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Carbohydrate interaction with monovalent ions. The effects of Li^+, Na^+, K^+, NH_4^+, Rb^+, and Cs^+ on the solid state and solution structures of D-glucono-1,5-lactone and D-gluconic acid

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ABSTRACT

The interaction of D-glucono-1,5-lactone with monovalent ions has been studied in aqueous solution at neutral pH. The D-gluconate salts of Li^+, Na^+, K^+, NH_4^+, Rb^+, and Cs^+ were studied by ^{13}C NMR, FTIR, and by X-ray powder diffraction. The spectroscopic evidence suggests that in aqueous solution, the alkali metal ions are hydrated, with no direct metal–sugar interaction. In the solid state, Li^+ is four-coordinated, binding to two different gluconate anions through the carboxylate O-1 and one of the acid anion OH groups. Na^+ binds to six oxygen atoms of six different acid anions. K^+ is six-coordinated in the anhydrous salt, binding to four oxygen atoms of the four anion carboxylate groups and to two sugar OH groups; the monohydrated shows two different types of crystals (A and B). In the A crystal, K^+ has eight-fold coordination, binding to six OH groups and two two H_2O, with no direct metal–carboxylate interaction, while in the B crystal, the eight coordination around K^+ is completed by the acid anion carboxylate and OH groups as well as a water molecule. the Rb^+ and K^+ salts are isomorphous with and rather different from the Cs^+ salt. The sugar intermolecular H-bonding network is rearranged upon acid ionization and salt formation.

INTRODUCTION

Interaction of carbohydrates with alkali metal ions has been known for a long time[1]. A recent paper by Burger and Nagy[2] reviews metal–sugar complex formation in the solid state and aqueous solutions. Crystal structures of the gluconate salts of sodium[3], potassium[4] (and its monohydrate)[5], and ammonium[6] have been determined, but little has been reported about their spectroscopic properties in the solid state and aqueous solution. We have recently described the FTIR spectra of the alkali metal D-glucuronate salts[7] and alkali metal–sucrose adducts[8].

The present work describes the spectroscopic and structural properties of D-glucono-1,5-lactone and D-gluconic acid in the presence of the cations Li^+, Na^+,

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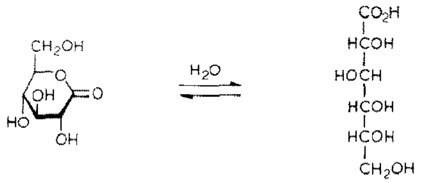

D-Glucono-1,5-lactone D-Gluconic acid

Scheme 1.

K^+, NH_4^+, Rb^+, and Cs^+, in the crystalline solid and aqueous solution, using Fourier-transform IR, ^{13}C NMR spectroscopy, and X-ray powder diffraction. These properties are compared with those of such structurally identified metal–gluconate complexes such as Mn(D-gluconate)$_2 \cdot 2H_2O$ (ref. 9) and Pb(D-gluconate)$_2$ (ref. 10). These comparisons allowed examination of characteristic features of the Li, Rb, and Cs salts, that are not structurally known. The complete assignments of the IR vibrational frequencies of D-glucono-1,5-lactone and D-gluconic acid (Scheme 1) are reported here.

EXPERIMENTAL

Materials and methods.—D-Glucono-1,5-lactone was purchased from Sigma Chemical Co., and used as supplied. D-Gluconic acid was prepared by slowly evaporating a satd aq solution of D-glucono-1,5-lactone, as reported earlier[1]. The alkali metal salts were reagent grade and were used without further purification. The D_2O (99.98%) used was from Cambridge Isotopic Laboratories.

