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# CARBOHYDRATE ADDUCTS WITH ZINC-GROUP-METAL IONS. INTERACTION OF β-D-FRUCTOSE WITH Zn(II), Cd(II), AND Hg(II) CATIONS, AND THE EFFECTS OF METAL-ION COORDINATION ON THE SUGAR ISOMER BINDING

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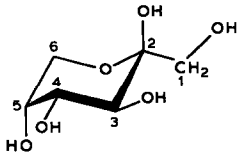
ABSTRACT

Interaction of β-D-fructose with hydrated salts of zinc-group-metal has been studied in aqueous solution and solid adducts of the type M(D-fructose)$X_2 \cdot nH_2O$, where M = Zn(II), Cd(II), and Hg(II) ions, X = $Cl^-$ or $Br^-$, and $n$ = 0–2, have been isolated, and characterized by means of F.t.-i.r. spectroscopy, X-ray powder diffraction, and molar conductivity measurements. The marked spectral similarities observed with the Mg(D-fructose)$X_2 \cdot 4\,H_2O$ (X = $Cl^-$ or $Br^-$) compounds indicated that the Zn(II) and Cd(II) ions are six-coordinated, binding to two D-fructose molecules through O-2, O-3 of the first D-fructose, and O-4, O-5 of the second, as well as to two $H_2O$. The Hg(II) ion binds to two sugar moieties in the same fashion as do the Zn(II) and Cd(II) ions, resulting in four-coordination geometry around the mercury ion. The crystalline sugar is in the β-D-fructopyranose form, and the coordination of the of the Ca(II) ion takes place through the β-D-fructopyranose isomer, whereas the binding of the Mg(II), Zn(II), Cd(II), Hg(II), and $UO_2^{2+}$ cations could be *via* the β-D-fructopyranose and the β-D-fructofuranose structures.

## INTRODUCTION




β-D-Fructopyranose-$^2C_5$

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It is well known[1] that crystalline β-D-fructose has the β-D-fructopyranose structure (1), and this has been demonstrated through X-ray[2] and neutron[3] diffraction measurements. When crystalline β-D-fructose is dissolved in water, an equilibrium is established[4] among β-D-fructopyranose, α-D-fructopyranose, β-D-fructofuranose, α-D-fructofuranose, and the acyclic isomer. The proportions of these isomers in aqueous solution are dependent on the pH, the temperature, and other factors. Recently, the effect of calcium ion coordination on the molecular structure, conformation, and hydrogen-bonding pattern of β-D-fructose has been studied in detail[2,5,6]. On the basis of infrared (i.r.) spectroscopy, it was shown[7] how the Ca(II) ion binds to the β-D-fructopyranose isomer of D-fructose; coordination of the Mg(II) and $UO_2^{2+}$ cations was found[8] to be *via* β-D-fructofuranose as well as β-D-fructopyranose.

Therefore, it was of interest to study the interaction of β-D-fructose with Zn(II), Cd(II), and Hg(II) ions, and the effects on the sugar isomeric coordination, of the binding of these metal ions. Now described are the synthesis and characterization of several adducts formed between β-D-fructose and the zinc group metal ions, using Fourier transform (F.t.)-i.r. spectroscopy, molar conductivity, and X-ray powder diffraction techniques that have not previously been reported. In addition, the spectroscopic properties of these metal–D-fructose adducts are compared with those of the corresponding, structurally identified[7,9] Mg(II)– and Ca(II)–D-fructose compounds, in order to detect the characteristic features of each structural type of adduct synthesized here for the zinc group of metal ions, and to establish a correlation between the spectral changes and the binding sites used by the D-fructose molecule. Furthermore, the effect of metal ion coordination on the binding of the sugar isomers is discussed.

## EXPERIMENTAL

β-D-Fructose was purchased from BDH, and recrystallized from water by slow evaporation. All other chemical compounds were reagent grade and were used as supplied.

