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Metal–ion interactions with sugars. The crystal structure and FTIR study of an $SrCl_2$–fructose complex

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Abstract—The single-crystal structure of $SrCl_2 \cdot 2C_6H_{12}O_6 \cdot 3H_2O$ was determined with $M_r = 572.88$, $a = 16.252(5)$, $b = 7.941(2)$, $c = 10.751(3)$ Å, $\beta = 127.652(4)°$, $V = 1098.5(6)$ Å^3, C2, $Z = 2$, $\mu = 0.71073$ Å and $R = 0.0296$ for 1998 observed reflections. The fructose moiety of the complex exists as a β-D-pyranose. The strontium atom is surrounded by eight oxygen atoms, which are arranged in symmetry-related pairs that are derived from four sugar and two water molecules. Three nonvicinal hydroxyl groups of fructose are involved in strontium binding. All the hydroxyl groups and water molecules are involved in forming an extensive hydrogen-bond network. The Sr–fructose complex is isostructural with the Ca–fructose complex, and the crystal structures and FTIR spectra of the two complexes are compared in this article. The O–H, C–O, and C–O–H vibrations are shifted, and the relative intensities changed in the complexes IR spectra, which indicate sugar metalation. By studying the metal-binding properties of fructose, it is hoped that such would aid in the understanding of the structural chemistry of metal ions interacting with saccharides, as an actual biological system, and thereby aid in the interpretation of some particular biological processes.

Keywords: Sr–D-fructose complex; Single-crystal X-ray structure; FTIR

1. Introduction

Solution studies show that simple carbohydrates strongly bind calcium ions only if they can provide three contiguous axial–equatorial–axial (ax–eq–ax) hydroxyl groups on six-membered rings or vicinal cis–cis–triol groups on five-membered rings,[1,2] and calcium–carbohydrate interactions have been implicated in a variety of biological processes.[3–7] However, only D-ribose, D-allose, and D-talose are present in solution in significant amounts of the 'complexing forms', and these sugars, except D-ribose, are not natural as the free sugars. D-fructose, which bears no 'complexing forms', is a well-known ketose occurring widely in nature. However, the stable single-crystal of Ca–fructose complex, Ca(β-D-fructose)$_2$Cl$_2$·3H$_2$O, has been reported, **8** shows that D-fructose can also coordinate with calcium ions by a different mode.

Such metal–fructose interactions in solutions may be concluded to be similar to those metal–saccharide interactions in biological fluids that take part in many diverse biological functions. Therefore, studying metal–sugar interactions is of particular significance. We are currently investigating the crystal structures of such metal–sugar complexes to elucidate the structural factors involved in these interactions.[9,10]

Sr^{2+} is an essential element in living things, and it also plays an important role in biological processes as does Ca^{2+}. In the present work, the first single crystal of a Sr–ketose complex, Sr(β-D-fructopyranose)$_2$Cl$_2$·3H$_2$O, was determined and compared with that of Ca(β-D-fructopyranose)$_2$Cl$_2$·3H$_2$O. These studies of the metal-binding properties of fructose are carried out in the hope that they would aid in the understanding of the structural chemistry of metal ions interacting with saccharides that bear no 'complexing forms' in an actual biological system. It is just such interactions that influence many biological processes in living things,[11–15] whereas the mechanism of action still remain obscure. In this article, the vibrational spectrum of the title complex was also

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assigned and interpreted in correlation with the single-crystal structure, and the FTIR technique was shown to be another useful method for detecting the formation of such complexes.

2. Experimental

2.1. Materials

D-Fructose (99.8%) was purchased from Acros and was used without purification. $SrCl_2 \cdot 6H_2O$ (AR) was purchased from Tianjin Chemical Reagent Co., Inc, Tianjin, China, and was used as supplied.