Preparation of alkali metal D-gluconates.—A solution of the alkali metal carbonate (1 mmol) or the alkali metal hydrogen carbonate (2 mmol) in H_2O (50 mL) was added to a hot solution of D-glucono-1,5-lactone (2 mmol) in H_2O (50 mL). The pH of the solution was adjusted to 7–7.5 and the mixture was then heated to 80°C for 10 min. The solution was cooled to room temperature and EtOH (100 mL) was added, producing a white precipitate, which was filtered off, washed with EtOH several times and dried ($CaCl_2$). These salts could also be prepared by the double decomposition of the alkali metal carbonate and the Ca(D-gluconate)$_2$ salt and filtering off the insoluble $CaCO_3$. Analysis showed the composition of M–D-gluconate (where M = Li, Na, K, NH_4, Rb , and Cs ions).

D-gluconate monohydrate was prepared by recrystallization of the anhydrous potassium salt from H_2O. The alkali salts were very soluble in water, and slightly so in EtOH but were insoluble in other common organic solvents.

Physical measurements.—The ^{13}C NMR spectra were recorded with a Bruker WP-80 MHz instrument for D_2O solution containing 1,3-dioxane as the reference. The IR spectra were recorded with a Digilab FTS 15D/C Fourier-transform interferometer equipped with an HgCdTe (nitrogen cooled) detector and KBr beam splitter. The solid spectra were taken as KBr pellets with a resolution of 2 to 4 cm^{-1}. The solution spectra were taken with 2% solutions in D_2O, using an AgCl

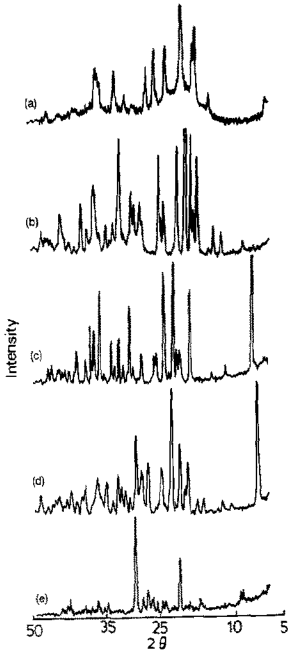

Fig. 1. X-ray powder diffraction patterns for the alkali metal D-gluconate salts: (a) Li; (b) Na; (c) K; (d) Rb; and (e) Cs.

window. The X-ray powder diagrams were recorded on a Philips PW 1011 diffractometer with Cu*Kα* radiation and a LiF monochromator.

RESULTS AND DISCUSSION

X-ray powder diagrams.—The X-ray powder patterns of the alkali metal gluconate salts (Fig. 1), demonstrate the structural similarities between these salts and also identify the materials in the KBr pellets used for IR spectra with the corresponding crystal structures. The potassium and rubidium salts are very similar (Fig. 1), whereas no such similarities were observed for the Li, Na, NH_4, and Cs salts. The observed differences in the powder patterns of these salts are reflected in their different crystal structures[3–6] and their IR spectra (see later). The formation of different coordination polyhedra and different binding-modes of the alkali metal ions are considered to be the main factors responsible for the observed spectral dissimilarities.

FTIR spectra.—The IR spectra of D-glucono-1,5-lactone, D-gluconic acid, and the alkali metal D-gluconate salts in the region of 4000–500 cm^{-1} are shown in part in Figs. 2 and 3 and Table I.

Lactone and acid OH stretching vibrations and alkali metal-ion interaction.—The correlation between hydrogen-bond geometry and the vibrational frequencies of

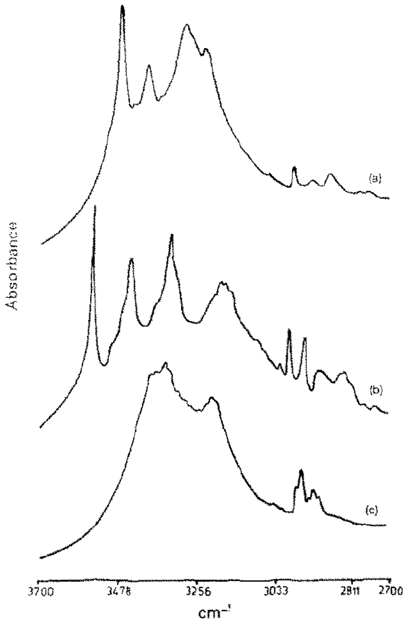

Fig. 2. FTIR spectra in the region 3700–2700 cm^{-1} of (a) D-glucono-1,5-lactone and its alkali metal salts: (b) Na; and (c) K.