*Synthesis of metal–D-fructose adducts.* — A metal (M) halide (3 mmol) in 1:3 water–methanol (20 mL) was added to a hot solution of D-fructose (1 mmol) in methanol (30 mL). The solution was heated for 1 h at 80°, the heating being used in order to prevent precipitation of the (less soluble) cadmium and mercury salts. After cooling to room temperature, the solution was kept for two weeks. Upon slow evaporation, colorless crystals were deposited (except for the Zn–D-fructose compounds, precipitated by addition of acetone). The compounds were then filtered off, washed several times with acetone, and dried over $CaCl_2$. The Zn–D-fructose adducts are very hygroscopic and should be kept in a desiccator. The analytical results showed the composition. M(D-fructose)$X_2 \cdot nH_2O$, where M = Zn(II), Cd(II), and Hg(II) ions, X = $Cl^-$ or $Br^-$, and $n$ = 0–2. These metal–sugar adducts are very soluble in water and in hot methanol, but are not soluble in any

of the other common organic solvents.

*Physical measurements.* — The F.t.-i.r. spectra were recorded with a DIGILAB FTS-15D/C Fourier-transform Michelson Interferometer equipped with a high-sensitivity CdHgTe detector and a KBr beam-splitter. The spectra were recorded, for KCl pellets, with a resolution of 2 to 4 $cm^{-1}$. A film of D-fructose was prepared by spreading an aqueous solution of the sugar (10%) on AgCl plate, followed by evaporation and respreading, as needed, to produce a uniform thickness. The X-ray powder diagrams were taken, for comparative purposes, with a camera (Phillips, Debye–Scherrer) with Cu$K_\alpha$ radiation. Conductance measurements were performed at room temperature, for mM solutions in $H_2O$, with a CDM2e type of conductivity meter (Radiometer, Copenhagen).

## RESULTS AND DISCUSSION

*F.t.-i.r. spectra.* — The F.t.-i.r. spectra of free β-D-fructose and its Zn(II), Cd(II), and Hg(II) adducts were recorded for the region of 4000–400 $cm^{-1}$, and comparisons were made with the spectra of the known Mg(II)– and Ca(II)–D-fructose compounds; the results of the spectral analysis are discussed. It should be noted that, on the basis of i.r. spectroscopy and chemical evidence, it was suggested[9] that the Mg(II) ion in the Mg(D-fructose)$X_2 \cdot 4\ H_2O$ (X = Cl or $Br^-$) adducts is six-coordinated, binding to two sugar molecules *via* O-2. O-3 of the first sugar and O-4, O-5 of the second, and to two $H_2O$ molecules. On the other hand, the X-ray structural information had shown[5,6] that the Ca(II) ion in the Ca(D-fructose)$X_2 \cdot 2\ H_2O$ (X = $Cl^-$ or $Br^-$) adducts is seven-coordinated, binding to three D-fructose units through O-2, O-3 of the first, O-4, O-5 of the second, and O-1 of the third sugar, as well as to two $H_2O$ molecules, whereas, in 2:1 Ca(D-fructose)$_2Cl_2 \cdot 3\ H_2O$, the calcium ion is eight-coordinated, binding to four sugar molecules *via* O-1 of two and O-4, O-5 of the other two, and to two $H_2O$ molecules[6]. In these structurally identified metal–sugar adducts the strong, intermolecular, sugar hydrogen-bonding network is rearranged to that of the sugar–$OH\cdots H_2O\cdots$halide system[5,6].

TABLE I

PATTERS IN THE HYDROGEN BONDING IN β-D-FRUCTOSE

| Type of hydrogen bond | O–H (pm) | H···O (pm) | O···O (pm) | $\nu_{OH}$[a] ($cm^{-1}$) |
|---|---|---|---|---|
| O-4–H···O-2′ | 94.8 | 206.3 | 297.2 | 3526 s |
| O-3–H···O-5′ | 96.4 | 197.7 | 293.0 | 3422 bs |
| O-1–H···O-3′ | 97.2 | 196.5 | 285.9 | 3406 s |
| O-5–H···O-2′ | 96.3 | 186.9 | 280.5 | 3266 s |
| O-2–H···O-1′ | 97.9 | 175.0 | 266.8 | 3180 m |

[a]b, broad; m, medium; s, strong; ν, stretching.