2.2. Preparation of $Sr(\beta\text{-D-fructose})_2Cl_2 \cdot 3H_2O$

D-Fructose (0.90 g, 5 mmol) and equivalent amounts of $SrCl_2 \cdot 6H_2O$ were dissolved in distilled water. Clear, stout, and prismatic crystals of $Sr(\beta\text{-D-fructopyranose})_2Cl_2 \cdot 3H_2O$ were grown by slowly evaporating the solution over several weeks at room temperature. Anal. Calcd for $SrCl_2 \cdot 2C_6H_{12}O_6 \cdot 3H_2O$: C, 25.16; H, 5.28. Found: C, 24.93; H, 5.28.

2.3. Physical measurements

The structure of $Sr(\beta\text{-D-fructopyranose})_2Cl_2 \cdot 3H_2O$ was determined on a Bruker Smart 1000 diffractometer using monochromatic MoKα radiation ($\lambda = 0.71073$ Å) in the θ range from 2.39° to 26.44° at 293 K. The final cycle of full-matrix least-squares refinement was based on 1998 observed reflections. Calculations were completed with the SHELX-97 program. For complete data, see supplementary material section.

The crystals of $Sr(\beta\text{-D-fructopyranose})_2Cl_2 \cdot 3H_2O$ were ground into a powder, and the FTIR spectra (4000–400 cm^{-1}) of $Sr(\beta\text{-D-fructopyranose})_2Cl_2 \cdot 3H_2O$ and D-fructose were recorded on a Nicolet Magna-IR 750 spectrometer. The spectra were taken as KBr pellets with resolution of 4 cm^{-1}.

3. Results and discussion

3.1. X-ray crystal structure

Crystal data are listed in Table 1. The structure and atom numbering scheme is shown in Figure 1. Figure 2 is the projection of the crystal cell in the crystal structure of $Sr(\beta\text{-D-fructopyranose})_2Cl_2 \cdot 3H_2O$. Selected bond lengths and bond angles are collected in Table 2.

The fructose exists in the title complex as a pyranose with the β-D configuration in the $^2C_5$ chair conformation. The strontium is surrounded by eight oxygen atoms as was determined previously for calcium

Table 1. Crystal data and structure refinement parameters for $SrCl_2 \cdot 2C_6H_{12}O_5 \cdot 3H_2O$

Formula	$SrCl_2 \cdot 2C_6H_{12}O_5 \cdot 3H_2O$
Formula weight	572.88
Crystal system, Space group	Monoclinic, C2
a (Å)	16.252(5)
b (Å)	7.941(2)
c (Å)	10.751(3)
β (°)	127.652(4)
V (Å^3)	1098.5(6)
Z	2
D_{calcd} (Mg/m^3)	1.732
Absorption coefficient (mm^{-1})	2.768
F(000)	588
Crystal size (mm)	0.35×0.30×0.25
θ range for data collection (°)	2.39–26.44
Index ranges	$-20 \leqslant h \leqslant 13$, $-9 \leqslant k \leqslant 9$, $-13 \leqslant l \leqslant 13$
Reflections collected/unique	3017/1998 [R(int)=0.0226]
Completeness to $\theta = 26.44$ (%)	98.9
Absorption correction	Semi-empirical from equivalents
Max/min transmission	1.000000 and 0.772097
Refinement method	Full-matrix least-squares on F^2
S	0.923
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0296$, $wR2 = 0.0581$
R indices (all data)	$R1 = 0.0349$, $wR2 = 0.0594$
Absolute structure parameter	0.010(8)
Largest difference peak and hole (e/Å^3)	0.403 and −0.573
Data/restraints/parameters	1998 /1/ 139