H-bonded OH groups is far from direct in carbohydrates[12]. Recent efforts have been made to establish correlations between the sugar OH stretching vibrations and the intermolecular O ··· O and O ··· H distances as well as the hydrogen-

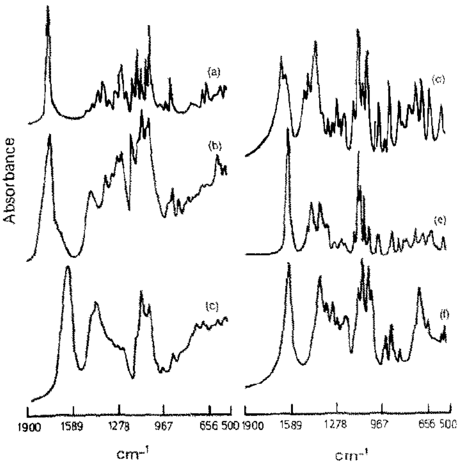

Fig. 3. FTIR spectra in the region 1900–500 cm^{-1} of (a) D-glucono-1,5-lactone, (b) D-gluconic acid, and the alkali metal D-gluconate salts: (c) Li; (d) Na; (e) K; and (f) Cs.

bonding geometry of the H-bonded OH groups[13–18]. X-ray structural data have shown[19] that there are four distinct H-bonded OH groups in the crystal structure of free D-glucono-1,5-lactone. A tentative assignment of the lactone OH stretching vibrations has been made on the basis of the intermolecular O ··· O and O ··· H distances (Table I). A sharp, intense band at 3462 cm^{-1} is assigned to the 6-OH ··· O-2, a strong band at 3387 cm^{-1} is related to 4-OH ··· O-1, a broad band with medium intensity at 3277 cm^{-1} is assigned to the 2-OH ··· O-3, and a strong band at 3225 cm^{-1} is due to the strongly H-bonded 3-OH ··· O-6 stretching vibrations (Fig. 2 and Table I). On the other hand, the crystal structure of the free D-gluconic acid monohydrate showed[11] eight different OH-bonding systems, including two from a water molecule. The IR spectrum of the free acid exhibited eight sharp, strong bands in the region 3500–3200 cm^{-1}, which are tentatively attributed to the following acid OH stretching frequencies: O-7(H_2O) ··· O-1 (O ··· O = 291.9 pm) (3415 cm^{-1}); 3-OH ··· O-7(H_2O) (O ··· O = 282.2 pm) (3353 cm^{-1}); 2-OH ··· O-1 (O ··· O = 280.6 pm) (3335 cm^{-1}); O-7(H_2O) ··· O-6 (O ··· O = 278.8 pm) (3259 cm^{-1}); 4-OH ··· O-6 (O ··· O = 278.5 pm) (3241 cm^{-1}); 6-OH ··· O-7(H_2O) (O ··· O = 272.7 pm) (3225 cm^{-1}); 5-OH ··· O-4 (O ··· O = 265.8 pm) (3207 cm^{-1}); and 1-OH ··· O-5 (O ··· O = 260.7 pm) (3190 cm^{-1}).

It should be noted that the assignments made for the IR vibrational frequencies in Table I are only used for the free lactone.

