Interactions of Cations with Sugar Anions. Part I. Crystal Structures of Calcium Sodium Galacturonate Hexahydrate and Strontium Sodium Galacturonate Hexahydrate

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The crystal structures have been determined for the isomorphous pair, calcium sodium galacturonate (I) and strontium sodium galacturonate (II), as models for the biologically important interactions between Ca^{2+} and the pyranose forms of sugar carboxylic acids. The space group is $P6_3$ and the cell dimensions are: a = 13·56(1), c = 9·70(1) Å (I); and a = 13·50(1), c = 9·63(1) Å (II). There are six galacturonate anions, twelve water molecules, two sodium ions, and two alkaline-earth cations in the hexagonal unit cell. The structures were solved by Fourier methods from photographic data, and refined by least-squares techniques to R 12·2 [(I), 837 observed reflections] and 8·4% [(II), 946 observed reflections]. Each divalent cation is co-ordinated by three sugar anions and three water molecules in a nine-co-ordinate trigonal prism arrangement. The sugar oxygen atoms which co-ordinate to the cation are those of the carboxylate and the sugar ring. We suggest that sugar anions will in general co-ordinate to Ca^{2+} through the carboxylate oxygen and the oxygen function on the α-carbon atom, with these two oxygens in an eclipsed or near-eclipsed conformation. In solution, however, the system may deviate from the eclipsed conformation to facilitate a terdentate complex with its entropic advantage.

ANIONIC sugar residues are often anchored to cell membranes, where they might function in the regulation of cation availability for key biological events such as biosynthesis or transmission of nervous impulses.[1,2] Their interactions with cations are also important in determining the surface charge,[3] and in facilitating various recognition and binding phenomena.[4] Such acidic sugar residues also exist in intercellular regions more remote from the membrane, and their interactions with cations then help to determine the strength, elasticity, permeability, hydration, and ion-exchange properties of the tissue.[5]

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Many of these functions seem to involve divalent cations, especially Ca^{2+}. In an attempt to work towards an understanding of the chemistry of the relevant interactions, we have already used solution methods to investigate the co-ordination of Ca^{2+} by uronic acids[6] and simple polymers.[7] We have now examined some relevant crystal structures and here report the results for calcium sodium galacturonate (I) and the isomorphous strontium sodium galacturonate (II). It is the first example of a crystal structure of the biological important class of Ca^{2+} salts of pyranose sugar acids.

EXPERIMENTAL

Both salts have been described before.[8] (I) Was prepared by neutralization of galacturonic acid (Sigma, recrystallized from ethanol) with reagent-grade calcium carbonate, in an attempt to prepare calcium galacturonate. On repeated crystallization from aqueous propan-2-ol, however, a product was obtained in low yield with an analysis that corresponded to the double salt. We presume that sodium ions were present as an impurity in the calcium carbonate and that the double salt was less soluble and crystallized out.

(II) Was prepared by neutralization of a solution of galacturonic acid with excess of strontium carbonate, the filtrate then being mixed with half a molar equivalent of sodium galacturonate solution, prepared by neutralization of galacturonic acid with sodium carbonate.

Both salts were recrystallized from aqueous alcohol [ethanol for (I), propan-2-ol for (II)] using isothermal distillation as a means to increase the alcohol concentration gradually.

Crystal Data.—These are summarized in Table 1. The hexagonal unit cell is slightly larger for (II) than for (I).

TABLE 1

Crystal data for galacturonate salts

Empirical formula	$NaSrC_{18}H_{39}O_{27}$	$NaCaC_{18}H_{39}O_{27}$
Space group	$P6_3$ (hexagonal)	$P6_3$ (hexagonal)
a/Å	13·56(1)	13·50(1)
c/Å	9·70(1)	9·63(1)
U/Å^3	1544	1520
D_m/g cm^{-3}	1·71	1·64
D_c/g cm^{-3}	1·70	1·64
M	798	750
Z	2	2
μ(Cu-K_α)/cm^{-1}	38·0	28·8
Needle crystals:		
Length/mm	0·4	0·2
Diameter/mm	0·1	0·05
F(000)	824	788

Unit-cell volume and density measurements indicate six galacturonate anions, two Na^+ ions, two divalent cations, and also twelve water molecules in the unit cell of each salt. This and the hexagonal symmetry of Weissenberg photographs mounted parallel to the needle axis, with the presence of $000l$ reflections for even orders only for crystals mounted perpendicular to the needle axis, indicate a space group of $P6_3$ for both salts.