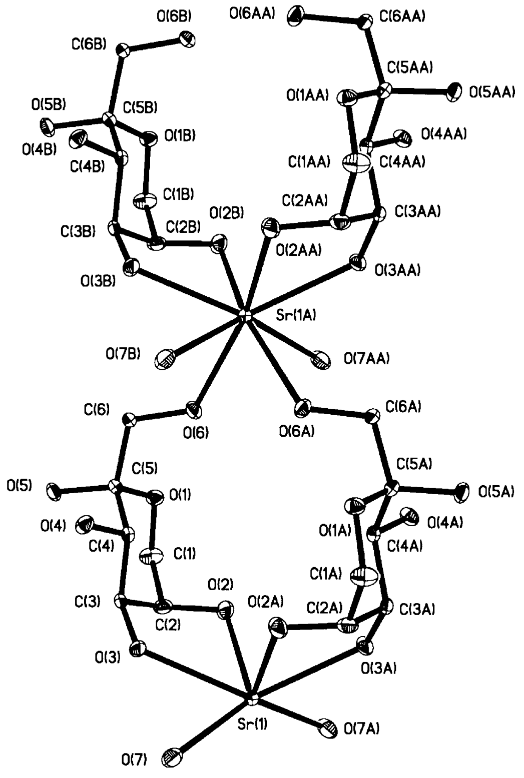

Figure 1. The structure and atom numbering scheme of $SrCl_2 \cdot 2C_6H_{12}O_6 \cdot 3H_2O$.

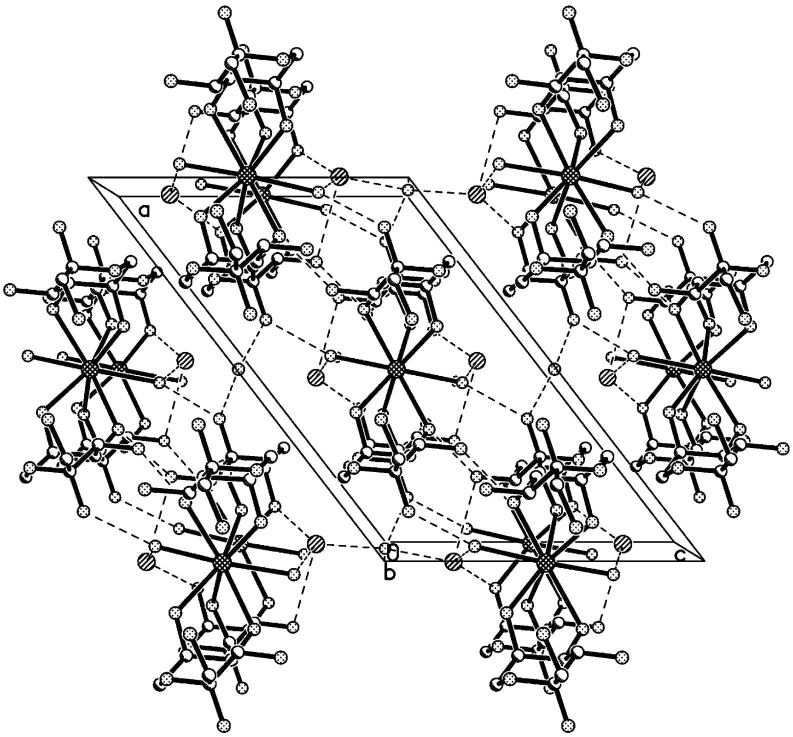

Figure 2. Projection of the unit cell in the structure of $SrCl_2{\cdot}2C_6H_{12}O_6{\cdot}3H_2O$. The D-fructose molecules are arranged in chains parallel to the *b*-axis, which is formed by coordination to translation-related strontium ions. The chains are separated by sheets parallel to the *a*–*b* plane containing the strontium and chloride ions and the water molecules.

ions,[8,16,17] with Sr–O distances from 2.551 to 2.619 Å that form a distorted square-antiprism. The oxygens, in symmetry-related pairs, are derived from four sugar and two water molecules. Of the five hydroxyls available in each fructose molecule, only O(6), O(2), and O(3) are involved in the complex formation. The D-fructose molecules are arranged in chains parallel to the *b*-axis, formed by coordination to translation-related strontium ions. The chains are separated by sheets parallel to the *a*–*b* plane containing the strontium and chloride ions and the water molecules.