TABLE II

F.T.-I.R. ABSORPTION BANDS[a] ($cm^{-1}$) FOR β-D-FRUCTOSE AND ITS METAL ADDUCTS IN THE REGION OF 4000–400 $cm^{-1}$ WITH POSSIBLE BAND ASSIGNMENTS

| *β-D-Fructose* | *Zn(D-fructose)$Cl_2$·2 $H_2O$* | *Zn(D-fructose)$Br_2$·2 $H_2O$* | *Cd(D-fructose)$Cl_2$·2 $H_2O$* | *Cd(D-fructose)$Br_2$·2 $H_2O$* | *Hg(D-fructose)$Cl_2$* | *Hg(D-fructose)$Br_2$* | *Assignments*[7–13] |
|---|---|---|---|---|---|---|---|
| 3526 s | 3510 s | 3500 s | 3515 s | 3510 s | 3520 s | 3518 s | ν O-4–H···O-2′ |
| 3422 bs | 3410 bs | 3410 vs | 3400 s | 3415 s | 3418 vs | 3415 vs | ν O-3–H···O-5′ |
| 3406 s | 3400 s | 3990 s | 3395 vs | 3390 s | 3395 s | 3400 s | ν O-1–H···O-3′ |
| 3366 s | 3345 s | 3350 s | 3350 s | 3355 vs | 3358 s | 3360 s | ν O-5–H···O-2′ |
| 3180 s | 3165 s | 3160 s | 3170 vs | 3160 s | 3165 vs | 3170 s | ν O-2–H···O-1′ |
| 3013 w | 3010 w | 3010 w | 3012 vw | 3010 vw | 3012 w | 3010 vw | ν as($CH_2$) of C-1 |
| 2990 w | 2995 vw | 2990 w | 2993 vw | 2990 w | 2992 vw | 2995 w | ν as($CH_2$) of C-6 |
| 2959 w | 2950 vw | 2954 w | 2955 w | 2955 w | 2960 w | 2956 w | ν(CH) of C-4 |
| 2934 m | 2930 m | 2933 w | 2930 m | 2930 m | 2935 m | 2932 m | ν(CH) of C-5 |
| 2900 m | — | — | — | — | — | — | ν sy($CH_2$) of C-6 |
| 2835 vw | — | — | — | — | — | — | ν sy($CH_2$) of C-1 |
| | 1640 mb | 1655 mb | 1645 mb | 1630 mb | | | δ($H_2O$) |
| 1470 w | — | — | — | — | — | — | δ(OCH) + δ(CCH) + δ(COH) |
| 1451 w | 1455 m | 1450 m | 1451 m | 1451 m | 1450 m | 1452 w | δ($CH_2$) + δ(OCH) |
| 1428 m | 1410 s | 1411 s | 1403 s | 1402 s | 1404 m | 1412 m | δ(OCH) + δ(CCH) |
| 1399 m | 1360 w | — | — | 1391 sh | 1383 m | 1382 sh | δ(OCH) + δ(COH) + δ(CCH) |
| 1372 vw | 1347 m | 1342 m | 1343 s | 1342 m | 1333 m | 1341 m | δ(OCH) + δ(CCH) + δ($CH_2$) |
| 1336 s | — | — | — | — | — | — | δ(CCH) + δ(COH) |
| 1320 vw | — | — | 1325 sh | — | — | — | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1265 m | — | — | — | 1245 sh | 1245 sh | 1240 m | $\delta$(CCH) + $\delta$(COH) |