Equi-inclination Weissenberg photographs were taken for layers $hki0$ to $hki7$ for the calcium salt and $hki0$ to $hki8$ for the strontium. Intensities were estimated visually with a calibrated intensity strip, and were put on a common scale by means of an $h0\bar{h}l$ photograph. Lorentz and polarization corrections but no absorption corrections were applied. Scattering factors from ref. 9 were used for calcium, sodium, and strontium, and from ref. 10 for carbon, hydrogen, and oxygen. Calculations were performed on the I.B.M. 360/50 computer at the Edinburgh Regional Computing Centre, using the programmes of '*X*-Ray '70.'[11]

Solution and Refinement of the Structure.—In space group $P6_3$, there are two types of two-fold special positions. The special conditions for an atom at $1/3,2/3,z$ and $2/3,1/3,1/2 + z$ could easily be seen in the diffraction pattern for (II), and could be detected by a statistical survey of the intensities for the data for (I). A difference-Fourier synthesis for the strontium compound phased by structure factors calculated for a strontium ion at 1/3,2/3,1/2, gave a centrosymmetric pattern from which the organic residue could be picked out. Two further syntheses were needed to give an unambiguous position for the sodium ion on $0,0,z$. A further synthesis enabled most of the hydrogen atoms to be located in plausible positions. Least-squares weights were applied such that $w = 1$ for $F_0 < A$, and $w = (A/F_0)^2$ otherwise, where $A = 30$. After anisotropic refinement of the metal ions only, and no refinement of the hydrogen atoms, the final R was 8·4% based on 946 observed reflections.

For (I), refinement was with initial parameters taken to be the same as those of (II) except for the hydrogen atoms which were located independently. The procedure was as before, with the same weighting scheme. The final R was 12·2% for 837 observed reflections. The poorer agreement for (I) could be largely attributed to the poorer quality of the calcium data, and was most marked for the centric reflections $hki0$, R_{Sr} 9·9%, R_{Ca} 16·8%.

Final positional and thermal parameters for both structures are given in Table 2, and observed and calculated structure factors in Supplementary Publication No. SUP 21168 (4 pp.).*

RESULTS

Description of the Structures.—Bonding distances and angles are given in Table 3, and torsion angles in Table 4. These are normal for a pyranosyl group.[12] Each galacturonate ion has the Reeves *C*1 conformation with the hydrogen-bonding pattern shown in Figure 1.

A projection of the structure along the *c* axis is shown in Figure 2. A prominent feature is the relatively open structure, which may be described as layers related by the 2_1 component of the 6_3 screw axis.

In both structures, the sodium ions have a distorted octahedral co-ordination, involving O(2) and O(3) of three sugar anions which are related by the 3 component of the 6_3 axis. The two polyhedra related by the 2_1 component have an inter-residue hydrogen bond, as is shown in Figure 1. As required by the symmetry, the sodium ions are evenly spaced at intervals of *ca*. 4·8 Å. The co-

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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TABLE 2

Fractional co-ordinates ($\times 10^4$), with standard deviations and thermal parameters ($Å^2 \times 10^4$)[a]

