Interactions of Calcium Ions with Carbohydrates. The Crystal Structure of Calcium D-Glycero-D-gulo-heptonate Tetrahydrate

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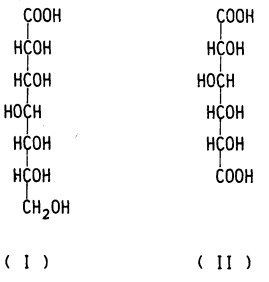
The crystal structure of the calcium salt of D-glycero-D-gulo-heptonic acid has been determined by the X-ray method. The crystal is monoclinic of space group $P2_1$ with unit-cell dimensions of a=10.064(1), b=10.540 (2), c=11.340(2) Å, and β=108.92(1)°. The intensity data for 1754 unique reflections were measured with an automatic diffractometer. A trial structure, obtained by the direct method, was refined by the full-matrix least-squares method to R=0.030. The two independent heptonate anions have different conformations, and they chelate a calcium ion in different ways. The calcium ion is surrounded by eight oxygen atoms in a deformed dodecahedral form, the Ca···O distances ranging from 2.40 Å to 2.48 Å. The distortion of the moleular strcuture of the heptonate anions due to the calcium chelation was discussed in relation to the calcium-binding sites on a linear carbohydrate chain.

The previous X-ray and NMR studies of interactions of calcium ions with carbohydrates in the solid and solution states have shown that the calcium ion is stereospecifically bound with a carbohydrate molecule and that the three-dimensional arrangement of the oxygen atoms of the carbohydrate chain is an important factor in forming a stable calcium–carbohydrate complex.[1] The geometry of the calcium–carbohydrate interactions in many crystalline complexes have been studied to date.[2] It has been reported that the C(6) carboxyl group of D-glucaric acid (II) is unlikely to interact with the calcium ion.[3-5] The carbohydrate chain of D-glycero-D-gulo-heptonic acid (I) has a relatively similar sequence to that of D-glucaric acid (II); the configurations around C(2), C(3), C(4), and C(5) in (I) correspond to the antipodal configurations around C(5), C(4), C(3), and C(2) respectively in (II). Thus the interactions of the calcium ions with the carboxylate (I) is of interest, and the X-ray analysis of the crystal structure of the title complex was undertaken. Since two crystallographically independent anions exist in the crystal structure, their molecular structures were compared in order to make clear the effect of the calcium chelation on the carbohydrate-chain structure.



(I) (II)

Scheme 1.

Experimental

Transparent needle-like crystals were grown by evapolating an aqueous 2-propanol solution of the calcium salt of D-glycero-D-gulo-heptonic acid. The crystal data are: $Ca^{2+}[C_7H_{13}O_8^-]_2 \cdot 4H_2O$, MW=564.5, monoclinic, $P2_1$, Z=2, a=10.064(1), b=10.540(2), c=11.340(2) Å, β=108.92(1)°, and D_x=1.647 g/cm³. The space group $P2_1$ was indicated by the systematic absence of $0k0$ reflections with k odd. The unit-cell parameters were determined by a least-squares analysis of the angular settings of 22 high-angle reflections, measured on a Rigaku AFC-5 diffractometer using a graphite-monochromated Cu $K\alpha$ radiation (λ=1.54178 Å).

The intensity data were collected with the AFC-5 diffractometer operating with a RU-200 X-ray generator (40 KV, 150 mA), using a crystal with dimensions of 0.10×0.14×0.33 mm. A total of 1894 reflections were recorded in the range of $2\theta<120°$ in the $\omega-2\theta$ scanning mode with a scan speed of 4° min^{-1} in ω. The scan width was $\Delta(\omega)=0.8°+0.5\tan\theta$. The data were corrected for Lorentz and polarization factors, and then converted to the F_o structure factors. No absorption correction was applied.

