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THE CRYSTAL STRUCTURE OF THE ADDUCT $3NaI \cdot 2SUCROSE \cdot 3H_2O$*

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ABSTRACT

The complex $3NaI \cdot 2Sucrose \cdot 3H_2O$ crystallizes in the $C2$ space group with cell constants $a = 17.177(3)$, $b = 8.388(1)$, $c = 29.696(4)$ Å, and $\beta = 94.72(1)°$, and forms infinite chains parallel to [001] interlinked by hydrogen bonds. The cations are located in the most negative potential zone compatible with the sum of the bond radii.

INTRODUCTION

Only in the last decade has particular attention been paid to complexes formed by alkali and alkaline-earth metals and polyhydroxylated ligands such as carbohydrates and inositols, often in connection with the role of these compounds in cellular transport in biological systems. The intracellular activity of Ca^{2+} is connected with polyhydroxylated ligands, and carbohydrates and amino acids are involved in the gastro-intestinal absorption of Ca^{2+} and other alkaline-earth cations[1]. Alkali metals usually form weak complexes with such "hard" donor atoms and, although their importance is accepted in the maintainance of water balance, the conduction of axon impulses, and the maintainance of neuromuscular activity[2], their biological behaviour is not completely understood.

Several studies have been undertaken on the thermodynamics of sugar–cation–water systems in relation to the ability of polyhydroxylated compounds to modify free energies and heat capacities[3]. It is reasonable to assume that the cation co-ordination in a salt–sugar–water mixed crystal is, in some respects, representative of the situation in solution. Thus, structural determination of such mixed crystals is a starting point for the construction of molecular models for these ternary systems.

In salt–sugar–water crystals, water, sugar and the anion compete to coordinate the cation, and both water and sugar molecules are able to bind the anion by means of hydrogen bonds. These factors contribute to hinder formation of ion

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pairs. A systematic analysis of the principles of co-ordination of M^{2+} ions must take into account both the co-ordination ability of the solvent and the properties of the ligand[4]. It has been found by electrophoretic methods that, in solution, the most suitable arrangement of the hydroxyl groups on the sugar co-ordinating the cation is *cis–cis* in glycofuranoses and *ax–eq–ax* in glycopyranoses[5], whereas two OH groups seem to be sufficient for complexation[6] in crystals.

We now report the crystal structure of the $3NaI \cdot 2Sucrose \cdot 3H_2O$ adduct and a detailed discussion on the co-ordinative modalities of the Na^+ cation in this particular salt–sugar–water ternary system.

EXPERIMENTAL

Preparation of $3NaI \cdot 2Sucrose \cdot 3H_2O$. — A solution of sucrose (10 g, 0.029 mol) and NaI (6.6 g, 0.044 mol) in water (10 mL) was allowed to concentrate slowly at room temperature, to give large crystals of dendritic shape.

Determination of crystal structure. — Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with monochromated MoK_α radiation and the

TABLE I

CRYSTAL DATA FOR $3NaI \cdot 2SUCROSE \cdot 3\ H_2O$

Formula	$C_{24}H_{50}Na_3I_3O_{25}$
Mol. wt.	1188.32
Space group	$C2$
a (Å)	17.177(3)
b (Å)	8.388(1)
c (Å)	29.696(4)
β (°)	94.72(1)
V (Å^3)	4264(1)
Z	4
$d_{calc.}$ (g.cm^{-3})	1.85
Crystal size (mm)	0.31 × 0.36 × 0.40
Radiation	MoK_α
Monochromator	Graphite
μ (MoK_α) (cm^{-1})	22.9
Temp. (°)	22
Scan method	$\omega/2\theta$
Data collection range (θ) (°)	2–27
No. of unique reflections	4967
No. of reflections with $I > 3\sigma(I)$	4335
No. of parameters refined	649
R^a	0.026
R_w^b	0.034
Weighting scheme	$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02\,F_o^2)^2]$
Largest shift/error, last cycle	0.40
S = error in an observation of unit weight	1.46
Largest peak in the final difference map outside I^- coordination sphere (eÅ^{-3})	0.391

[a] $\Sigma|\Delta F_o|/\Sigma|F_o|$. [b] $(\Sigma_w|\Delta F_o|^2/\Sigma_w|F_o|^2)^{1/2}$.