Atom	(II)				(I)			
	x	*y*	*z*	*U*	*x*	*y*	*z*	*U*
Sr or Ca	[3333]	[6667]	[5000]	194, 236[b]	[3333]	[6667]	[5000]	209, 98[b]
Na	[10000]	[10000]	6855(11)	217, 332[b]	[10000]	[10000]	6858(15)	244, 279[b]
C(1)	6583(9)	7666(9)	4748(14)	200	6604(12)	7689(13)	4677(20)	232
C(2)	7337(10)	8520(10)	5818(14)	190	7338(12)	8542(12)	5726(20)	210
C(3)	7474(9)	7930(9)	7063(14)	157	7493(13)	7967(13)	7008(21)	208
C(4)	6340(10)	7029(10)	7640(14)	194	6347(13)	7036(13)	7593(21)	208
C(5)	5660(10)	6230(10)	6434(15)	204	5631(14)	6215(14)	6389(23)	289
C(6)	4470(10)	5294(10)	6970(15)	227	4456(13)	5331(13)	6889(20)	246
O(1)	7148(7)	7120(8)	4230(12)	278	7151(10)	7103(10)	4120(17)	322
O(2)	8452(7)	9263(8)	5284(11)	292	8454(9)	9295(10)	5243(16)	333
O(3)	8144(7)	8765(7)	8103(12)	231	8154(9)	8772(9)	8043(15)	221
O(4)	5742(8)	7515(8)	8289(11)	250	5746(10)	7517(10)	8263(16)	289
O(5)	5525(6)	6854(6)	5351(9)	180	5500(8)	6858(8)	5288(14)	184
O(6)	3634(9)	5389(9)	6627(12)	267	3624(9)	5434(10)	6582(16)	246
O(7)	4471(9)	4531(8)	7650(12)	354	4427(11)	4540(11)	7608(16)	380
W(1)	3518(9)	5434(10)	3187(14)	322	3564(10)	5513(10)	3263(10)	326
W(2)	5782(20)	7591(20)	1183(30)	1050	5752(20)	7623(22)	1176(28)	955
Hydrogen atoms attached to:[c]								
C(1)	6430	8110	3890		6500	8090	3720	
C(2)	6940	9030	6150		6930	9050	6020	
C(3)	7950	7520	6780		7950	7550	6670	
C(4)	6480	6540	8420		6500	6540	8370	
C(5)	6130	5820	6050		6120	5800	6030	
O(1)	6990	7010	3200		7210	7430	3190	
O(2)	8590	9570	4230		8500	9510	4060	
O(3)	7870	9230	8630		8180	9430	8450	
O(4)	5950	8240	7850		6190	8300	7860	
W(1)	4410	5570	3100		4350	5460	3030	
	2920	4910	2290		2850	5030	2510	
W(2)	5700	6800	1700		5710	6810	1650	
	5790	7570	190		5770	7600	150	

[a] Standard deviations are not given for hydrogen atoms. Thermal parameters are in the form: isotropic, exp $(-8\pi^2U^2\sin^2\theta/\lambda^2)$; anisotropic, exp $(-2\pi^2\Sigma h_ia^*_ih_ja^*_jU_{ij})$. [b] U_{11} and U_{33} are given. [c] Hydrogen atoms were assigned the thermal parameters of the atoms to which they are bonded.

ordination distances are not significantly different for the two structures.

TABLE 3

Bond lengths (Å) and angles (deg.)

	(I)	(I)
C(1)–C(2)	1·51(2)	1·48(2)
C(2)–C(3)	1·51(2)	1·52(3)
C(3)–C(4)	1·51(2)	1·52(3)
C(4)–C(5)	1·55(2)	1·56(3)
C(5)–O(5)	1·42(2)	1·44(3)
O(5)–C(1)	1·43(1)	1·47(2)
C(1)–O(1)	1·40(2)	1·43(3)
C(2)–O(2)	1·43(2)	1·41(2)
C(3)–O(3)	1·45(2)	1·42(2)
C(4)–O(4)	1·42(2)	1·42(3)
C(5)–C(6)	1·56(2)	1·51(2)
C(6)–O(6)	1·25(2)	1·24(2)
C(6)–O(7)	1·23(2)	1·26(3)
C(1)–C(2)–C(3)	111(1)	111(1)
C(2)–C(3)–C(4)	112(1)	112(1)
C(3)–C(4)–C(5)	107(1)	109(2)
C(4)–C(5)–O(5)	111(1)	110(1)
C(5)–O(5)–C(1)	113(1)	112(1)
O(5)–C(1)–C(2)	110(1)	110(2)
O(5)–C(1)–O(1)	110(1)	110(1)
C(2)–C(1)–O(1)	108(1)	111(2)
C(1)–C(2)–O(2)	111(1)	113(2)
C(3)–C(2)–O(2)	107(1)	105(1)
C(2)–C(3)–O(3)	110(1)	112(1)
C(4)–C(3)–O(3)	111(1)	111(2)
C(3)–C(4)–O(4)	112(1)	111(1)
C(5)–C(4)–O(4)	112(1)	112(2)
C(4)–C(5)–C(6)	109(1)	111(2)
O(5)–C(5)–C(6)	110(1)	108(2)
C(5)–C(6)–O(6)	117(1)	119(2)
C(5)–C(6)–O(7)	115(1)	115(2)
O(5)–C(6)–O(7)	128(1)	126(1)

The alkaline-earth ions are effectively nine-co-ordinate in both structures, and lie on three-fold rotation axes.