| 1250 sh | 1246 sh | 1235 s | 1235 s | 1235 s | 1235 s | 1230 s | |
| 1235 sh | 1236 mb | 1237 m | — | — | — | — | |
| 1176 m | 1180 s | 1180 m | 1181 m | 1180 s | 1179 m | 1179 m | $\delta$(OCH) + $\delta$(CCH) |
| 1150 s | 1140 s | 1141 s | 1146 s | 1140 s | 1145 m | 1143 sh | $\nu$(CO) + $\nu$(CC) |
| 1100 sh | 1085 sh | 1080 sh | 1085 sh | 1086 sh | 1085 sh | 1080 sh | $\nu$(CO) + $\nu$(CC) |
| 1094 s | 1080 sh | 1075 sh | 1071 sh | 1076 sh | 1075 sh | 1070 sh | $\nu$(CO) + $\nu$(CC) |
| 1079 vs | 1057 vs | 1055 vs | 1054 bs | 1055 vs | 1066 bs | 1057 bs | $\nu$(CO) |
| 1053 vs | — | — | — | — | — | — | |
| 1025 sh | 990 sh | 995 sh | — | 1000 sh | 1005 sh | 1003 sh | $\nu$(CO) + $\nu$(CC) |
| 978 s | 976 s | 977 s | 975 s | 975 s | 876 m | 976 m | $\nu$(CO) + $\delta$(CCO) |
| 924 m | 920 m | 925 m | 910 m | 920 m | 920 m | 920 m | $\nu$(CO) + $\delta$(CCH) |
| 874 m | 866 m | 865 s | 867 m | 864 m | 865 m | 865 m | $\delta$(CH) + $\beta$-anomer |
| 818 m | 817 s | 818 s | 817 s | 816 s | 816 s | 816 s | $\delta$(CH) |
| 783 s | 778 s | 779 s | 779 s | 777 s | 779 s | 777 s | $\tau$(CO) + $\delta$(CCO) + $\delta$(CCH) |
| 688 m | 690 m | 695 m | 693 m | 740 vw | 699 m | 685 m | $\delta$(CCO) + $\tau$(CO) + $\delta$(OCO) |
| 665 sh | 655 m | 650 w | 678 w | 698 m | 680 sh | 677 sh | |
| 628 s | 615 w | 626 m | 622 m | 621 m | 624 m | 622 m | $\delta$(CO) |
| 596 sh | 596 w | 599 m | 595 w | 590 m | 588 m | 588 m | $\tau$(CO) + $\delta$(CCO) |
| 560 m | 550 vw | 567 w | 569 w | 569 w | 569 m | 568 m | $\delta$(CCO) + $\tau$(CO) |
| 528 m | 530 w | 549 m | 534 w | 528 m | 530 m | 535 w | |
| 488 sh | 490 m | 516 m | 515 m | 515 m | 515 sh | 520 w | |
| 476 w | 460 m | 465 w | 485 w | 480 w | 505 m | 510 w | $\delta$(CCO) + $\delta$(CCC) |
| 454 w | 445 w | 440 w | 450 w | — | 450 m | 415 vw | |