TABLE II

POSITIONAL ($\times 10^4$) AND THERMAL PARAMETERS FOR $3NaI \cdot 2$SUCROSE $\cdot 3H_2O$ WITH E.S.D.'S IN PARENTHESES

Atom	x	y	z	B_{eq}
I-1	1342.2(3)	5256.8(5)	4557.0(1)	4.255(8)
I-2	1319.9(2)	13.5	538.5(1)	3.588(7)
I-3	918.7(2)	7698.6(5)	2626.6(1)	3.616(6)
Na-1	−700(1)	301(3)	4561.6(6)	2.91(4)
Na-2	−727(1)	4910(3)	353.2(6)	2.81(4)
Na-3	−839(1)	2385(3)	2432.8(6)	2.60(4)
O-1A	−520(2)	3849(4)	1641.1(9)	1.62(5)
O-2A	181(2)	1182(4)	2021(1)	2.86(6)
O-3A	1692(2)	2606(6)	2176(1)	3.21(7)
O-4A	1803(2)	5715(5)	1725(1)	2.98(7)
O-5A	241(2)	3679(4)	1022.7(9)	1.87(5)
O-6A	567(2)	6127(5)	429(1)	3.30(7)
O-1′A	−1724(2)	1820(5)	1736(1)	3.91(8)
O-2′A	−1274(2)	5286(4)	1087.0(9)	2.10(5)
O-3′A	−1240(2)	4971(5)	2280(1)	3.38(7)
O-4′A	−1866(2)	8222(4)	1859(1)	2.32(6)
O-6′A	−1245(3)	7590(6)	446(1)	4.82(9)
C-1A	−92(2)	2827(5)	1372(1)	1.68(7)
C-2A	543(2)	2069(6)	1683(2)	2.17(8)
C-3A	1078(2)	3340(6)	1894(2)	2.04(8)
C-4A	1393(2)	4379(6)	1535(1)	1.90(8)
C-5A	755(2)	4945(6)	1179(1)	1.93(7)
C-6A	1133(3)	5522(7)	769(2)	2.77(9)
C-1′A	−1801(2)	2860(6)	1363(2)	2.60(9)
C-2′A	−1288(2)	4306(5)	1478(1)	1.77(7)
C-3′A	−1585(2)	5381(5)	1851(1)	1.97(7)
C-4′A	−1391(2)	7034(5)	1690(1)	1.72(7)
C-5′A	−1540(3)	6862(5)	1182(1)	1.95(8)
C-6′A	−1117(3)	8044(6)	910(2)	3.3(1)
O-1B	−508(2)	1138(4)	3279(1)	1.81(5)
O-2B	35(2)	3888(5)	2961(1)	3.56(7)
O-3B	1694(2)	3100(6)	3071(1)	4.59(9)
O-4B	2007(2)	160(6)	3526(1)	3.89(8)
O-5B	193(2)	1518(4)	3985.2(9)	1.87(5)
O-6B	605(2)	−803(5)	4623(1)	3.16(7)
O-1′B	−1928(2)	2460(6)	2934(1)	4.59(9)
O-2′B	−1178(2)	−387(4)	3774(1)	2.23(6)
O-3′B	−1001(2)	−565(4)	2595(1)	2.34(6)
O-4′B	−1744(2)	−3640(5)	3021(1)	3.08(7)
O-6′B	−1210(3)	−2353(6)	4481(1)	6.0(1)
C-1B	−173(2)	2263(5)	3596(1)	1.88(7)
C-2B	432(3)	3207(6)	3356(2)	2.44(8)
C-3B	1091(2)	2159(7)	3236(2)	2.59(9)
C-4B	1434(3)	1274(7)	3644(2)	2.62(9)
C-5B	819(2)	459(6)	3907(1)	2.00(8)
C-6B	1184(3)	−75(7)	4366(2)	2.97(9)
C-1′B	−1878(3)	1701(6)	3364(2)	2.63(9)
C-2′B	−1239(2)	471(5)	3360(1)	1.74(7)
C-3′B	−1427(2)	−785(6)	2985(1)	1.95(8)
C-4′B	−1298(2)	−2371(6)	3219(1)	2.20(8)
C-5′B	−1477(3)	−1973(5)	3702(2)	2.28(8)
C-6′B	−1095(4)	−3052(7)	4055(2)	4.0(1)
O-1W	0	2890(7)	0	3.2(1)
O-2W	0	2395(7)	5000	3.5(1)
O-3W	−1744(3)	2122(7)	4560(2)	5.9(1)
O-4W	−1846(3)	3399(7)	167(2)	6.4(1)

$\omega/2\theta$ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centered reflections in the range $9 < \theta < 15°$. The crystal data are reported in Table I. Intensities were corrected for Lorentz, polarization, and absorption (minimum transmission factor, 64.7%). Scattering factors and anomalous dispersion parameters were taken from International Tables for X-Ray Crystallography[7].

The positions of two I^- ions were located from the Patterson map and all other non-H atoms from subsequent Fourier maps. All H atoms were found in the difference map. After a few cycles of isotropic refinement, the structure was refined by full-matrix least-squares, using anisotropic temperature factors for all non-H atoms. Positional and thermal parameters of some hydrogen atoms were kept fixed during refinement*. Weights for the last cycle were applied according to the scheme given in Table I. All calculations were done by the SDP system of programs[8]. Final positional and thermal parameters for non-H atoms are given in Table II.

DESCRIPTION OF THE STRUCTURE

Bond distances and a selection of torsion angles are reported in Tables III and IV, respectively. The asymmetric unit (Fig. 1) consists of two sucrose molecules, three Na^+ ions, three I^- ions, and three water molecules. Such units, related by two-fold symmetry axes at 0, *y*, 1/2 and 0, *y*, 0 passing through the two water molecules W1 and W2 on the opposite ends, generate infinite chains parallel to the [001] direction. The chains have a tunnel "zigzag" shape and include all the Na^+ ions, whereas the I^- ions are arranged three-by-three on the opposite sides of the chain. The chains are cross-linked by a network of hydrogen bonds (some bifurcated) and by I^- ions co-ordinated to both water molecules and sugar hydroxyl groups. Fig. 2 shows the crystal packing, and hydrogen bonds are indicated by dashed lines. Table V lists the intra- and inter-molecular hydrogen bonds.