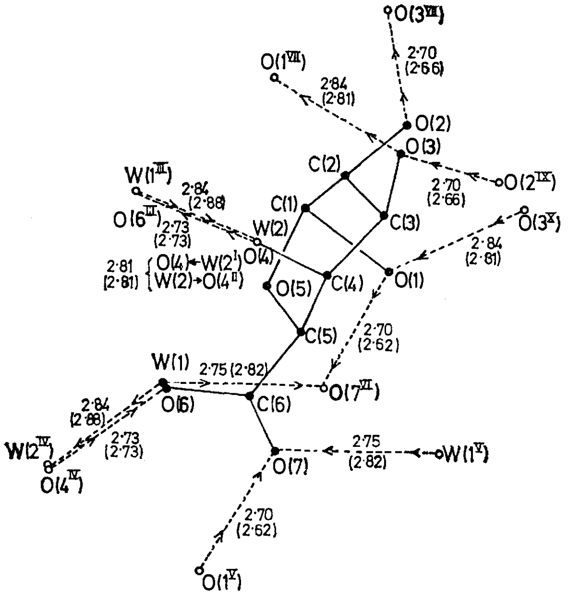

FIGURE 1 Molecular conformation and hydrogen bonding. Symmetry operations are: I $x, y, 1 + z$; II $x, y, z - 1$; III $1 - y, 1 + x - y, z$; IV $y - x, 1 - x, z$; V $1 - x, 1 - y, \frac{1}{2} + z$; VI $1 - x, 1 - y, z - \frac{1}{2}$; VII $y, 1 + y, \frac{1}{2} + z$; VIII $y, 1 + y - z, z - \frac{1}{2}$; IX $1 + x - y, x, \frac{1}{2} + z$; X $1 + x - y, x, z - \frac{1}{2}$. Hydrogen-bond lengths (Å) are given for (II) with those for I in parentheses. The direction of proton donation is shown by arrows

They lie *ca.* 0·3 Å above the plane defined by three related ring-oxygen atoms [O(5)]. In both structures, these atoms are >2·8 Å from the metal ions, which are more closely co-ordinated by three carboxylate oxygens and three water molecules, forming an almost regular trigonal prism. This type of co-ordination is found in some minerals, notably apatite.[13] There is a significant difference in these co-ordination distances in the two compounds, but it parallels the difference of 0·14 Å in ionic radii.[14]

TABLE 4

Torsion angles (deg.), compared with mean literature values for related compounds (from ref. 12)

Angle	(II)	(I)	Lit.
O(5)–C(1)–C(2)–C(3)	53·8	55·4	56·0 ± 4·0
C(1)–C(2)–C(3)–C(4)	−52·5	−51·8	−53·2 ± 3·3
C(2)–C(3)–C(4)–C(5)	52·9	50·8	53·0 ± 3·3
C(3)–C(4)–C(5)–O(5)	−57·7	−56·0	−55·4 ± 4·0
C(4)–C(5)–O(5)–C(1)	63·6	62·5	61·1 ± 3·8
C(5)–O(5)–C(1)–C(2)	−60·7	−62·5	−62·2 ± 3·3
O(1)–C(1)–C(2)–O(2)	52·6	52·1	
O(2)–C(2)–C(3)–O(3)	61·6	59·3	
O(3)–C(3)–C(4)–O(4)	52·6	53·4	
O(4)–C(4)–C(5)–C(6)	−52·4	−55·6	