As would be expected, there is an extensive network of hydrogen bonds involving hydroxyl groups, water molecules, and chloride ions, which appears to use all of the hydrogen atoms that are covalently bonded to oxygen atoms (see Table 3). It is by the extensive network of intramolecular and intermolecular hydrogen bonds, these chains are joined and form a sheet, and the sheets are thus organized to form the whole packed crystal structure.

The title complex appears to be isostructural with the calcium chloride analogue,[8] which shows that the Ca^{2+} and Sr^{2+} have similar coordination modes. However, in the IIA group metal ions, no stable similar complex of $MgCl_2$ or $BaCl_2$ from D-fructose was obtained by the same synthesis method, which indicates that the size effect plays an important role in the coordinating process. Of the two metal–fructose complexes obtained, the bond lengths of Sr–O (2.551–2.619 Å) are longer than those of Ca–O (2.450–2.502 Å), which indicates that the coordination ability of Sr^{2+} to fructose is weaker than that of Ca^{2+}.

3.2. FTIR spectroscopic study of Sr(β-D-fructose)$_2$Cl$_2$·3H$_2$O

The FTIR spectra of D-fructose and the Sr–fructose complex were recorded in the region of 4000–400 cm^{-1}. The absorption bands and tentative assignments are given in Table 4. The results of the spectral analysis are discussed below.

3.2.1. Region of wavenumbers 3600–2800 cm^{-1}. This region of wavenumbers is characteristic of O–H and C–H stretching vibrations. The absorption bands at 3600–3100 cm^{-1} can be assigned to the hydrogen-bonded OH groups. Upon strontium coordination, the sugar OH stretching vibrations showed considerable intensity changes and shifted toward lower wavenumbers (Table 4). The changes observed are mainly due to the participation of the sugar OH groups in the metal–ligand bonding. However, the rearrangements of the strong intermolecular hydrogen-bonding network of the free D-fructose to that of the sugar $OH{\cdots}H_2O{\cdots}Cl$ system found in the crystal structure of the Sr–fructose complex, which result in a weakening of the H-bond network upon complex formation, should lead to a shift toward higher wavenumbers.[18] The two effects are

Table 2. Selected bond lengths (Å) and angles (°) for $SrCl_2 \cdot 2C_6H_{12}O_6 \cdot 3H_2O$[a]