[a]b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak; $\nu$, stretching; $\delta$, bending; $\tau$, internal rotation.

*Sugar OH stretching vibrations and binding modes.* — In previous reports[7–9], the assignments for free β-D-fructose were based on the intermolecular O···O distances found by X-ray and neutron diffraction analysis[3]. On the basis of the neutron diffraction measurements, the patterns given in Table I exist in the hydrogen-bonding structure of β-D-fructose. The order of the hydrogen-bonding strengths, based on the intermolecular O···O distances are summarized as O-2–H > O-5–H > O-1–H > O-3–H > O-4–H.

The five strong absorption bands observed here at ~3500–3200 $cm^{-1}$ in the i.r. spectrum of free β-D-fructose are assigned to the hydrogen-bonded, OH stretching frequencies (see Table II).

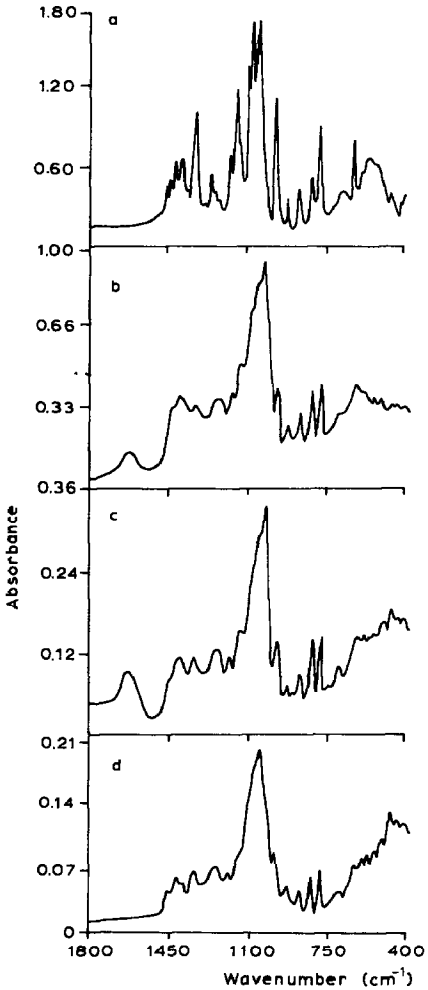


Fig. 1. F.t.-i.r. spectra of crystalline β-D-fructose and its zinc-group metal adducts in the region of 1800–400 $cm^{-1}$ for a, β-D-fructose; b, Zn(D-fructose)$Cl_2 \cdot 2\ H_2O$; c, Cd(D-fructose)$Br_2 \cdot 2\ H_2O$; and d, Hg(D-fructose)$Cl_2$.

The OH stretching vibrations of D-fructose exhibited considerable intensity changes, and shifted towards lower frequencies in the spectra of the Zn(II)–, Cd(II)–, and Hg(II)–D-fructose adducts (see Table II). The spectral changes are related[7–9] to the participation of the sugar OH groups in metal–ligand bondings. Similar behavior was observed in the spectra of the structurally characterized Mg–D-fructose compounds, where it was suggested[9] that the Mg(II) ion bonded to the two sugar molecules through O-2, O-3 of the first sugar and O-4, O-5 of the second, as well as to two $H_2O$ molecules. Thus, the binding modes of free D-fructose would be similar in these zinc-group-metal–sugar adducts. It should be noted that the rearrangements of the intermolecular H-bonding network in the free sugar to that of the sugar–OH···$H_2O$···halide system, which was observed[5,6] in the crystal structures of the calcium halide–D-fructose adducts, are also responsible for the alterations in the sugar OH stretching vibrations.

*Sugar C–H stretching vibrations.* — The assignments of the free $\beta$-D-fructose C–H stretching vibrations had been reported[7–9]; they were in good agreement with the results of Szarek *et al.*[10]. The D-fructose has seven fundamental C–H stretching vibrations, but, due to the inherent width of some bands, and possible overlap, six of these vibrational frequencies have been observed here and these were assigned to the antisymmetric and symmetric stretchings of the $CH_2$ and CH groups (see Table II). The C–H stretching vibrations of the free sugar showed no marked changes as a result of the zinc-group-metal ion interaction (see Table II).

*Water coordination.* — Due to the overlapping of the sugar OH stretchings with those of the bonded $H_2O$ molecules in the region of 3500–3200 $cm^{-1}$, it is rather difficult to draw with certainty conclusions as to the nature of the metal–$H_2O$ bonding. However, there is present, in the spectra of the Zn(II)– and the Cd(II)–D-fructose compounds, a broad absorption band with medium intensity at ~1640 $cm^{-1}$ that is absent from the spectra of the free sugar and the Hg–D-fructose adducts (see Fig. 1), and that is assigned to the bending mode of the coordinated $H_2O$ molecule[7,9].