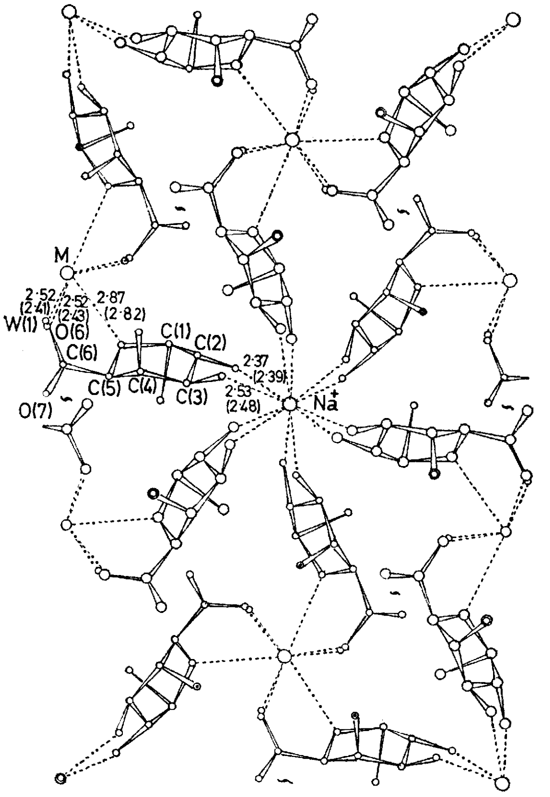

FIGURE 2 Projection of the structures of (I) ($M = Ca^{2+}$) and (II) ($M = Sr^{2+}$) along *c*. The corners of the unit cell are defined by the sodium ions. Co-ordination distances (Å) are given for (II), with those for (I) in parentheses. Note that pairs of Na^+ ions are eclipsed in this projection, as also are W(2) and O(4); W(2) is therefore shown as a smaller circle. Large and small circles are also used to distinguish the sets of oxygen atoms related by the 2_1 component of the 6_3 axis, and hence to distinguish, *inter alia*, between the co-ordination polyhedra of the two eclipsed Na^+ ions

DISCUSSION

The formation of Ca^{2+} complexes of neutral sugars in solution is favoured [15] when the sugar can adopt a stable conformation in which three oxygen atoms form an equilateral triangle of side *ca.* 2·8 Å. All three atoms are presumed to enter the co-ordination shell of the cation with displacement of three water molecules. The triangular arrangement is most commonly formed by oxygen functions which are adjacent and axial-equatorial-axial on a pyranose ring.

In the solid state, many crystalline adducts are known in which this triangular geometry is evidently not required to form a stable complex. In the structures [16] of α-D-xylose,$CaCl_2$,$3H_2O$, α-lactose,$CaBr_2$,$7H_2O$, αα′-trehalose,$CaBr_2$,H_2O, and *myo*-inositol,$CaBr_2$,$5H_2O$, it is common to find that pairs of adjacent oxygen atoms chelate the cations, but only in the structure of β-D-mannofuranose,$CaCl_2$,$4H_2O$ is there an example of chelation by a set of three oxygen atoms.[17] This difference between the solution and solid states is not surprising because the occupation of any set of three co-ordination positions on the same cation by oxygen atoms from the same sugar residue will be favoured by entropic factors in solution which are not important in the solid state. Conversely, the relative stabilities of different co-ordination possibilities in the solid state will be influenced by packing considerations which are not important in the solution.

Corresponding differences seem to be evident when we compare what is known about the co-ordination geometry of calcium galacturonate in solution with the crystal structure which we have now characterized. From a comparison of the stability complexes of the calcium complexes of various uronic acids, we previously concluded that the axial oxygen function at O(4) of galacturonate is likely to be involved in co-ordination to Ca^{2+}.[6] This is confirmed by ^1H n.m.r. using Eu^{3+} as a paramagnetic probe for the Ca^{2+} site.[18] A model was derived in which O(4), O(5), and O(6) form a triangular arrangement in which they all co-ordinate simultaneously to Ca^{2+} [see (A)]. This geometry is not found in the crystal structures of (I) and (II), nor in a related disaccharide structure.[19] Indeed it involves an unusual [20] and probably unstable [21,22] conformation about the C(5)–C(6) bond. In the crystal, the conformation

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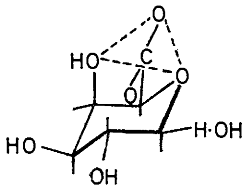
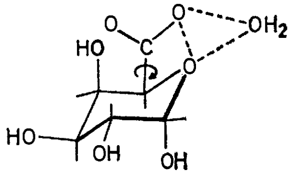
about C(5)–C(6) relaxes to its usual position[20] of near-eclipse between the carboxylate group and C(5)–O(5). Two of the same oxygens co-ordinate to Ca^{2+} in solution and in the crystal. The third position of the ' co-ordinating triangle ' is occupied by a water molecule in the crystal. These relationships are shown schematically in (A) and (B).