The structure was solved with MULTAN78[6] using 445 reflections for phase-generation. The first E-map revealed one calcium ion and eight oxygen atoms surrounding the calcium ion. Subsequent E-map synthesized with the phases including the contributions of these atoms produced a complete non-hydrogen-atom structure. The trial structure was refined by the full-matrix least-squares method using a modified version of the ORFLS program.[7] The minimized quantity was $\sum w(|F_o|-k|F_c|)^2$, where k was the scale factor, and the weight w was equal to $1/[\sigma^2(F_o)+0.0023F_o)^2]$. All the hydrogen atoms were located from the difference Fourier maps synthesized after several cycles of the least-squares refinement optimizing the positional and anisotropic thermal parameters of the non-hydrogen atoms. The refinements including the positional and isotropic thermal parameters of the hydrogen atoms converged to R=0.030 and R_w=0.041 [$R_w=(\sum w|F_o-kF_c|^2/\sum|F_o|^2)^{1/2}$] for 1754 reflections [$F_o>3\sigma(F_o)$]. Scattering factors for Ca^{2+}, C, O, and H were obtained from the International Tables for X-ray Crystallography (1974).[8] All the computations were performed on a FACOM M-382 in the Data-processing Center of Kyoto University.

Results and Discussion

Table 1 lists the non-hydrogen-atom parameters and their estimated standard deviations. Table 2 lists the hydrogen-atom parameters and their estimated standard deviations. The bond distances and the bond

angles, and the torsion angles, for the non-hydrogen atoms are listed in Table 3 and Table 4 respectively. The anisotropic thermal parameters of the non-hydrogen atoms and the observed and calculated structure factors are preserved at the Chemical Society of Japan (Document No. 8503).

The crystal structure, stereographically illustrated in Fig. 1, is stabilized by the hydrogen bonds and the calcium-oxygen interactions. All the hydrogen atoms of the hydroxyl groups and of the water molecules participate in the hydrogen-bond network. The distances and angles for the hydrogen bonds are listed in Table 5. As is shown in Fig. 2, one calcium ion binds four heptonate anions and one water molecule. One heptonate anion chelates the calcium ion through the carboxyl oxygen O(1A) atom, together with the α-hydroxyl O(2) atom, a second anion through the O(4′) and O(5′) pair of hydroxyl groups, a third anion through the O(6) and O(7) pair of hydroxyl groups, and a fourth anion through the single carboxyl O(1B) atom. Consequently, the calcium ion is surrounded by eight oxygen atoms in a deformed dodecahedron arrangement, as is shown in Fig. 3. The Ca···O distances range from 2.40 Å to 2.48 Å. These distances are the usual distances observed in the other calcium-carbohydrate complex crystals.[9] As has been described in the Introduction, the carboxyl group of the heptonate anion was assumed to be unfavorable to the calcium binding. Actually, in the present crystal structure, the carboxyl oxygen atoms of the primed anion have no direct interactions with the calcium ion, although those of the unprimed anion are bound to the calcium ion.