*Sugar ring vibrational frequencies and metal ion bindings.* — The strongly coupled sugar COH, $CH_2$, and CCH bending modes[11–13], observed as several absorption bands with medium intensities in the region of 1470–1170 $cm^{-1}$ of the free D-fructose spectrum, exhibited major intensity changes and shifting upon sugar metalation (see Fig. 1 and Table II). The spectral changes for the COH bendings are consistent with the modifications of the sugar hydroxyl stretching vibrations (3500–3200 $cm^{-1}$), which are indicative of the involvement of the sugar OH groups in metal–sugar bondings[7–9].

The sugar C–O stretching vibrations appeared as several strong bands at 1150, 1094, 1078, 1054, and 978 $cm^{-1}$ in the spectrum of free D-fructose; these showed major intensity changes and shifted towards lower frequencies on sugar adduct formation (see Fig. 1 and Table II). The shifts of the C–O stretchings towards lower frequencies are due to the metal binding *via* sugar oxygen atoms[7–9].

The sugar ring skeletal deformations C–O–C and C–C–C[11–13] in the region of 900–400 $cm^{-1}$ exhibited major alterations in the spectra of the zinc-group-metal–D-fructose adducts (see Fig. 1 and Table II). Since the ring vibrational modes are strongly coupled, metalation of the sugar moiety causes a large perturbation to the ring electron distribution, where the vibrations are mostly localized, and finally causes ring distortion[7–9]. Similar spectral changes were observed for the sugar ring vibrational frequencies in the i.r. spectra of the calcium– and magnesium–D-fructose compounds[7–9], where the metal–sugar binding was through O-2, O-3, O-4, and O-5 of the two sugar molecules.

*Sugar isomeric binding.* — Crystalline D-fructose is β-D-fructopyranose[2,3]; in aqueous solution, the sugar has mainly the β-D-fructopyranose (57%), β-D-fructofuranose (31%), and the α-D-fructofuranose (9%) isomeric forms[14]. The F.t.-i.r. spectra of the crystalline solid is substantially different from that of the aqueous

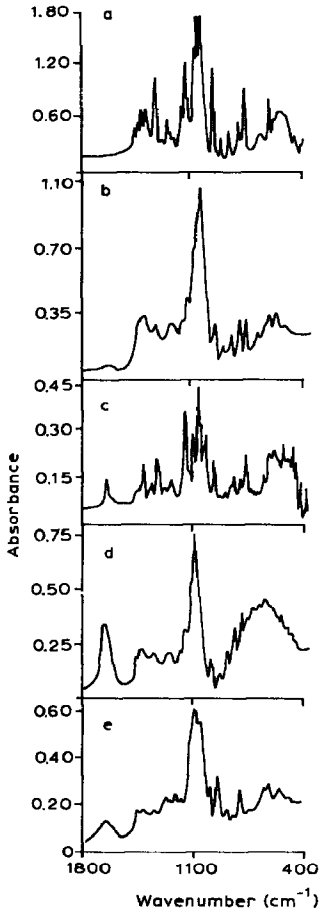


Fig. 2. F.t.-i.r. spectra of β-D-fructose in solid form and in aqueous solution with its metal ion adducts in the region of 1800–400 $cm^{-}$ for a, crystalline β-D-fructose; b, β-D-fructose (film cast); c, Ca(D-fructose)$Cl_2 \cdot 2\ H_2O$; d, Mg(D-fructose)$Cl_2 \cdot 4\ H_2O$; and e, $UO_2$(D-fructose)$Cl_2 : 2\ H_2O$.

