The Crystal Structures of Calcium and Strontium 3-Deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentonate and Some Extended Hückel Calculations on the Corresponding Acid

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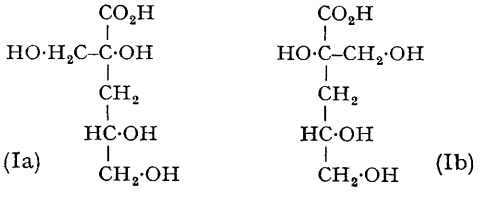
THE crystal structures of two isomorphous D-glucoisosaccharates, $Ca(C_6H_{11}O_6)_2$ and $Sr(C_6H_{11}O_6)_2$, have been determined by *X*-ray diffraction methods in order to elucidate the molecular structures of the two glucoisosaccharinic acids. The crystal structure analyses have established that α-D-glucoisosaccharinic acid[1] is 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentonic acid. The salts are formed by neutralizing α-D-glucoisosaccharinic acid by calcium and strontium hydroxide, respectively.[1] The possible Fischer diagrams of the corresponding acid are



The *X*-ray analyses show that the α-D-glucoisosaccharate ion (Figure 1) agrees with the representation I(a).

Powder specimens of calcium and strontium α-D-glucoisosaccharate were kindly supplied by A. Ishizu (Swedish Forest Products Research Laboratory). Single crystals suitable for *X*-ray analysis were obtained by slowly cooling saturated aqueous solutions. Three-dimensional *X*-ray data were collected by using a General Electric single-crystal orienter equipped with a scintillation detector and a pulse-height analyser set to collect about 90% of the Cu-K_α radiation used.

The structure of the cation is shown in Figure 1. The carbon chain has a twist at C(4) and therefore only C(2′), C(2), C(3), and C(4) form a planar zigzag chain. The twist may be regarded as a rotation of about 75° around the C(3)—C(4) bond from a planar carbon chain. A calculation of a least-squares plane through O(0), O(1), C(1), and C(2)

TABLE

Crystallographic data of calcium and strontum α-D-glucoisosaccharate

	Strontium salt	Calcium salt
Lattice constants:	a = 20·034 Å	a = 19·604 Å
	b = 6·909	b = 6·782
	c = 5·730	c = 5·749
Cell volume:	793·1 Å^3	764·4 Å^3
Density (X-ray):	1·867 g. cm.$^{-3}$	1·418 g. cm.$^{-3}$
Molecules per unit cell:	2	2
Space group:	$P2_12_12$	$P2_12_12$
Measuring technique:	θ—2θ scanning	peak intensity measurements
Anisotropic temperature factors applied on:	Sr, O, and C	Ca
Isotropic temperature factors applied on:	—	O and C
R-Value	0·058	0·108

shows that these atoms are without significant deviation coplanar, but atom O(2) deviates slightly, 0·30 Å, from this plane. Therefore, the intramolecular distance O(0)—O(2) is as short as 2·60 Å.

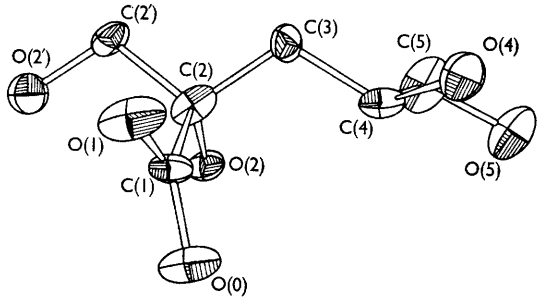


FIGURE 1. *Structure of the α-D-glucoisosaccharate ion as illustrated by means of the plot programme.*[2]

Eight oxygen atoms related by a two-fold axis form a distorted Archimedean antiprism around each metal ion. This co-ordination polyhedron consists of oxygen atoms from four different cations. Each cation is thus co-ordinated to two anions.

On each cation there are four hydrogen atoms available for hydrogen bonding and there are four intermolecular O–O distances less than or equal to 2·90 Å outside the co-ordination polyhedron. This gives a plausible intermolecular hydrogen bonding scheme involving all the oxygen atoms. The assumed hydrogen bonds link the molecules in all directions so that a three-dimensional network is formed.

Extended Hückel calculations on the acid show an energy minimum for an almost planar group C(1), O(0), O(1), C(2), O(2) and it is concluded that there is no tendency for the free acid to increase the short O(0)—O(2) distance by rotation of the carboxylic group. The energy calculated for a planar-staggered zigzag chain C(2'), C(2), C(3), C(4), and C(5) is 0·8 ev higher than the energy calculated for the configuration obtained from the crystal structure. Therefore, the possibility may not be excluded that the carbon chain has a twist at C(4) in the solvated acid also. Furthermore, it is noticeable that C(3) is the only carbon atom with a calculated negative net charge.

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[1] A. A. J. Feast, B. Lindberg, and O. Theander, *Acta Chem. Scand.*, 1965, **19**, 1127.
[2] C. K. Johnson, ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal-Structure Illustrations, Oak Ridge National Laboratory, ORNL-3794.