Cations and anions are separately solvated by sucrose and water molecules, and Tables VI and VII give the bond distances of Na^+ and I^- co-ordination polyhedra. Although the asymmetric unit contains three different Na^+ and I^- ions, I-1,2 and Na-1,2 are similar from the point of view of co-ordination because the whole unit has a pseudo-two-fold axis that is almost parallel to *a* and passes through Na-3. The I-3 ion is co-ordinated, in a distorted octahedron, to six hydroxyl groups [average H---I distance 2.94(14)Å] belonging to six different sugar molecules of three different asymmetric units together with two hydrogens bonded to the carbon skeleton of the asymmetric unit sugar molecule, but at a greater distance. The co-ordination around I-1 and I-2 is similar, does not correspond to any definite geometrical form, and involves five hydroxyl groups of five different asymmetric units, two from sugar molecules and three from water molecules [average H---I

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*Tables of anisotropic thermal parameters and bond angles are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/410 *Carbohydr. Res.*, 191 (1989) 91–104.

TABLE III

BOND DISTANCES (Å) IN $3NaI \cdot 2SUCROSE \cdot 3H_2O$ WITH E.S.D.'S IN PARENTHESES

O-1A–C-1A	1.418(4)	O-1B–C-1B	1.422(5)
O-1A–C-2′A	1.419(5)	O-1B–C-2′B	1.413(4)
O-2A–C-2A	1.431(5)	O-2B–C-2B	1.427(5)
O-3A–C-3A	1.430(5)	O-3B–C-3B	1.421(5)
O-4A–C-4A	1.416(5)	O-4B–C-4B	1.422(6)
O-5A–C-1A	1.418(4)	O-5B–C-1B	1.415(5)
O-5A–C-5A	1.433(5)	O-5B–C-5B	1.428(5)
O-6A–C-6A	1.435(6)	O-6B–C-6B	1.438(7)
O-1′A–C-1′A	1.408(6)	O-1′B–C-1′B	1.423(7)
O-2′A–C-2′A	1.426(5)	O-2′B–C-2′B	1.421(5)
O-2′A–C-5′A	1.434(5)	O-2′B–C-5′B	1.435(5)
O-3′A–C-3′A	1.403(5)	O-3′B–C-3′B	1.432(5)
O-4′A–C-4′A	1.406(5)	O-4′B–C-4′B	1.411(6)
O-6′A–C-6′A	1.430(6)	O-6′B–C-6′B	1.423(7)
C-1A–C-2A	1.510(6)	C-1B–C-2B	1.527(5)
C-2A–C-3A	1.511(6)	C-2B–C-3B	1.499(7)
C-3A–C-4A	1.511(7)	C-3B–C-4B	1.498(6)
C-4A–C-5A	1.535(5)	C-4B–C-5B	1.527(6)
C-5A–C-6A	1.506(7)	C-5B–C-6B	1.519(6)
C-1′A–C-2′A	1.522(6)	C-1′B–C-2′B	1.507(6)
C-2′A–C-3′A	1.546(5)	C-2′B–C-3′B	1.548(5)
C-3′A–C-4′A	1.513(6)	C-3′B–C-4′B	1.509(6)
C-4′A–C-5′A	1.517(5)	C-4′B–C-5′B	1.528(5)
C-5′A–C-6′A	1.502(6)	C-5′B–C-6′B	1.495(7)

TABLE IV

A SELECTION OF TORSION ANGLES (°) IN $3NaI \cdot 2SUCROSE \cdot 3H_2O$ WITH E.S.D.'S IN PARENTHESES

C-2A–C-1A–O-1A–C-2′A	−159.6(3)		C-2B–C-1B–O-1B–C-2′B	−160.3(3)
O-5A–C-1A–O-1A–C-2′A	79.9(4)		O-5B–C-1B–O1-B–C-2′B	79.6(4)
C-1A–O-1A–C-2′A–O-2′A	−66.6(4)		C-1B–O-1B–C-2′B–O-2′B	−61.6(4)
C-1A–O-1A–C-2′A–C-3′A	179.2(3)		C-1B–O-1B–C-2′B–C-3′B	−176.0(3)
O-5A–C-5A–C-6A–O-6A	61.3(5)	g	O-5B–C-5B–C-6B–O-6B	56.9(5)
C-4A–C-5A–C-6A–O-6A	−177.8(4)	t	C-4B–C-5B–C-6B–O-6B	178.3(4)
O-1′A–C-1′A–C-2′A–O-1A	50.0(4)		O-1′B–C-1′B–C-2′B–O-1B	59.1(5)
O-1′A–C-1′A–C-2′A–O-2′A	172.7(3)	t	O-1′B–C-1′B–C-2′B–O-2′B	−177.5(3)
O-1′A–C-1′A–C-2′A–C-3′A	−69.2(4)	g	O-1′B–C-1′B–C-2′B–C-3′B	−60.5(5)
O-2′A–C-5′A–C-6′A–O-6′A	55.7(5)	g	O-2′B–C-5′B–C-6′B–O-6′B	53.8(6)
C-4′A–C-5′A–C-6′A–O-6′A	173.0(4)	t	C-4′B–C-5′B–C-6′B–O-6′B	170.1(4)

distance 2.84(8)Å] distributed on one hemisphere, the remaining empty space being occupied by contacts of two, in I-2, or three, in I-1, hydrogens of the sugar skeleton.