Sr(1)–O(7)#1	2.551(3)	C(1)–C(2)	1.501(5)
Sr(1)–O(7)	2.551(3)	O(1)–C(5)	1.407(4)
Sr(1)–O(6)#2	2.579(3)	C(2)–O(2)	1.424(5)
Sr(1)–O(6)#3	2.579(3)	C(2)–C(3)	1.502(5)
Sr(1)–O(3)#1	2.591(3)	C(3)–O(3)	1.426(5)
Sr(1)–O(3)	2.591(3)	C(3)–C(4)	1.533(5)
Sr(1)–O(2)#1	2.619(3)	C(4)–O(4)	1.414(4)
Sr(1)–O(2)	2.619(3)	C(4)–C(5)	1.520(5)
C(1)–O(1)	1.425(5)	C(5)–O(5)	1.404(4)
C(5)–C(6)	1.514(5)	C(6)–O(6)	1.417(5)
O(6)–Sr(1)#4	2.579(3)		
O(7)#1–Sr(1)–O(7)	138.08(13)	O(7)#1–Sr(1)–O(6)#2	70.85(9)
O(7)-Sr(1)–O(6)#2	77.86(10)	O(7)#1–Sr(1)–O(6)#3	77.86(9)
O(7)-Sr(1)–O(6)#3	70.85(9)	O(6)#2–Sr(1)–O(6)#3	82.38(14)
O(7)#1–Sr(1)–O(3)#1	66.41(8)	O(7)–Sr(1)–O(3)#1	133.92(9)
O(6)#2–Sr(1)–O(3)#1	136.89(8)	O(6)#3–Sr(1)–O(3)#1	83.52(9)
O(7)#1–Sr(1)–O(3)	133.92(9)	O(7)–Sr(1)–O(3)	66.41(8)
O(6)#2–Sr(1)–O(3)	83.52(9)	O(6)#3–Sr(1)–O(3)	136.89(8)
O(3)#1–Sr(1)–O(3)	131.58(11)	O(7)#1–Sr(1)–O(2)#1	127.39(9)
O(7)–Sr(1)–O(2)#1	81.09(9)	O(6)#2–Sr(1)–O(2)#1	158.95(7)
O(6)#3–Sr(1)–O(2)#1	91.06(9)	O(3)#1–Sr(1)–O(2)#1	61.27(8)
O(3)–Sr(1)–O(2)#1	87.82(9)	O(7)#1–Sr(1)–O(2)	81.09(9)
O(7)–Sr(1)–O(2)	127.39(9)	O(6)#2–Sr(1)–O(2)	91.06(9)
O(6)#3–Sr(1)–O(2)	158.95(7)	O(3)#1–Sr(1)–O(2)	87.82(9)
O(3)–Sr(1)–O(2)	61.27(8)	O(2)#1–Sr(1)–O(2)	101.54(13)
O(1)–C(1)–C(2)	112.4(3)	C(5)–O(1)–C(1)	115.1(3)
O(2)-C(2)–C(1)	114.1(3)	O(2)–C(2)–C(3)	109.1(3)
C(1)–C(2)–C(3)	110.0(3)	C(2)–O(2)–Sr(1)	115.8(2)
O(3)–C(3)–C(2)	108.4(3)	O(3)–C(3)–C(4)	109.1(3)
C(2)–C(3)–C(4)	109.5(3)	C(3)–O(3)–Sr(1)	123.2(2)
O(4)–C(4)–C(5)	109.6(3)	O(4)–C(4)–C(3)	111.0(3)
C(5)–C(4)–C(3)	109.6(3)	O(5)–C(5)–O(1)	110.8(3)
O(5)–C(5)–C(6)	109.6(3)	O(1)–C(5)–C(6)	104.2(3)
O(5)–C(5)–C(4)	108.7(3)	O(1)–C(5)–C(4)	110.0(3)
C(6)–C(5)–C(4)	113.5(3)	O(6)–C(6)–C(5)	112.0(3)
C(6)–O(6)–Sr(1)#4	126.4(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $(-x, y, -z+1)$; #2, $(x, y-1, z)$; #3, $(-x, y-1, -z+1)$ #4, $(x, y+1, z)$.

antagonistic: for the Sr–fructose complex molecule, the weakening of the OH band by coordinating with metal ions appears more distinct than the strengthening of the original OH band caused by the rearrangements of the H-bond network. The absorption bands at about 3100–2800 cm^{-1} are related to the asymmetric, symmetric CH_2 and C–H stretching vibrations of the free sugar. They are also observed to be shifted to lower wavenumbers upon strontium coordination.

3.2.2. Region of wavenumbers 1800–400 cm^{-1}.

This region is related to the sugar ring vibrations and drastic spectral changes occur in this region upon sugar metalation.