The OH stretching vibrations of the free lactone exhibited major spectral changes (broadening, shifting, and splitting), upon ionization of the aldonic acid, and of the formation of the alkali metal salt (Fig. 2 and Table I). Shifting and broadening of the sugar OH stretching vibrations were observed in the IR spectrum of the Li salt. In the Na salt, the OH stretchings exhibited splitting and shifting towards higher frequencies, whereas in the K salt, they exhibited broadening and were shifted towards lower frequencies (Table I). The spectral changes observed for the Rb salt were similar to those of the K salt (as in the case of their X-ray powder patterns). In the NH_4 salt, major broadening of the sugar OH stretching vibrations was observed (attributable to strong hydrogen-bonding of NH_4^+ with sugar OH groups). Similarly, broadening and shifting of the sugar OH stretching vibrations occurred in the spectrum of the Cs salt (Table I). The observed spectral changes are attributed to ionization of the sugar and the participation of the sugar OH groups in alkali metal–gluconate binding in the solid state. The observed dissimilarities of the OH vibrations in the spectra of the alkali metal salts can be related to the different binding modes of the sugar anion in these salts[3–6]. It should be noted that ionization and salt formation cause drastic alterations of the sugar H-bonding network[3–6]. Such rearrangements of the H-bonding system in the acid may contribute considerably to the spectral modifications of the OH stretching vibrations. Evidence to support these conclusions comes from the structural and spectral properties of the potassium gluconate monohydrate. Two different forms of crystals exist for this salt (A and B crystals), in which

TABLE I

FTIR Absorption bands [a] (cm^{-1}) for D-glucono-1,5-lactone, D-gluconic acid and their monovalent D-gluconate salts in the region 4000–500 cm^{-1}, with possible assignments

D-Glucono-1,5-lactone	D-Gluconic acid	Li D-gluconate	Na D-gluconate	K D-gluconate	NH_4 D-gluconate	Cs D-gluconate	Assignments
			3533 vs				
3462 vs	3415 vs	3450 s	3475 sh		3460 s	3445 vs	$\nu_{6\text{-OH}\ldots0\text{-}2}$
3387 bs	3353 vs	3360 s	3455 sh	3375 s	3420 s	3425 s	$\nu_{4\text{-OH}\ldots0\text{-}1}$
3277 bs	3335 s	3250 b s	3432 vs	3362 s	3380 bs	3375 bs	$\nu_{2\text{-H}\ldots0\text{-}3}$
3225 bs	3259 bs	3220 s	3344 bs	3330 bs	3280 m	3275 s	$\nu_{3\text{-OH}\ldots0\text{-}6}$
	3241 s		3100 s	3299 s		3200 s	
	3207 s		3080 s	3260 m			
	3190 s			3220 m			
				3200 bs			
2978 s	2980 m	2982 m	2990 m	2960 sh	2965 m	2960 m	ν_{CH_2}
2940 w	2945 s	2550 m	2975 s	2930 s	1940 m	2940 m	ν_{CH}
2900 m	2910 vw	2912 w	2925 s	2930 s	2910 m	2910 m	ν_{CH}
2850 s	2860 w	2855 vw	2900 mb	2880 m	2880 m	2880 w	ν_{CH}
			2800 mb	2860 m			overtone
1728 vs	1716 bs						$\nu_{C_1=O}$
	1640 mb						δ_{H_2O}
		1599 bs	1636 bs	1599 vs	1599 bs	1607 bs	ν COO$^-$ antisym.
		1410 vs	1401 vs	1431 s	1408 vs	1393 vs	ν COO$^-$ sym.
1427 m	1433 vs	1435 sh	1445 s	1439 sh	1439 sh	1433 sh	$\delta_{CH_2} + \delta_{OCH}$
1392 s	1365 sh	1370 sh		1377 s	1375 sh	1376 sh	$\delta_{COH} + \delta_{COH}$