The central Na-3 ion is surrounded by eight sugar oxygens (Fig. 1). The co-ordination polyhedron can be described as an octahedron whose opposite O-2, O-1′, O-3′ faces are capped by the two O-1 atoms. This arrangement is determined mainly by the geometrical constraints induced by the two conformationally rather

TABLE V

INTER- AND INTRA-MOLECULAR HYDROGEN BONDS IN $3NaI \cdot 2$SUCROSE$\cdot 3H_2O$ (DISTANCES IN Å WITH E.S.D'S IN PARENTHESES)

Bond		$d_{O\cdots O}$	d_{O-H}	$d_{H\cdots O}$	*Translational vector*
O-3B–H(O-3B)---O-3A	I[a]	2.690(4)	0.74(5)	1.95(3)	0,0,0
O-3A–H(O-3A)---O-4′A	III	2.770(5)	0.70(5)	2.09(5)	0, −1,0
O-1′A–H(O-1′A)---O-4A′	III	2.663(5)	0.85	1.89	−1, −1,0
O-1′A–H(O-1′A)---O-4′A	I	3.050(5)	0.85	2.56	0, −1,0
O-3′A–H(O-3′A)---O-4′B	I	2.695(5)	0.97(5)	1.78(4)	0,1,0
O-4′A–H(O-4′A)---O-3′B	I	2.736(4)	0.57(6)	2.18(6)	0,1,0
O-6B–H(O-6B)---O-6′B	II	3.065(5)	0.89(7)	2.89(6)	0,0,1
O-4′B–H(O-4′B)---O-3B	III	3.069(5)	0.97	2.50	−1, −1,0
O-4′B–H(O-4′B)---O-4B	III	2.897(5)	0.97	1.96	−1, −1,0

[a] I, x,y,z; II, $-x,y,-z$; *III*, $x + 1/2, y + 1/2, z$.

rigid sucrose molecules acting as tetradentate ligands. Such a geometrical solid is somewhat deformed towards a C_2 symmetry, the angle between the two opposite triangular faces being 155.8°. Each Na-1 and Na-2 ion co-ordinates seven oxygen atoms, four from the adjacent sucrose molecule and two from water molecules; the seventh oxygen is O-6 of another sucrose molecule related by a crystallographic two-fold axis. The co-ordination is approximately bipyramidal pentagonal with O-6 and a water molecule at the apices.

Conformational modifications induced in the ligand by the co-ordination have been studied mainly for complexes with crown-ethers and cyclic antibiotics[9,10], and limited data are available for complexes involving carbohydrates and Ca^{2+} ions[1]. Sucrose alone or as a moiety in trisaccharides has remarkable conformational stability[11] in that the glucose ring adopts the $^4C_1$ conformation and the fructose ring

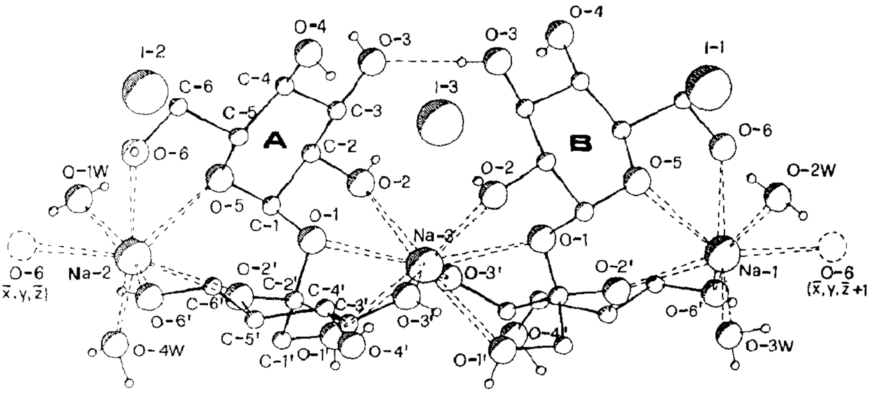

Fig. 1. A view of the content of the asymmetric unit. The dashed lines show the co-ordination around the cations.