Table 1. Atomic parameters for non-hydrogen atoms in Ca glucoheptonate $4H_2O$

Atom	x	y	z	B_{eq}/Å^2
CA2+	0.6039(1)	0.0 (0)	0.3985(1)	1.25(5)
C(1)	0.5431(3)	0.3072(3)	0.4248(3)	1.33(12)
C(2)	0.6755(3)	0.3151(3)	0.3860(3)	1.47(13)
C(3)	0.7990(3)	0.3696(3)	0.4920(3)	1.40(12)
C(4)	0.8023(3)	0.5132(4)	0.5134(3)	1.33(12)
C(5)	0.7982(3)	0.5895(3)	0.3980(3)	1.35(12)
C(6)	0.8011(3)	0.7316(3)	0.4222(3)	1.38(12)
C(7)	0.8293(3)	0.8070(4)	0.3183(3)	1.73(12)
O(1A)	0.4969(2)	0.1994(2)	0.4359(2)	1.83(8)
O(1B)	0.4940(2)	0.4109(2)	0.4448(2)	1.63(8)
O(2)	0.7127(2)	0.1911(2)	0.3589(2)	1.79(8)
O(3)	0.8038(2)	0.3113(2)	0.6084(2)	1.63(8)
O(4)	0.9310(2)	0.5430(2)	0.6093(2)	1.60(7)
O(5)	0.9177(2)	0.5523(3)	0.3631(2)	1.80(7)
O(6)	0.6663(2)	0.7743(2)	0.4223(2)	1.89(8)
O(7)	0.8106(2)	0.9390(2)	0.3376(2)	1.88(8)
C(1′)	0.0640(3)	1.0547(4)	0.0711(3)	2.11(12)
C(2′)	0.1561(3)	1.0968(4)	−0.0058(3)	1.90(12)
C(3′)	0.3131(3)	1.1078(4)	0.0688(3)	1.78(12)
C(4′)	0.3954(3)	0.9839(4)	0.0892(3)	1.54(13)
C(5′)	0.3376(3)	0.8809(3)	0.1528(3)	1.38(10)
C(6′)	0.4064(3)	0.7535(4)	0.1469(3)	1.54(12)
C(7′)	0.3588(4)	0.6515(4)	0.2175(3)	2.08(12)
O(1A′)	−0.0207(3)	0.9664(4)	0.0306(3)	3.60(13)
O(1B′)	0.0813(3)	1.1169(3)	0.1695(2)	2.82(10)
O(2′)	0.1353(3)	1.0216(3)	−0.1142(2)	2.95(10)
O(3′)	0.3780(3)	1.1879(3)	0.0008(3)	2.69(12)
O(4′)	0.5357(2)	1.0101(3)	0.1682(2)	1.86(7)
O(5′)	0.3689(2)	0.9215(2)	0.2801(2)	1.66(7)
O(6′)	0.3699(2)	0.7172(3)	0.0190(2)	2.03(8)
O(7′)	0.4266(3)	0.5362(3)	0.2067(2)	2.58(10)
O(W1)	0.7971(2)	1.0335(3)	0.5905(2)	2.25(9)
O(W2)	0.8261(4)	0.8726(3)	0.7854(3)	4.09(15)
O(W3)	0.7006(3)	0.9328(3)	0.0269(2)	2.38(10)
O(W4)	0.8461(3)	0.2466(4)	0.1943(3)	3.57(13)

Estimated standard deviations are given in parentheses. B_{eq} is isotropic equivalent of the anisotropic thermal parameter (Hamilton, 1959).

Table 2. Fractional coordinates and isotropic thermal parameters for hydrogen atoms in Ca glucoheptonate $4H_2O$

Atom	x	y	z	B_{iso}/Å^2
H2	0.649(4)	0.359(4)	0.317(3)	1.7(8)
HO2	0.770(5)	0.194(6)	0.314(4)	4.5(12)
H3	0.882(4)	0.345(5)	0.478(4)	2.4(8)
HO3	0.798(4)	0.229(5)	0.601(4)	3.3(10)
H4	0.721(4)	0.545(4)	0.543(4)	2.3(8)
HO4	0.913(4)	0.564(5)	0.680(4)	3.3(10)
H5	0.697(4)	0.578(4)	0.328(3)	1.4(7)
HO5	0.894(5)	0.540(6)	0.288(4)	5.0(13)
H6	0.878(4)	0.752(4)	0.501(4)	2.3(8)
HO6	0.627(5)	0.743(6)	0.468(4)	4.4(12)
H7A	0.768(4)	0.792(5)	0.249(4)	2.8(9)
H7B	0.920(4)	0.797(5)	0.308(4)	2.8(9)
HO7	0.891(4)	0.972(4)	0.357(4)	2.1(8)
H2′	0.115(4)	1.184(4)	−0.036(4)	2.3(8)
HO2′	0.132(6)	0.949(8)	−0.110(6)	6.8(16)
H3′	0.310(4)	1.148(5)	0.144(4)	2.4(8)
HO3′	0.339(4)	1.267(6)	−0.005(4)	3.5(10)
H4′	0.389(4)	0.952(5)	0.007(4)	2.3(9)
HO4′	0.585(4)	0.987(5)	0.129(4)	2.2(8)
H5′	0.234(4)	0.874(4)	0.112(3)	1.5(8)
HO5′	0.321(4)	0.891(5)	0.316(4)	2.6(9)
H6′	0.507(3)	0.761(4)	0.186(3)	0.8(7)
HO6′	0.438(4)	0.707(5)	0.004(4)	3.2(10)
H7A′	0.356(5)	0.677(6)	0.298(5)	4.6(12)
H7B′	0.250(4)	0.639(5)	0.185(4)	3.1(9)
HO7′	0.422(5)	0.484(6)	0.280(4)	4.4(12)
H(W1A)	0.874(4)	1.047(5)	0.590(4)	3.3(10)
H(W1B)	0.793(5)	0.967(6)	0.647(5)	4.7(11)
H(W2A)	0.831(5)	0.793(6)	0.786(4)	4.5(12)
H(W2B)	0.876(6)	0.901(7)	0.861(6)	6.4(15)
H(W3A)	0.795(5)	0.944(6)	0.052(4)	3.9(11)
H(W3B)	0.661(5)	0.964(6)	−0.041(4)	4.6(12)
H(W4A)	0.771(4)	0.220(5)	0.122(4)	2.6(9)
H(W4B)	0.915(5)	0.210(5)	0.179(4)	3.8(10)