1358 s	1332 s	1357 m	1349 s	1368 sh	1363 s	1341 s	$\delta_{COH}+\delta_{COH}$
1316 m			1310 m	1325 s	1322 s		$\delta_{COH}+\delta_{OCH}$
1303 m							$\delta_{COH}+\delta_{COH}$
1274 m	1285 s	1256 m	1282 m	1279 m	1270 s	1268 s	
1260 m	1254 s		1248 m				$\delta_{COH}+\delta_{COH}$
1225 s	1223 s		1231 m	1238 w	1226 w	1225 sh	$\delta_{COH}+\delta_{COH}$
1193 m			1202 s	1201 m	1216 s	1213 vs	$\nu_{CO}+\delta_{COO}$
1142 s	1150 s	1128 m	1133 s	1140 m	1136 s	1119 s	$\nu_{OC}+\nu_{CO}$
1109 vs	1105 m		1095 vs	1107 vs	1103 vs	1091 vs	$\nu_{CO}+\delta_{COO}$
1078 s	1078 vs	1089 vs	1065 vs	1091 s	1087 vs	1050 vs	$\nu_{CO}+\nu_{OC}$
1050 s	1050 sh	1040 vs		1064 s	1060 s		$\nu_{CO}+\delta_{COO}$
1025 vs	1033 vs		1039 vs	1036 m	1032 s	1025 s	$\nu_{CO}+\delta_{OCH}$
950 w	987 m	951 w	974 m	973 m	964 s	950 sh	$\nu_{CO}+\delta_{OCH}$
908 w			950 s	966 m	930 sh	922 s	$\nu_{CO}+\nu_{OC}$
880 s	861 s	877 s	874 vs	864 m	866 m	887 s	δ_{CH}
	818 m	814 w	808 s	821 m	819 m	826 m	δ_{CH}
744 vw	758 m		789 m	786 m	760 m		$\delta_{CO}+\delta_{COO}$
725 vw	707 vw	709 m	734 s	706 m	705 m	723 sh	δ_{OCH}
660 m	658 m	652 m	694 s	654 m	652 s	690 vs	δ_{COO}
631 m	623 vw	630 sh	651 s	614 sh		638 m	$\delta_{COO}+\delta_{COO}$
610 vw	602 vw	610 w	594 s	613 sh	590 m	605 w	$\delta_{CO}+\delta_{COO}$
565 vw	560 s	568 m	556 m	599 s	554 sh	554 w	
534 m	5635 sh		515 m	511 m	511 w	536 w	$\delta_{CO}+\delta_{COO}$
506 w	508 w	512 w				519 m	

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

the binding modes of the gluconate anions are different, with dissimilar hydrogen bonding patterns[5]. One involves σ-bonded cooperativity and the other π-bond cooperativity in their hydrogen-bonding systems. The IR spectra of the two crystals were dissimilar in the region 3500–3200 cm^{-1}; these dissimilarities are related to the different H-bonding networks and binding modes of the acid anions observed in the crystal structures of the two crystalline forms of potassium gluconate monohydrate[5].

The C–H stretching vibrations of the free lactone and D-gluconic acid appeared as several absorption bands in the region 3000–2800 cm^{-1} and showed no major spectral changes upon acid ionization and salt formation (Fig. 2 and Table I).

Lactone and acid carbonyl-stretching vibrations and alkali metal-ion binding.— The C=O stretching vibration of the free lactone was observed at 1728 cm^{-1}, whereas in free D-gluconic acid it appeared at 1716 cm^{-1} (Fig. 3). Similarly, the carbonyl-stretching vibration of D-glucurono-1,4-lactone[20] occurred at 1758 cm^{-1}, whereas in free D-glucuronic acid it was observed[7] at 1707 cm^{-1}. Upon alkali metal-ion interaction, the stretching vibration of the free lactone C=O at 1728 cm^{-1} shifted towards lower frequencies and split into two components at ~ 1600 and 1400 cm^{-1} (Fig. 3 and Table I). The two absorption bands observed in the spectra of the alkali metal–gluconate salts are related to the antisymmetric and symmetric stretching vibrations of the acid anion OCO^- group, respectively[21]. The shape and the intensity of the antisymmetric OCO^- band at ~ 1600 cm^{-1} are rather different in the alkali metal–gluconate salts (Fig. 3). The band was strong and broad (at 1599 cm^{-1}) in the Li salt, as two components at 1636 and 1600 cm^{-1} in the Na salt, as a sharp band at 1599 cm^{-1} in the K salt, as a strong band at 1600 cm^{-1} in the Rb salt, and as a strong and broad band at 1607 cm^{-1} in the spectrum of the Cs salt (Fig. 3 and Table I). The variations in shape and intensity of the antisymmetric carboxylate band in the spectra of these salts are related to the different extents of the sugar carboxylate group interaction in these alkali metal salts.