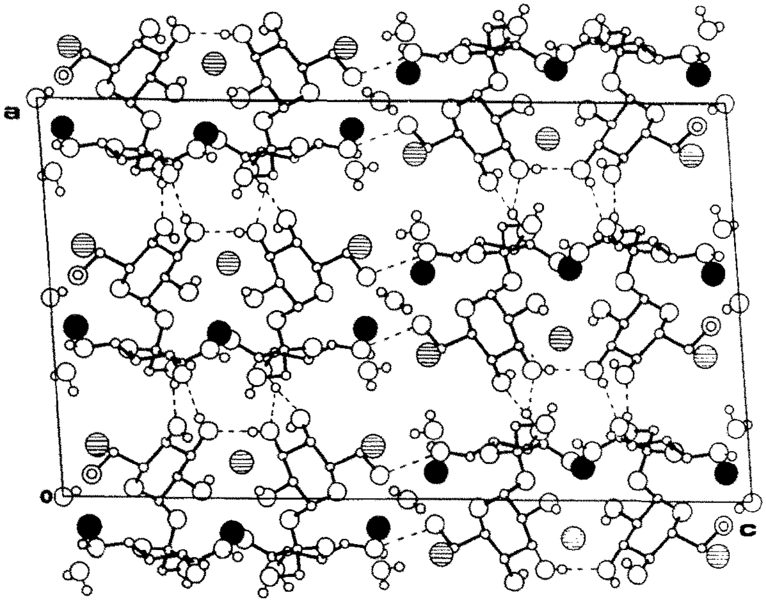

Fig. 2. View along axis *b* of the packing in the unit cell. The dashed lines represent the hydrogen bonds. The Na^+ ions are drawn as full circles and the I^- ions as hatched circles.

TABLE VI

Na–O DISTANCES FOR $3NaI \cdot 2$SUCROSE$\cdot\cdot 3H_2O$ IN THE CO-ORDINATION POLYHEDRA OF Na^+ IONS

Atoms		*Distance (Å)*[a]	*Translational vector*
Na-1–O-5B	I[b]	2.599(3)	0,0,0
Na-1–O-6B	I	2.419(4)	0,0,0
Na-1-O-2′B	I	2.483(3)	0,0,0
Na-1–O-6′B	I	2.397(5)	0,0,0
Na-1–O-W2	I	2.443(4)	0,0,0
Na-1–O-W3	I	2.355(5)	0,0,0
Na-1–O-6′B	II	2.585(4)	0,0,1
Na-2–O-5A	I	2.691(3)	0,0,0
Na-2–O-6A	I	2.439(4)	0,0,0
Na-2–O-2′A	I	2.464(3)	0,0,0
Na-2–O-6′A	I	2.442(5)	0,0,0
Na-2–O-W1	I	2.397(4)	0,0,0
Na-2–O-W4	I	2.331(5)	0,0,0
Na-2–O-6′A	II	2.573(4)	0,0,0
Na-3–O-1A	I	2.747(3)	0,0,0
Na-3–O-2A	I	2.437(4)	0,0,0
Na-3–O-1′A	I	2.510(4)	0,0,0
Na-3–O-3′A	I	2.310(4)	0,0,0
Na-3–O-1B	I	2.737(3)	0,0,0
Na-3–O-2B	I	2.432(4)	0,0,0
Na-3–O-1′B	I	2.485(4)	0,0,0
Na-3–O-3′B	I	2.540(4)	0,0,0

[a] With e.s.d's in parentheses. [b] I, *x,y,z*; II, $-x,y,-z$.

TABLE VII

I–H DISTANCES FOR THE CO-ORDINATION POLYHEDRA OF I^- IONS IN $3NaI \cdot 2$SUCROSE $\cdot 3H_2O$

Atoms		*Distance (Å)*[a]	*Translational vector*
I-1–H-21W	I[b]	2.88	0,0,0
I-1–H-2B	I	3.23(6)	0,0,0
I-1–H-4B	I	3.56(4)	0,0,0
I-1–H-26B	I	3.66(6)	0,0,0
I-1–H(O-6B)	I	2.72(6)	0,1,0
I-1–H(O-6′B)	II	2.84	0,1,1
I-1–H-31W	II	2.79	0,0,1
I-1–H-32W	III	2.92	0,0,0
I-2–H-11W	I	2.93(6)	0,0,0
I-2–H-2A	I	3.18(5)	0,0,0
I-2–H-16A	I	3.77(5)	0,0,0
I-2–H(O-6A)	I	2.86(7)	0, −1,0
I-2–H(O-6A)	II	2.70(6)	0, −1,0
I-2–H-42W	II	2.89	0,0,0
I-2–H-41W	III	2.81	0, −1,0
I-3–H(O-4A)	I	2.86(6)	0,0,0
I-3–H(O-2B)	I	3.10(6)	0,0,0
I-3–H(O-2A)	I	2.67(6)	0,1,0
I-3–H(O-4B)	I	3.02(6)	0,1,0
I-3–H(O-3′B)	I	2.99	0,1,0
I-3–H(O-1′B)	III	2.99(5)	0,0,0
I-3–H-3A	I	3.52(4)	0,0,0
I-3–H-3′A	I	3.72(5)	0,0,0

[a] With e.s.d's in parentheses. [b] I, x,y,z; II, $-x,y,-z$; III, $x + 1/2$, $y + 1/2$, z.

is limited mainly to the rather narrow E_3–$^4T_3$ range. Moreover, the relative positions of the two rings, which are defined by the torsion angles ϕ (O-5–C-1–O-1–C-2′) and ψ (O-2′–C-2′–O-1–C-1), are confined (with the exception of raffinose) to the range $84.7° < \phi < 108.7°$ and $-65.8° < \psi < -26.8°$. In the $3NaI \cdot 2$Sucrose $\cdot 3H_2O$ complex, in spite of the co-ordination of the Na^+ ions, the $^4C_1$ conformation of the glucose moiety is maintained and that of the fructose ring is shifted only slightly towards E_4 or $^4T_5$, an arrangement which is stabilized both by the anomeric effect, which forces the C-2′–O-1 bond perpendicular to the ring, and the transoid arrangement of the C-3′–O-3′, C-4′–O-4′, and C-5′–O-2′ bonds. The puckering co-ordinates[12] used for assessing the ring conformations are reported in Table VIII.