A perspective drawing of the structures of the two independent heptonate anions with thermal ellipsoids of 50% probability is shown in Fig. 4. The backbone conformations of the two moieties differ from each other mainly in the torsion angles around the C(2)–C(3) bonds: the C(1)–C(2)–C(3)–C(4) torsion angle is −77.4(4)°, while the corresponding angle for the primed anion is 82.1(4)°. The conformational difference may be caused by the different intermolecular interactions around the carboxyl groups, since the calcium-oxygen interactions about the carboxyl groups differ remarkably, as has been described above. Apart from the large conformational difference about the C(2)–C(3) bonds, the bond distortions due to the calcium chelation became apparent upon comparing the corresponding bond distances and angles of the two anions (see Table 3). In particular, the C–C–O valence angles are greatly changed by the calcium chelation, and the internal C–C–O angles of the five-membered ring formed by the O–C–C–O linkage with the calcium ion are smaller than those in the absence of the calcium ion. The change in the torsion angles due to the calcium chelation is also remarkable (see Table 4). The calcium chelation tends to decrease the absolute values of the O–C–C–O torsion angles, and the O···O nonbonding distances between the adjacent hydroxyl groups are significantly shorter than the corresponding distances without calcium chelation: O(4′)···O(5′) 2.585(4) Å and O(6)···O(7) 2.636(3) Å for calcium chelation, while O(4)···O(5) 2.753(3) Å and O(6′)··· O(7′) 2.776(4) Å without calcium chelation. These O···O distances in the case of the calcium chelation are smaller than the sum of van der Waals radii (3.04 Å) and also of the ionic radii (2.80 Å) of oxygen atoms. Concerning a calcium chelation by the two hydroxyl oxygen atoms of a linear carbohydrate

TABL 3. BOND LENGTHS(l/Å) AND VALENCE ANGLES(ϕ/°) IN Ca GLUCOHEPTONATE $4H_2O$

Bond	Length	Bond	Length
C (1) - C (2)	1.535 (5)	C (1′) - C (2′)	1.530 (5)
C (1) - O (1 A)	1.249 (4)	C (1′) - O (1 A′)	1.245 (5)
C (1) - O (1 B)	1.250 (4)	C (1′) - O (1 B′)	1.257 (4)
C (2) - C (3)	1.533 (4)	C (2′) - C (3′)	1.536 (4)
C (2) - O (2)	1.420 (4)	C (2′) - O (2′)	1.420 (4)
C (3) - C (4)	1.532 (5)	C (3′) - C (4′)	1.523 (6)
C (3) - O (3)	1.443 (4)	C (3′) - O (3′)	1.435 (5)
C (4) - C (5)	1.525 (5)	C (4′) - C (5′)	1.520 (5)
C (4) - O (4)	1.430 (3)	C (4′) - O (4′)	1.433 (3)
C (5) - C (6)	1.521 (4)	C (5′) - C (6′)	1.522 (5)
C (5) - O (5)	1.437 (4)	C (5′) - O (5′)	1.439 (4)
C (6) - C (7)	1.522 (5)	C (6′) - C (7′)	1.508 (6)
C (6) - O (6)	1.430 (4)	C (6′) - O (6′)	1.428 (4)
C (7) - O (7)	1.430 (5)	C (7′) - O (7′)	1.418 (5)

