–OH (sugar) binding, with no direct metal halide interaction[12,30,31].

SUMMARY AND CONCLUSIONS

On the basis of the spectroscopic properties of solid D-glucose and in solution and its alkaline-earth metal adducts, the following remarks may be made. (*a*) There is a strong interaction between D-glucose and the alkaline-earth metal cations in the solid and in non-aqueous solutions, whereas, in H_2O solution, such interaction is less significant. (*b*) In the 1:1, solid, metal–D-glucose adducts, the Mg(II) ion may be six-coordinate, binding to a sugar molecule (possibly through O-1-H and O-2-H) and to four H_2O, while the Ca(II) ion may be seven-coordinate, binding to a D-glucose (possibly through O-1-H, O-2-H and other sugar donor atoms) and to four H_2O. (*c*) In the 1:2 Ca(II)–D-glucose adduct, the calcium ion may be eight-coordinate, binding to two sugar units bidentately *via* O-1-H and O-2-H and four H_2O. (*d*) The 1:1 and 1:2 calcium–sugar adducts are spectrally dissimilar. (*e*) The binding of D-glucose to these alkaline-earth metal ion is through its α-anomeric structure.

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