As regards the geometry of the glucopyranosyl-fructofuranosyl linkage, the relative energy map has been computed in the atom–atom approximation[11] for the sucrose molecule as a function of ϕ and ψ. The calculations revealed the minimum values 108° and −48°, which correspond to the experimentally determined conformation, the minimum being in the middle of a deep diagonal canyon of low energy, where the representative points of all sucrose moieties so far investigated are located. This finding shows that the sucrose molecule can co-ordinate the Na^+ ions

TABLE VIII

PUCKERING CO-ORDINATES[12]

Ring	*Q*	ϕ	θ	*Conformation*
Glc (A)	0.601(5)	−34(4)	173.6(4)	$^4C_1$
Glc (B)	0.536(4)	85(3)	170.7(5)	$^4C_1$
Fru (A)	0.378(4)	−72.8(5)		$^4T_5$
Fru (B)	0.350(4)	−54.6(6)		E_4

without changes in the conformations of the two rings and of the ring junction. The data in Table IV show that "the best" co-ordination is achieved mainly by rotation of the three $-CH_2OH$ groups. In the free sucrose molecule, conformations about O-2′–C-5′–C-6′–O-6′, O-2′–C-2′–C-1′–O-1′, and O-5–C-5–C-6–O-6 are typically g,g, g,t, and g,g, whereas, in the complex, the conformations are g,t, a rearrangement that allows O-6, O-6′, and O-1′ to achieve optimal co-ordination distances with the cations (Table VI).

DISCUSSION

The c.n. (co-ordination number) is seven for Na-1 and Na-2, but eight for Na-3. Comparison of the structural data[10] for complexes of sodium with neutral oxygenated ligands shows that the c.n. is in the range 5–8, with values of 6 and 7 being the most common. The co-ordination is irregular as far as both polyhedral geometry and Na–O distances are concerned. Table IX summarizes some metal co-ordination parameters for the $3NaI \cdot 2Sucrose \cdot 3H_2O$, $CaCl_2 \cdot$ *allo-allo*-trehalose $\cdot 5H_2O$ (c.n. 9), $CaCl_2 \cdot \beta$-D-fructopyranose $\cdot 2H_2O$ (c.n. 7), $CaBr_2 \cdot$ lactose $\cdot 7H_2O$ (c.n. 8), and $MgCl_2 \cdot$ *myo*-inositol $\cdot 4H_2O$ (c.n. 6) complexes. Volumes of the co-ordination polyhedra (calculated by the computing program VOLCAL[13]) show a definite trend with the c.n. both for Na^+ and Ca^{2+} ions, the smallest volume being associated with the small Mg^{2+} ion. This trend is paralleled by the variation of the mean M^{z+}–O distances ($\langle d \rangle$). Assuming the values reported by Shannon[14] for the ionic radii (r_+) of the three cations having different values of c.n., the mean radius of neutral oxygen (r_0) can be calculated (column 8 of Table IX) in the narrow range 1.19–1.22 Å with an average values of 1.20[1] Å, which is identical to the accepted value of 1.20 Å reported for HO^- with c.n. 3.

The dispersion of the M^{z+}–O distances (*d* in Table IX) has a maximum for Na^+ in c.n. 8 and a minimum for Mg^{2+} in c.n. 6, and appears to decrease in a continuous way according to the value of the ratio z/r_+. The cation co-ordination can be rationalized in terms of the concept of *bond valence*[15,16], which assumes that the total charge of the cation has to be saturated by $\Sigma_1 s_1$, *i.e.*, the summation of the separated bond valences (s_1) of each co-ordinated atom or ion *i*. Quantities *s* can be calculated by the expression $s = s_0(R/R_0)^{-N}$, where *R* is the actual M^{z+}–L distance, and R_0, s_0, and N are parameters empirically determined for each M^{z+}

TABLE IX

SELECTED PARAMETERS[a] OF NEUTRAL OXYGEN CO-ORDINATION FOR $3NaI \cdot 2$SUCROSE$\cdot 3H_2O$

Ion	*C.n.*	*Volume* (Å^3)	d_{min}–d_{max}	⟨d⟩	r_+^{14}	z/r_+	r(0)	Σs^b	*Ref.*
Na^+	8	27.12(4)	2.309–2.747	2.52[15]	1.32	0.76	1.20	1.10	
	7	22.19(4)	2.331–2.691	2.48[12]	1.26	0.79	1.22	1.06	
	7	22.34(4)	2.355–2.599	2.47[9]	1.26	0.79	1.21	1.06	
Ca^{2+}	9	31.46(3)	2.420–2.613	2.51[6]	1.32	1.52	1.19	1.91	22
	8	26.41(6)	2.379–2.537	2.45[6]	1.26	1.59	1.19	1.98	23
	7	21.03(5)	2.328–2.458	2.39[5]	1.20	1.67	1.19	1.95	24
Mg^{2+}	6	11.63(2)	2.032–2.143	2.07[4]	0.86	2.32	1.21	2.01	25