Bond	Angle	Bond	Angle
C (2) - C (1) - O (1 A)	117.7 (3)	C (2′) - C (1′) - O (1 A′)	118.4 (3)
C (2) - C (1) - O (1 B)	115.8 (3)	C (2′) - C (1′) - O (1 B′)	114.8 (3)
O (1 A) - C (1) - O (1 B)	126.5 (3)	O (1 A) - C (1′) - O (1 B′)	126.8 (4)
C (1) - C (2) - C (3)	110.7 (3)	C (1′) - C (2′) - C (3′)	114.4 (3)
C (1) - C (2) - O (2)	109.0 (3)	C (1′) - C (2′) - O (2′)	112.6 (3)
C (3) - C (2) - O (2)	108.1 (2)	C (3′) - C (2′) - O (2′)	110.8 (3)
C (2) - C (3) - C (4)	117.7 (2)	C (2′) - C (3′) - C (4′)	115.5 (3)
C (2) - C (3) - O (3)	109.6 (3)	C (2′) - C (3′) - O (3′)	108.3 (3)
C (4) - C (3) - O (3)	106.5 (3)	C (4′) - C (3′) - O (3′)	105.4 (3)
C (3) - C (4) - C (5)	113.1 (3)	C (3′) - C (4′) - C (5′)	114.3 (3)
C (3) - C (4) - O (4)	107.8 (3)	C (3′) - C (4′) - O (4′)	107.9 (3)
C (5) - C (4) - O (4)	107.6 (3)	C (5′) - C (4′) - O (4′)	107.0 (3)
C (4) - C (5) - C (6)	111.8 (3)	C (4′) - C (5′) - C (6′)	111.1 (3)
C (4) - C (5) - O (5)	107.5 (2)	C (4′) - C (5′) - O (5′)	105.7 (2)
C (6) - C (5) - O (5)	110.5 (3)	C (6′) - C (5′) - O (5′)	110.6 (2)
C (5) - C (6) - C (7)	111.8 (3)	C (5′) - C (6′) - C (7′)	112.2 (3)
C (5) - C (6) - O (6)	110.3 (2)	C (5′) - C (6′) - O (6′)	108.1 (3)
C (7) - C (6) - O (6)	104.6 (2)	C (7′) - C (6′) - O (6′)	109.1 (3)
C (6) - C (7) - O (7)	108.8 (3)	C (6′) - C (7′) - O (7′)	108.7 (3)

TABLE 4. TORSION ANGLES (ϕ/°) IN Ca GLUCOHEPTONATE $4H_2O$

Bond	Angle	Bond	Angle
C(3)-C(2)-C(1)-O(1A)	−113.5(3)	C(3')-C(2')-C(1')-O(1A')	−130.7(3)
C(3)-C(2)-C(1)-O(1B)	65.0(3)	C(3')-C(2')-C(1')-O(1B')	50.7(4)
C(4)-C(3)-C(2)-C(1)	−77.4(4)	C(4')-C(3')-C(2')-C(1')	82.1(4)
C(4)-C(3)-C(2)-O(2)	163.2(3)	C(4')-C(3')-C(2')-O(2')	−46.6(4)
C(5)-C(4)-C(3)-C(2)	−56.7(3)	C(5')-C(4')-C(3')-C(2')	−56.5(4)
C(5)-C(4)-C(3)-O(3)	179.9(2)	C(5')-C(4')-C(3')-O(3')	−176.1(2)
C(6)-C(5)-C(4)-C(3)	179.8(2)	C(6')-C(5')-C(4')-C(3')	168.8(2)
C(6)-C(5)-C(4)-O(4)	−61.3(3)	C(6')-C(5')-C(4')-O(4')	−71.9(3)
C(7)-C(6)-C(5)-C(4)	167.5(2)	C(7')-C(6')-C(5')-C(4')	175.8(2)
C(7)-C(6)-C(5)-O(5)	47.9(3)	C(7')-C(6')-C(5')-O(5')	58.8(2)
O(2)-C(2)-C(1)-O(1A)	5.3(3)	O(2')-C(2')-C(1')-O(1A')	−2.9(4)
O(2)-C(2)-C(1)-O(1B)	−176.2(2)	O(2')-C(2')-C(1')-O(1B')	178.5(2)
O(3)-C(3)-C(2)-C(1)	44.4(3)	O(3')-C(3')-C(2')-C(1')	−160.0(3)
O(3)-C(3)-C(2)-O(2)	−75.0(3)	O(3')-C(3')-C(2')-O(2')	71.4(4)
O(4)-C(4)-C(3)-C(2)	−175.5(3)	O(4')-C(4')-C(3')-C(2')	−175.4(3)
O(4)-C(4)-C(3)-O(3)	61.0(3)	O(4')-C(4')-C(3')-O(3')	65.1(3)
O(5)-C(5)-C(4)-C(3)	−58.9(2)	O(5')-C(5')-C(4')-C(3')	−71.2(3)
O(5)-C(5)-C(4)-O(4)	60.1(3)	O(5')-C(5')-C(4')-O(4')	48.1(3)
O(6)-C(6)-C(5)-C(4)	−76.6(2)	O(6')-C(6')-C(5')-C(4')	−63.9(3)
O(6)-C(6)-C(5)-O(5)	163.8(2)	O(6')-C(6')-C(5')-O(5')	179.1(2)
O(7)-C(7)-C(6)-C(5)	171.8(1)	O(7')-C(7')-C(6')-C(5')	179.6(2)
O(7)-C(7)-C(6)-O(6)	52.4(2)	O(7')-C(7')-C(6')-O(6')	59.9(2)