The bands at about 1645 cm^{-1} in the spectra of the metal–fructose complexes can be assigned to the δ_{HOH} vibration of the coordinated water. The absorption bands at 1470, 1453, 1429, 1399, 1251, 1232, and 1177 m^{-1} in the free D-fructose spectrum, which are assigned mainly to the COH, CCH, and CH_2 bending

Table 3. Hydrogen bonds for $SrCl_2 \cdot 2C_6H_{12}O_5 \cdot 3H_2O$ with H···A < (A)+2.000 Å and ⟨DHA > 110°[a]

D-H···A	d(D-H)	d(H···A)	d(D···A)	⟨(DHA)
O2–H2B···Cl1#1	0.930	2.260	3.120	153.56
O3–H3B···O4#2	0.930	2.059	2.756	130.55
O4–H4B···Cl1	0.820	2.697	3.101	112.19
O5–H5A···O7#3	0.820	2.117	2.835	146.19
O5–H5A···O4	0.820	2.337	2.757	112.55
O6–H6···Cl1#1	0.849	2.589	3.392	158.13
O7–H7A···O5#2	0.854	1.997	2.835	166.72
O7–H7B···Cl1#4	0.851	2.265	3.113	174.08
O8–H81···O5#2	0.850	2.290	2.714	111.12

[a] Symmetry transformations used to generate equivalent atoms: #1, $(-x, y, -z+1)$; #2, $(-x-1/2, y-1/2, -z+1)$; #3, $(-x-1/2, y+1/2, -z+1)$; #4, $(x, y-1, z)$.

Table 4. IR data for D-fructose, Sr(β-D-fructose)$_2$Cl$_2$·3H$_2$O and Ca(β-D-fructose)$_2$Cl$_2$·3H$_2$O

D-Fructose	Ca-fructose	Sr-fructose	Possible assignment[19–23,a]
3526	3483	3467	νO–H
	3454	3442	
	3413	3414	
3422	3350	3346	νO–H
3406	3311	3307	νO–H
3366	3293	3295	νO–H
	3279	3273	
3180	3174	3176	νO–H
3014	3006	3000	$\nu_{asy}CH_2$ of C(6)
2990	2981	2987	$\nu_{asy}CH_2$ of C(1)
2960	2941	2944	ν_{sy}CH of C(3)
2938	2922	2921	ν_{sy}CH of C(2)
2901	2892	2887	$\nu_{sy}CH_2$ of C(1)
1633	1652	1645	δH_2O
1470	1463	1465	$\delta CH_2+\delta OCH+\delta CCH$
1453	1450	1453	$\delta OCH+\delta CCH$
1429	1424	1422	
1399	1392	1389	$\delta OCH+\delta COH+\delta CCH$
1373	1376	1374	$\delta OCH+\delta CCH+\delta CH_2$
1336	1338	1332	$\delta CCH+\delta COH$
1296	1292	1301	
1265	1270	1268	
1251	1251	1249	
1177	1169	1168	$\delta OCH+\delta CCH$
1150	1143	1142	$\nu CO+\nu CC+\delta CCC+$ (pyranose)
1095	1112	1111	$\nu CO+\nu CC$
	1083	1082	
1079	1068	1067	$\nu CO+\delta CC$
1053	1049	1049	νCO
1025	1035	1035	$\nu CO+\nu CC$
978	984	981	$\nu CO+\delta CCO$
924	920	918	$\nu CO+\delta CCH+\nu_{asy}$ (ring of pyranose)
875	877	875	$\nu CC+\delta CCH+\delta CH$ (β-pyranose)
	860	862	
819	823	822	δCH
783	785	783	$\tau CO+\delta CCO+\delta CCH$
689	667	674	$\delta CCO+\tau CO+\delta OCO$
628	634	634	

[a] δ, Bending mode; ν, stretching mode; τ, twisting.

vibrations,[19–21] showed major intensity changes and shifted toward lower wavenumbers upon sugar metalation (Table 4). The changes observed for the COH bending vibrations in this region, together with the shifts of the OH stretching vibrations (3600–3100 cm^{-1}) to lower wavenumbers, are indicative of the participation of the sugar OH groups in metal–ligand bondings.