[a] Distances in Å and e.s.d.'s in parentheses; $d = d_{M^{z+}-O}$. [b] Calculated from the paremeters given in ref. 16.

cation–ligand L couple. Parameters for the bonds M^{z+}–O ($M^{z+} = Na^+, Ca^{2+}, Mg^{2+}$) are those given in the original paper[16]. Calculated values of s_i for the structures considered are reported in Table IX. The average values obtained for Na^+ (1.07), Ca^{2+} (1.95), and Mg^{2+} (2.01) fit reasonably well with the charge values of 1 or 2, with differences which are commonly observed in such analyses. However, a better understanding of cation co-ordination can be achieved by considering Fig. 3, which shows the cumulative values of s_i obtained by progressive addition of the ligand atoms in order of increasing M^{z+}–O distance. The observed curvature of each Σs *vs.* c.n. curve is a measure of the dispersion of the distances in the co-ordination polyhedron. The curvature increases in the order Mg^{2+}, Ca^{2+}, *hepta, octa,* and *ennea* co-ordinated, and Na^+ *hepta* and *octa* co-ordinated. This result shows that rigid and regular co-ordination polyhedra are associated with cations having high charge and small c.n. (hard cations), such as Mg^{2+}, whereas irregular polyhedra are associated with cations of small charge and large c.n. (softer cations). This situation accords with the well-known fact that Mg^{2+} co-ordination is mostly regular octahedral[10].

The bond valence model[15,16] is also useful for understanding the co-ordination around the I^- ion. The parameters reported[16] for H---O interactions have been used for H---I^-, with re-scaling[17] of the H–I distances for the difference of the experimental O-radius (1.20 Å, see Table IX) and the value[14] of the radius of the I^- ion (2.06 Å). By totalling the contributions of the five OH groups around I-1 and I-2 and of the six around I-3, the values of 0.83, 0.83, and 0.90, respectively, were obtained, which are smaller than the expected unit value. However, the analysis of the packing shows that I-1, I-2, and I-3 are involved, respectively, in three, two, and two further weak interactions having $d_{H---I} > 3.18$ Å [for comparison, $r_{vdw}(I^-) + r_{vdw}(H) = 3.14$–$3.32$ Å][18] with C–H groups. Addition of these contributions gives final Σs values of 1.10, 1.02, and 1.05 for I-1, I-2, and I-3, respectively, in agreement with the idea that C–H hydrogens are to be considered as part of the I^- co-ordination sphere. This rather unusual situation may be ascribed to an increased C–H acidity caused by the geminal oxygens.

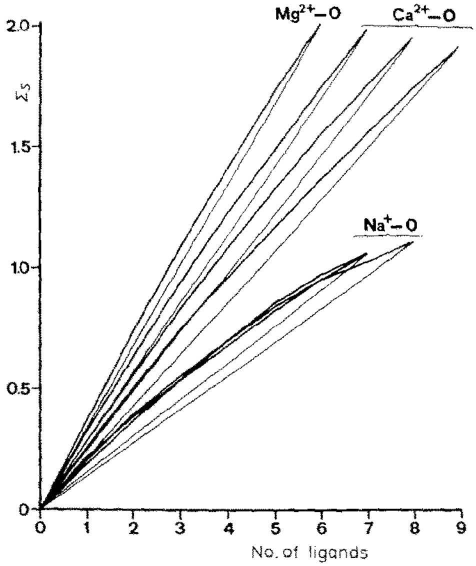

Fig. 3. A scatterplot[16] of Σ*s* *vs.* the number of ligands. The straight lines reflect identical M^{z+}–O distances.

A more comprehensive view of the cation co-ordination can be achieved in terms of the electrostatic potential V^{ES} spanned by the sucrose ligand, which, in turn, can be obtained for any point R from partial point atomic charges q_i of any different atom *i* at position R_i, *i.e.*, $V^{ES}(R) = \Sigma_i q_i/|R_i - R|$.

The q_i values were calculated by the Gasteiger–Marsili method[19] based on the partial equalization of orbital electronegativities. Such a method has been considered sufficient, in spite of its approximate nature, to give a qualitative picture of the crystal packing and cation co-ordination. All calculations and graphical representations were carried out by the CHEM-X system of programs[20].

Figs. 4 and 5 are sections of V^{ES} spanned by one or a pair of sugar molecules arranged in such a way as to reproduce the experimental crystal geometry. V^{ES} in each section corresponds to that of the plane parallel to the best least-squares plane (through one or two sucrose molecules) containing the appropriate Na^+ ion. The positions of the cations correspond to the lowest values of the electrostatic potential compatible with the impenetrability of the core shells. This situation can be shown by drawing the 3-dimensional envelope of the ligand molecule, giving to any oxygen a van der Waals radius of 2.46–2.52 Å, corresponding to the sum of $r_+(Na^+) =$ 1.26–1.32 and $r(0) = 1.20$ Å (see Table IX). The Na-1 and Na-3 ions are located in pockets created by the sphere intersections having the most negative V^{ES} values. From a more quantitative point of view, this equilibrium position is achieved at $V^{ES} = -45$ kcal.mol^{-1} for Na-1 (Fig. 4) if only one sugar molecule is considered, and $V^{ES} = -83$ kcal.mol^{-1} if the remaining co-ordinated groups (two water molecules and a further sugar molecule; see Table VI) are included in the calculation. For