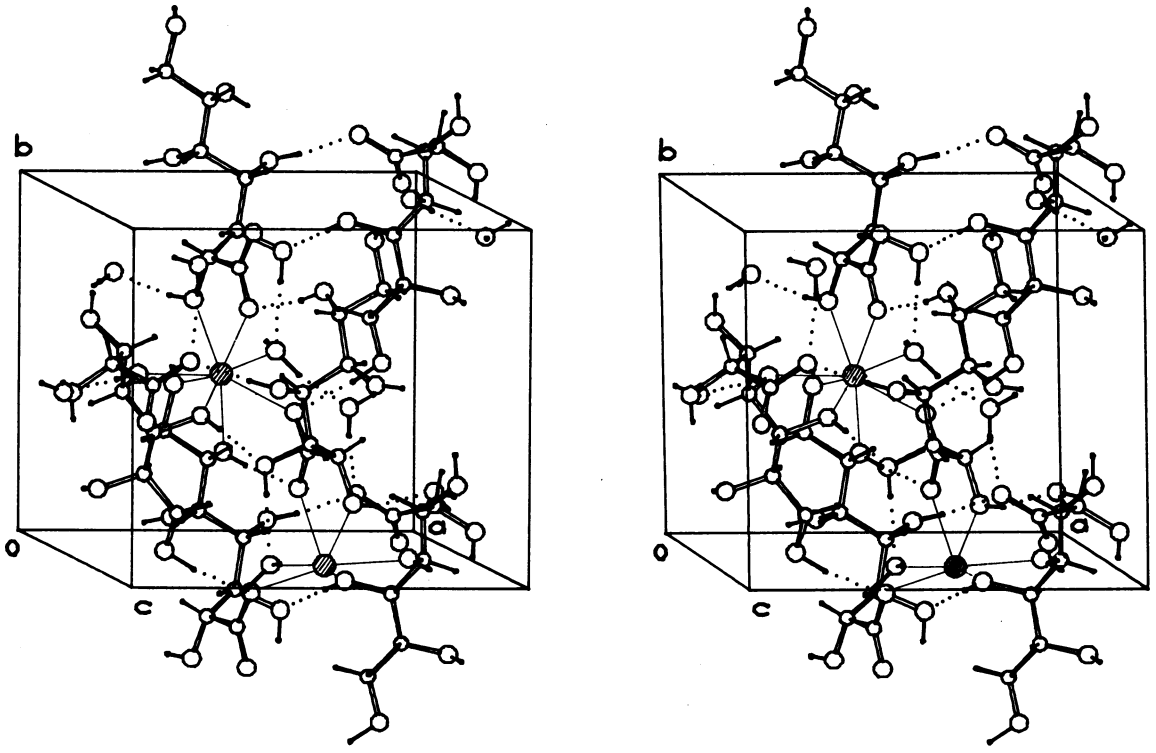


Fig. 1. Stereo view of the unit cell viewed approximately down the *c* axis. Thin and broken lines represent Ca···O interactions and hydrogen-bonds, respectively.