The crystal structure of the Na gluconate shows the sugar carboxylate group strongly involved in Na–sugar binding[3]. Similarly, the K-carboxylate binding is evident in the anhydrous K salt[4], whereas the monohydrate contains two different (A and B) types of crystals[5]. In the A crystal, binding of the potassium ion is through the acid anion OH groups and the H_2O molecule, with no metal–carboxylate interaction, whereas in the B crystal, the potassium–sugar bindings are through the OCO^- group and the anion OH groups as well as the water molecule[5]. The IR spectra of the hydrated and anhydrous potassium gluconate are substantially different in the OH stretching regions (3500–3200 cm^{-1}), as was the case for the A and B crystals of the hydrated form (because of the presence of different H-bonding arrangements in these salts). However, in the fingerprint region (1800-500 cm^{-1}) of the spectra, no such marked spectral differences was observed (Fig. 3). The presence of a moderate band at 1650 cm^{-1} in the hydrated salt (absent in the anhydrous salt) was attributed to the H_2O bending mode. The

OCO^- stretching vibrations were observed as broader bands in the spectra of the anhydrous and hydrated B crystals, as compared with that of the A crystal. Such broadening of the carboxylate vibrational frequencies observed in potassium gluconate and the monohydrate (B crystal only) may be related to participation of the OCO^- group in metal–sugar binding; such binding does not occur in the the A crystal[4,5].

There are marked similarities between the IR spectra of lithium gluconate and that of the structurally identified[9] $Mn(D\text{-gluconate})_2 \cdot 2H_2O$, in which the Mn(II) ion is bonded to two sugar anions through a carboxylate oxygen atom and an OH group of each anion, as well as by two H_2O molecules. Thus, it is possible to assume, that in the Li salt, the OCO^- group is involved in direct metal–sugar binding in concert with D-gluconate OH group. It is worth mentioning that, although the nature of alkali metal–sugar interactions are largely regarded as ionic, with M–O distances ranging from 234–254 pm for the Na–O (ref. 3) and 260–330 pm for K–O (ref. 5), the magnitude of separation of the two OCO^- components (antisymmetric and symmetric stretchings) ($\Delta\nu$ = 170–190 cm^{-1}) observed for the alkali metal gluconate salts are fairly large (Table I). These separations are similar to those of the structurally characterized $Mn(D\text{-gluconate})_2 \cdot 2H_2O$ (ref. 21) and $Pb(D\text{-gluconate})_2$ (ref. 22) salts ($\Delta\nu$ = 150–170 cm^{-1}), with M–O distances of 209–271 pm and strong metal–sugar interaction[9,10].

In the spectrum of the free D-gluconic acid monohydrate, the carbonyl stretching vibration was observed as a strong and broad band at 1716 cm^{-1} (Fig. 3). The broadening of the carbonyl stretching vibration is due to the H-bonding of the CO_2H group with a water molecule, as observed in the crystal structure of the free acid[11]. The presence of a band at 1640 cm^{-1} in free D-gluconic acid is related to the bending mode of the H-bonded H_2O molecule (Fig. 3). The N–H stretchings of the NH_4^+ cation at 3400–3200 cm^{-1} together with the N–H bending mode at about 1650 cm^{-1} were overlapped by the strong OH stretchings of the sugar and the OCO^- vibrations in the NH_4 salt (Table I).