The ring skeletal deformation bands (δCOC and δCCC) of the free D-fructose, mainly in the region of 1150–400 cm^{-1} show considerable changes on complex formation (Table 4). This may be interpreted that the metalation of the sugar perturbs the electron distribution within the sugar ring system where the vibrations are mostly localized and finally brings up the ring distortion, which then results in alteration of the spectrum. The band at about 1150 cm^{-1} in the spectrum of the free D-fructose, which is assigned as a complicated ring vibration mode of the free sugar, is characteristic of pyranose.[21] This absorption band is observed to be shifted to lower wavenumber in each spectrum of the complexes, which also indicates the pyranose configuration is retained in each complex. Other absorption bands at 1095, 1079, 1053, and 978 cm^{-1} in the spectrum of the free D-fructose, assigned mainly to the C–O stretching vibrations,[19–21] exhibited shifting and splitting in the spectra of the complexes (Table 4). The changes (splitting and shifting) observed are consistent with the participation of the sugar hydroxyl groups in metal–ligand bonding, which thus affect the corresponding C–O stretching vibrations.

The absorption bands at about 870 and 840 cm^{-1} in the sugar spectra are usually assigned to the presence of the β and α anomers of pyranose, respectively.[22,23] In the spectra of the free D-fructose and its complexes, the presence of a strong absorption band at about 870 cm^{-1} and the absence of any absorption bands at 840 cm^{-1} are indicative of the presence of the sugar moiety in the β-fructopyranose conformation. This is consistent with the X-ray results reported in this article.

The FTIR data indicate that the hydroxyl groups of D-fructose take part in the metal–oxygen interaction. The sugar moiety of the Sr–fructose complex is in the β-fructopyranose conformation. The similar FTIR spectra of the Sr–fructose and Ca–fructose complexes indicate similar structures. Furthermore the FTIR results are in accord with those of the X-ray diffraction analysis. Thus the FTIR technique has proven to be another useful method for detecting the formation of such complexes.

4. Conclusions

The X-ray results indicate that Sr^{2+} shows similar coordination behavior to that of Ca^{2+} in aqueous solution of D-fructose. Because two coordinated hydroxyl groups are vicinal in the fructose molecule, the size effect appears important. Of the IIA group metal ions, no stable metal–fructose complex from Mg^{2+} or Ba^{2+}, which have a shorter or longer ionic radius, respectively, was obtained by the same synthetic method. This indicates that the divalent metal ions with ionic radii from 0.99 Å (Ca^{2+}) to 1.12 Å (Sr^{2+}) are in the suitable size range for coordinating with fructose.

As predicated by solution studies, simple carbohydrates bind metal ions only if they can provide three contiguous axial–equatorial–axial (ax–eq–ax) hydroxyl groups on six-membered rings or vicinal cis–cis triol groups on five-membered rings. Our results indicate that a fructose molecule provides three nonvicinal hydroxyl groups for metal–ion binding. Consequently, single, isolated fructose is not likely to have high affinity for the metal ions. However, if four fructose molecules are close enough and are geometrically suited so that each can utilize hydroxyl groups for metal–ion coordination, then a strong binding site can result. Such a site is found in the crystal structures of the Sr(β-D-fructopyranose)$_2$Cl$_2$·3H$_2$O and Ca(β-D-fructopyranose)$_2$Cl$_2$·3H$_2$O where the crystal packing permits fructose molecules to form a chain by coordinating to a translation-related strontium or calcium ion that leads to interactions of six hydroxyl groups with a alkaline-earth metal ion. In biological systems, similar binding sites might also be provided by different neighboring molecules with sugar residues. In the crystal structure of the title complex, the additional ligands are provided by water molecules. In some biological processes, these sites might also be occupied by oxygen atoms from phosphate or carbonate ions, thus leading to the formation of mineral nuclei, which initiate the corresponding biological function(s). Therefore, studies of the geometrical nature of such metal–fructose complexes are carried out in the hope that they would aid in the understanding of the structural chemistry of metal ions interacting with saccharides in actual biological systems that involved in many biological processes.

Supplementary material

Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre, deposition no. CCDC 220667. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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