TABLE 5. HYDROGEN-BOND GEOMETRY

	Symmetry operation	O···O	H···O	H-O···O
O(2)-HO2···O(W4)		2.693(5) Å	1.84(6) Å	14(3)°
O(3)-HO3···O(W1)	i	2.934(4)	2.07(5)	2(2)
O(4)-HO4···O(1B')	ii	2.667(4)	1.77(5)	9(2)
O(5)-HO5···O(2')	iii	2.717(3)	1.91(5)	6(3)
O(6)-HO6···O(1A)	iv	2.760(3)	1.96(6)	9(3)
O(7)-HO7···O(4)	v	2.704(3)	1.87(4)	2(3)
O(2')-HO2'···O(W4)	vi	3.061(5)	2.38(8)	23(5)
O(3')-HO3'···O(W3)	vi	2.688(4)	1.79(6)	9(3)
O(4')-HO4'···O(W3)		2.777(4)	1.97(5)	2(3)
O(5')-HO5'···O(3)	iv	2.719(3)	1.93(5)	3(3)
O(6')-HO6'···O(3')	iii	2.637(4)	1.89(5)	8(3)
O(7')-HO7'···O(1B)		2.882(3)	1.94(5)	16(2)
O(W1)-H(W1A)···O(5)	v	2.752(3)	1.99(4)	13(3)
O(W1)-H(W1B)···O(W2)		2.725(4)	1.79(6)	12(3)
O(W2)-H(W2A)···O(1B')	ii	2.843(4)	2.05(6)	16(3)
O(W2)-H(W2B)···O(1A')	vii	2.882(4)	1.99(6)	2(4)
O(W3)-H(W3A)···O(1A')	viii	2.814(4)	1.96(5)	17(3)
O(W3)-H(W3B)···O(7')	vi	2.765(3)	1.96(5)	2(4)
O(W4)-H(W4A)···O(6')	iii	2.695(3)	1.76(3)	10(3)
O(W4)-H(W4B)···O(1B')	ix	2.825(5)	1.97(5)	6(4)

i $+x, -1+y, +z$ iv $1-x, 1/2+y, 1-z$ vii $1+x, +y, 1+z$
ii $1-x, 1/2+y, 1-z$ v $2-x, 1/2+y, 1-z$ viii $1+x, +y, +z$
iii $1-x, -1/2+y, -z$ vi $1-x, 1/2+y, -z$ ix $1+x, -1+y, +z$

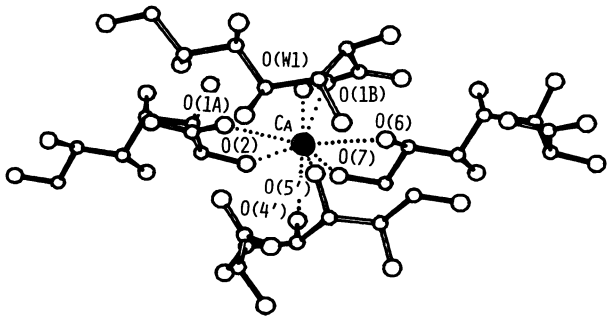


Fig. 2. Representation of the environment of the calcium ion.

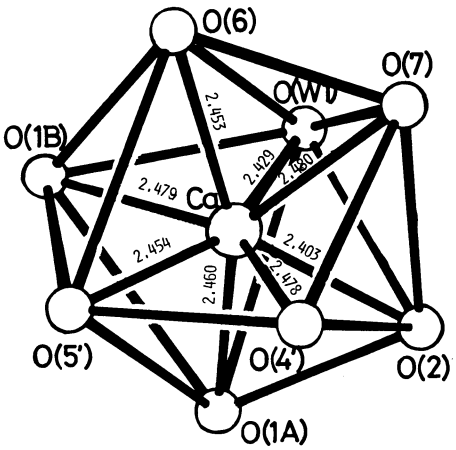


Fig. 3. Calcium-ion coordination shell.
Estimated standard deviations are 0.003 Å for the Ca···O distances.