solution (see Fig. 2). The dissimilarities observed are due to the different isomeric compositions present in aqueous solution. The i.r. spectra of the solid Ca–D-fructose adduct[7] showed marked similarities to that of crystalline β-D-fructose (see Fig. 2), and this is indicative[7] of Ca–sugar binding *via* the β-D-fructopyranose isomer; this is consistent with the results of X-ray structural analysis of the calcium–D-fructose adducts[5,6], which showed that the sugar moiety is in its β-D-fructopyranose form. On the other hand, the i.r. spectra of the Mg(II)– and $UO_2^{2+}$–D-fructose complexes reported earlier[8,9] and the zinc-group-metal–D-fructose adducts studied here exhibited marked similarities to that of β-D-fructose in aqueous solution (film cast) (see Figs. 1 and 2). The marked spectral similarities observed could be related to coordination of these metal cations through both the β-D-fructopyranose and the β-D-fructofuranose isomers of the D-fructose molecule. The reason for this would be mainly related to the larger ionic radius of the Ca(II) ion, which enables the calcium ion to form higher coordination numbers (7 or 8) and the ability of this metal ion to bind and accommodate three or four D-fructose molecules in their extended D-fructopyranose forms[5,6]. However, the shorter ionic radii of the Mg(II), $UO_2^{2+}$, and Zn(II) cations (with respect to those of the calcium ion) lead to formation of smaller coordination numbers (4 or 6) around these metal ions. Therefore, each of these metal ions can bind to two D-fructose molecules, one with β-D-fructopyranose and the other with β-D-fructofuranose (smaller form) structures. Similar conclusions were drawn as to the nature of the $UO_2$–D-fructose binding reported earlier[8]. The i.r. spectra of D-fructose in the solid form and in solution (film cast) were studied by Tamic and Hartman[15], and their observations on free D-fructose in crystalline form and in aqueous solution were confirmed.

*X-Ray powder diffraction and molar conductivity.* — The X-ray powder diagrams of the Zn(II)–, Cd(II)–, and Hg(II)–D-fructose adducts exhibited no marked similarities to those of the seven- and eight-coordination Ca–D-fructose complexes[5,6]. The dissimilarities observed are related to the higher coordination numbers formed for the Ca(II) ion with respect to those of the four- or six-coordination obtained for the zinc-group-metal ions. On the other hand, the X-ray powder patterns of these metal–sugar adducts showed distinct similarities to those of the Mg–D-fructose compounds[9], and this is indicative of similar coordination numbers (except for the mercury ion) and binding arrangements around these metal–D-fructose complexes. It should be noted that the coordination numbers of the magnesium ion are rather different from those of the calcium ion[16] and show similarities to those of the zinc and cadmium ions[17]. The dissimilarities of the zinc-group-metal–D-fructose adducts to those of the corresponding calcium compounds are also reflected in their i.r. spectra, whereas the isomorphic patterns of these metal adducts with the Mg–D-fructose compounds can be seen in their identical i.r. spectra (Figs. 1 and 2).

The high molar conductivities (150–190 $\Omega^{-1}.cm^2.mol^{-1}$) observed in aqueous solutions for the zinc-group-metal–D-fructose adducts are indicative of dissociation of these metal–sugar compounds in $H_2O$ solution and of the ionic nature of the

metal–halide interaction in these metal–sugar complexes. These findings are consistent with the structural analysis of the Ca–D-fructose adducts[5,6], which showed no direct calcium halide interaction.

## CONCLUSIONS

Based on comparisons of the structural and spectroscopic properties of the Zn(II)–, Cd(II)–, and Hg(II)–D-fructose adducts with those of the corresponding, structurally identified, Ca(II)– and Mg(II)–D-fructose compounds, the following conclusions were reached. (*a*) The strong, intermolecular, sugar hydrogen-bonding network is altered to that of the sugar–OH$\cdots$H$_2$O$\cdots$halide system on sugar metalation. (*b*) The possible mode of binding of each metal ion is by coordination to two D-fructose molecules through O-2, O-3 of the first sugar and O-4, O-5 of the second, as well as to two $H_2O$ molecules, resulting in six-coordination geometry around each metal ion, except for the mercury ion, which is four-coordinated (no bonded $H_2O$ molecule). (*c*) The zinc-group-metal–D-fructose adducts are isomorphous with the Mg–D-fructose compounds, and rather different from those of the Ca–D-fructose complexes. (*d*) The Ca(II) ion binds to $\beta$-D-fructopyranose, whereas binding of the Mg(II), Zn(II), Hg(II) and $UO_2^{2+}$ cations is to both $\beta$-D-fructopyranose and $\beta$-D-fructofuranose.

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