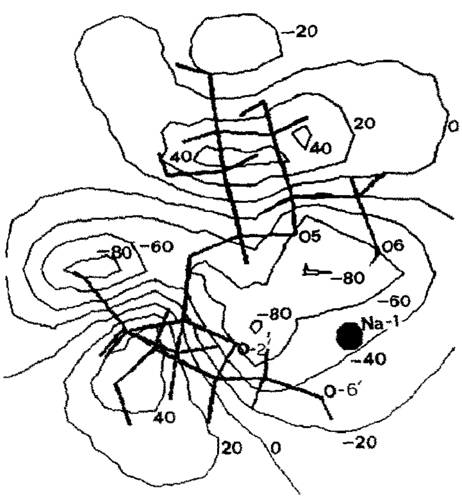

Fig. 4. V^{ES} spanned by a single sucrose molecule on the plane parallel to the best least-squares plane and passing through Na-1. V^{ES} in kcal.mol^{-1}.

Na-3, the equilibrium V^{ES} is −80 kcal.mol^{-1} if the full co-ordination, *i.e.* two sugar molecules, is considered (Fig. 5). The V^{ES} values of −83 and −80 kcal.mol^{-1} for the two ions correspond to the value of the solvation enthalpy of a single Na$^+$ ion in the crystal environment and can be compared with the hydration molar enthalpy $\Delta H^{\circ}_{\text{solv.m}}$ (298 K) of 96.8 kcal.mol^{-1} reported[21] for the same ion. The formation of the salt–sugar–water complex is energetically unfavourable at least as far as the cation co-ordination is concerned. This finding accords with the experimental observation that such mixed salts can be prepared only with great difficulties and only in very concentrated solutions, and suggests that the crystal represents a metastable phase containing a chemical species not present in dilute solution. A reason why the phase is obtained might be suggested by Fig. 6, which shows the envelope of

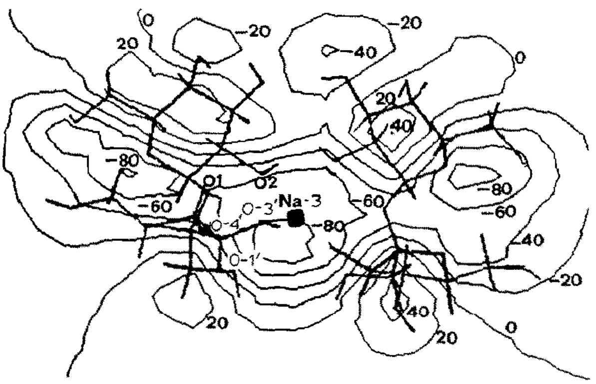

Fig. 5. V^{ES} spanned by the two sucrose molecules of the asymmetric unit on a plane parallel to the overall least-squares plane passing through Na-3. V^{ES} in kcal.mol^{-1}.

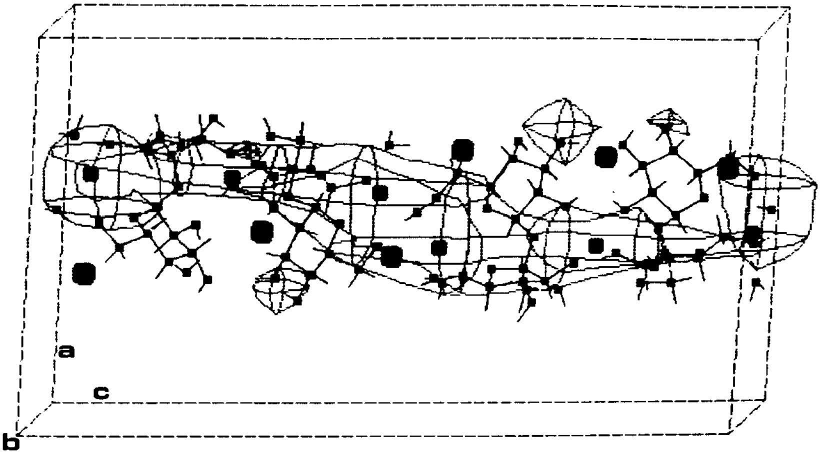

Fig. 6. A representation of the electrostatic potential inside a portion of the unit cell. Only the sugar and water molecules shown in the figure have been included in the calculations and only the envelope corresponding to $V^{ES} = -40$ kcal.mol^{-1} is shown. Na^+ and I^- positions are indicated by smaller and larger full-squares, respectively. All Na^+ atoms are located inside the negative potential cage.

the electrostatic potential corresponding to $V^{ES} = -40$ kcal.mol^{-1} inside a portion of the unit cell. The sugar and water molecules form a continuous zigzag tunnel of negative potential, with all Na^+ cations located on the central line and thus segregated by the I^- ions which are outside the tunnel. This arrangement could give rise to kinetic effects making the crystal possible in spite of its thermodynamic lack of stability.

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