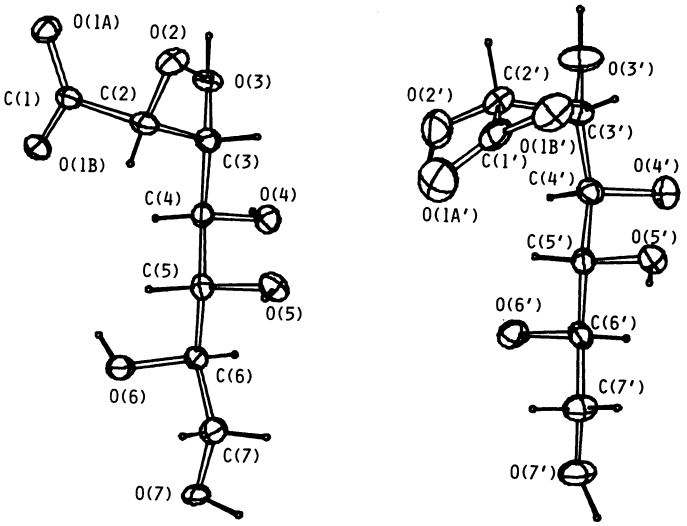
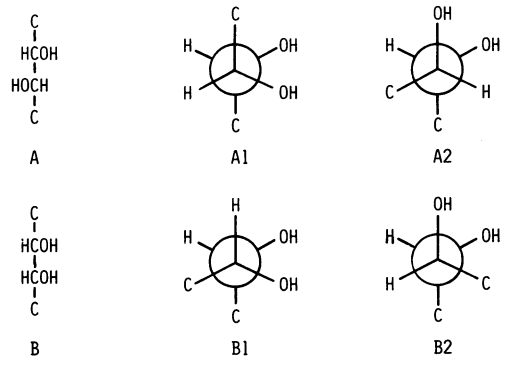


Fig. 4. Comparison of the molecular conformations of the two heptonate anions.

chain, it seems possible for four stable gauche conformations, represented as A1, A2, B1, and B2, to chelate a calcium ion. From a consideration of the bond distortions due to the calcium chelation described above, the B conformations are, however, unfavorable to the calcium chelation, because the calcium binding to B1 and B2 will decrease the absolute values of the O-C-C-O and C-C-C-C torsion angles and result in energetically unfavorable backbone conformations. On the other hand, the effects



Scheme 2.

of such bond distortions on the A conformers are small. For A2, a decrease in the absolute O–C–C–O torsion angle accompanies the increase in the absolute C–C–C–C torsion angle. The calcium chelation through the O(4′) and O(5′) atoms in the present crystal corresponds to Al. To our knowlege, there are no calcium chelation by the B conformations in the reported crystal structures of the calcium linear-carbohydrate complexes.[10–12] In conclusion, the calcium chelation by the two hydroxyl oxygen atoms decreases the absolute value of the O–C–C–O torsion angle; this fact indicates that, in general, the calcium chelation by the linear carbohydrate chain occurs selectively at the site of the configuration A in which the two hydoxyl groups are located on opposite sides of the carbon chain in the Fischer notation.

References

1) S. L. Angyal, *Chem. Soc. Rev.*, **9**, 415 (1980).
2) H. Einspahr and C. E. Bugg, *Acta Crystallogr.*, **37**, 1044 (1981).
3) T. Taga and K. Osaki, *Bull. Chem. Soc. Jpn.*, **49**, 1517 (1976).
4) T. Taga, Y. Kuroda, and K. Osaki, *Bull. Chem. Soc. Jpn.*, **50**, 3079 (1977).
5) T. Taga, Y. Kuroda, and M. Ohashi, *Bull. Chem. Soc. Jpn.*, **51**, 2278 (1978).
6) P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, "MULTAN 78. A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Date," Universities of York and Louvain (1978).
7) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS. Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee (1962).
8) International Tables for X-ray Crystallography, Vol. IV, Birmingham, Kynoch Press (1974), pp. 71—151.
9) T. Taga, M. Ohashi, and K. Osaki, *Bull. Chem. Soc. Jpn.*, **51**, 1697 (1978).
10) S. Furberg and S. Helland, *Acta Chem. Scand.*, **16**, 2373 (1962).
11) R. Norrestam, P.-E. Werner, and M. Glehn, *Acta Chem. Scand.*, **22**, 1395 (1968).
12) W. J. Cook and C. E. Bugg, Acta Crystallogr., Sect. B., **29**, 215 (1973).