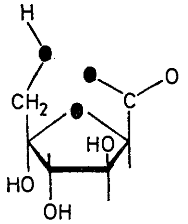


(A)

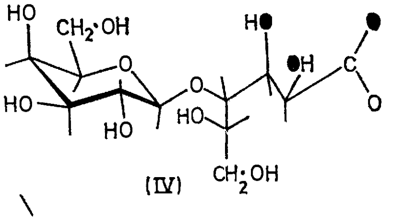


(B)

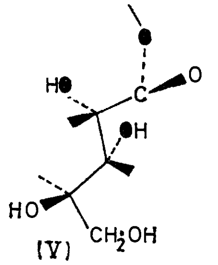
Amongst the calcium and strontium salts of sugar-like acids, whose crystal structures have been determined, are calcium D-*xylo*-hex-5-ulosonate–2-water (III),[23] the double salt CaBr,lactobionate–4-water (IV),[24] calcium D-arabinonate–5-water (V),[25] calcium 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentoate (VI),[22] the calcium salt of the lactone of (—)-hydroxycitric acid (VII),[26] and strontium 4-*O*-(4-deoxy-α-L-*threo*-hex-4-enopyranosyluronate)-D-galacturonate–4·5-water (VIII).[19] Terdentate complexes occur in the crystal structures of (III), (IV), and (V): the oxygen atoms involved are shown as filled circles. In these and in the bidentate complexes [(VI)—(VIII)] apart from certain qualifications which will be added elsewhere,[19] a carboxylate oxygen and an α-oxygen substituent are always involved together in co-ordination to Ca^{2+}. In so doing, they adopt a near-eclipsed conformation in a five-membered ring O·C·C·O·Ca. The terdentate complexes are formed only when the structure of the ligand happens to permit a third oxygen to be placed within 2·8 Å of each of the other two [*cf.* (III)—(V)]. In solution, it would seem that the eclipsing condition can be outweighed by the entropic advantage of the terdentate complex [*cf.* (A) and (B)].



(III)

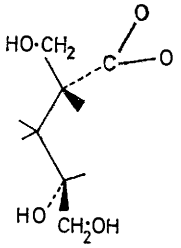


(IV)

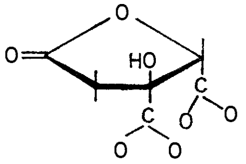


(V)

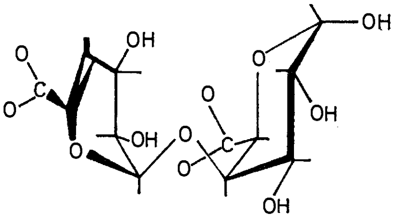
In polysaccharide chains there is the possibility that stable multidentate complexes can be formed by the co-ordination of the hydroxy-groups of neighbouring sugar residues to the same cation. Such an arrangement, in which the planarity of the carboxylate-ring oxygen system is conserved, has indeed been suggested for polyguluronate (IX) and polygalacturonate, in solutions[27] and in the junction zones of Ca^{2+} induced gels.[7]



(VI)

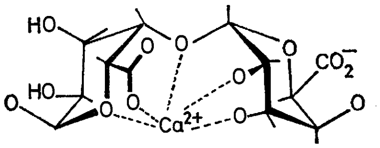


(VII)



(VIII)

This first example of a crystal structure which illuminates the biologically important co-ordination of Ca^{2+} by a pyranose carboxylate anion, therefore suggests that some features of the co-ordination pattern are predictable. These features have more in common with co-ordination by other hydroxycarboxylate anions than with co-ordination by neutral sugars. For example, the ring oxygen is important in co-ordination by the sugar anions, but not usually in the adducts of neutral sugars. The carboxylate oxygen is likewise important whereas the formal charge (as halide anion) is excluded from co-ordination in the adducts. Neutral sugars are usually distorted in their co-ordination to Ca^{2+}, in that pairs of vicinal hydroxy-groups are squeezed



(IX)

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[27] O. Smidsrød, A. Haug, and S. G. Whittington, *Acta Chem. Scand.*, 1972, **26**, 2563.

ca. 0·2 Å inside their usual separation distances, with consequent changes in torsion and bond angles within the ring.[16] The sugar anions appear quite normal in their geometry, although pairs of closely spaced oxygens are provided by the carboxylate and α-oxygens in the near-eclipsed arrangement is discussed earlier.

In almost all the crystalline complexes we have mentioned, the cation is eight-co-ordinate to form a distorted square antiprism. In the calcium halide adducts of D-xylose and αα'-trehalose, the co-ordination is seven-fold in a distorted pentagonal bipyramid. Our galacturonate crystals are the only Ca^{2+} complexes of either neutral or acidic carbohydrates to show nine-fold co-ordination. The geometry, in which the six closest oxygen atoms form an almost regular trigonal prism, has however been found in some Ca^{2+} minerals including apatite.[13]

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