Vibrational frequencies of the lactone ring and interaction of the alkali metal cation.—The strongly coupled sugar-ring COH, CH_2, and OH bending modes[23] were observed as several sharp bands at ~ 1460–1100 cm^{-1} in the IR spectrum of the free lactone, and exhibited considerable intensity changes and were shifted towards higher frequencies upon acid ionization and salt formation (Fig. 3 and Table I). The observed spectral modifications are related to ionization of the sugar, upon interactions with the alkali metal ion. The shift of the OH bending modes towards higher frequencies, together with the shift of the OH stretching vibrations (3500-3200 cm^{-1}), are indicative of rearrangements of the sugar H-bonding network network upon acid ionization and the participation of the sugar OH groups in metal–gluconate interaction. The C–O and C–C stretching vibrations of the free lactone[23] were observed as several strong bands at ~ 1100–900 cm^{-1} and exhibited shifting and splitting in the spectra of the salts (Fig. 3 and Table I). The observed spectral changes are due to involvement of the sugar anion

TABLE II

^{13}C NMR chemical shifts [a] of D-glucono-1,5-lactone, D-gluconic acid and their monovalent ion salts in D_2O solution

Compounds	C-1	C-2	C-3	C-4	C-5	C-6
D-Glucono-1,5-lactone	175.20	82.24	73.50	72.0	67.95	60.80
D-Gluconic acid	176.40	73.25	72.30	71.95	71.50	63.50
Li D-gluconate	179.29	74.84	73.33	71.95	71.78	63.42
Na D-gluconate	179.38	74.88	73.35	71.97	71.76	63.40
K D-gluconate	179.05	74.85	73.40	72.00	71.71	63.45
NH_4D-gluconate	179.22	74.80	73.31	71.97	71.87	63.40
Rb D-gluconate	179.38	74.88	73.42	72.00	71.87	63.37
Cs D-gluconate	179.36	74.95	73.38	72.00	71.85	63.36

[a] Employing 1,4-dioxane as reference (67.4 ppm).

oxygen atoms in metal–gluconate binding. Similar behaviour has been observed in the spectra of the alkaline earth and zinc group metal ions, plus lead(II) and manganese(II)-gluconate salts, where direct metal–sugar bindings were observed through acid anion OH and C–O groups[21,22,24]. The sugar skeletal C–O–C and C–C–C deformation modes[23] occurred in the region of 900–500 cm^{-1} in the spectrum of the free lactone and showed major changes upon metal-ion interaction (Fig. 3). These spectral changes are due to ionization of the acid in the presence of the alkali metal cations.

Solution spectra.—The IR spectra of the alkali metal gluconate salts were studied in D_2O solution and marked similarities were observed in the solution spectra of these salts (in contrast to their solid-state spectra). This observation is indicative of the presence of alkali metal cations in the hydrated $M(H_2O)_n^+$ forms, with no direct metal–sugar interaction. Evidence to support this comes from a ^{13}C NMR study of these metal gluconate salts in D_2O solution, which exhibited almost identical patterns (Table II). Upon ionization of the free acid, major downfield shifts were observed for the (3.1), C-2 (1.5), and C-3 (1.0 ppm), whereas the C-4, C-5, and C-6 atoms were not affected (Table II). The marked similarities observed in the ^{13}C NMR spectra of the gluconate salt (particularly with that of the NH_4 salt) are indicative of the presence of these metal cations in aqueous solution as hydrated forms having no major metal–sugar interactions. However, an indirect metal–gluconate interaction through the hydration shell of the metal ion cannot be excluded. The major downfield shifts of the C-1, C-2, and C-3 signals[25] may be due to the ionization of the carboxyl group and distribution of the negative charge around 0-1, 0-2, and 0-3.

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