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Coordination Complex of Na^+ and α-D-Glucose

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Abstract. The structure of α-D-glucose–NaCl is presented. $C_6H_{12}O_6.1/2(NaCl).0{\cdot}39(H_2O)$, $M_r = 216{\cdot}40$, trigonal, $P3_121$, $a = b = 9{\cdot}721\ (3)$, $c = 17{\cdot}06\ (1)$ Å, $V = 1396\ (1)$ Å^3, $D_m = 1{\cdot}54\ (1)$, $D_x = 1{\cdot}54$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 2{\cdot}859$ cm^{-1}, $F(000) = 683{\cdot}4$, $T = 293$ K, final $R = 0{\cdot}044$ for 744 reflections with $I \geq 3\sigma(I)$. The Na^+ residues on a crystallographic twofold axis and is coordinated by six hydroxyls orginating from four separate glucose molecules. The chloride ion is not involved in direct ionic interactions with the sodium ion.

Introduction. In the course of developing chemically modified carbohydrates of potential value to industry, Dr John Robyt and co-workers (Department of Biochemistry and Biophysics, Iowa State University) reacted succinyl dichloride with sucrose. The initial product was an intramolecularly crosslinked form of sucrose, whose covalent structure could not be deduced by spectroscopic analysis. Upon standing for several months, the purified product, a syrup, yielded crystals. The crystal structure revealed only a glucose molecule interacting with Na^+ and Cl^-. The presence of Na^+ and Cl^- was unexpected. As the small amount of crystalline sample precluded chemical analysis, new crystals were grown from an aqueous solution of glucose and NaCl. The new structure, identical to the original, appears below. Results of limited chemical analysis of the new crystals agree with the model from X-ray refinement. The crystal structure represents the only example in the literature where hydroxyls from carbohydrates occupy the entire coordination shell of an Na^+. Furthermore, the interaction of Na^+ and glucose observed here may be relevant to the mechanism of action of the α-D-glucose:Na^+ cotransporter in biological systems (Wright, Seckler & Overath, 1986).

Experimental. All chemicals used were of reagent grade. Crystals were grown by slow evaporation of water from a solution of D-glucose:NaCl in a 2:1 molar ratio. Dr John Robyt kindly provided crystals used in the original analysis, as mentioned above. The crystal used for the structure reported here measured approximately $0{\cdot}5 \times 0{\cdot}4 \times 0{\cdot}65$ mm. All data were collected on a Syntex $P2_1$ diffractometer using a graphite monochromator and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å). Unit-cell parameters resulted from a least-squares analysis of 15 reflections ($22 \leq 2\theta \leq 25°$). Data were collected to $2\theta = 50°$ [$(\sin\theta/\lambda)_{\max} = 0{\cdot}595$ Å^{-1}] over two asymmetric units of reciprocal space ($0 \leq h \leq 11$, $-10 \leq k \leq 0$, $0 \leq l \leq 20$) using variable-speed ω scans. A single standard reflection showed no decrease in intensity throughout data collection. Intensities were corrected for Lp effects and an empirical absorption correction (transmission factors varied from 0·82–0·87) was applied. Systematic absences occurring at $l \neq 3n$ for

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00*l* reflections in conjunction with Laue symmetry in axial photographs implied the space groups $P3_121$ or $P3_221$. Averaging of symmetry-equivalent data in the space group $P3_121$ ($P3_221$) gave a reasonable value for R_{int} of 0·057. The number of unique reflections was 958, 744 of which had $I \geq 3\sigma(I)$. Positions for all non-H atoms came from *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The appearance of the expected chirality for D-glucose confirmed the initial assignment of space group as $P3_121$. Coordinates for all H atoms came from difference maps.

All refinement employed full-matrix least squares using statistical weights of $1/\sigma^2(F)$, reflections with $I \geq 3\sigma(I)$ and anisotropic thermal parameters for non-H atoms. The H atoms were included in the structure-factor calculations using isotropic thermal factors ($B = 6{\cdot}0$ Å^2), but otherwise were not refined. Atomic scattering factors came from *International Tables for X-ray Crystallogaphy* (Cromer & Waber, 1974). All calculations were performed on a VAX3000 using computer programs provided by R. A. Jacobson (Karcher, 1981; Powell & Jacobson, 1980; Lapp & Jacobson, 1979). Initially, O atoms corresponding to water molecules were placed at sites eventually assigned to Na^+ and Cl^-. The thermal parameters for these O atoms refined to unreasonably low values. The refined occupancy factor of the O atom located at the Na^+ site inferred an electron number of ten. The assignment of Na^+ to this location, following refinement of thermal and occupancy parameters, gave an occupancy to within 1% of 0·5. In the refinement, the sodium ion was fixed to a crystallographic twofold axis with the appropriate symmetry constraints applied to its anisotropic thermal parameters (Peterse & Palm, 1966). A Cl^- was assigned to the other site where the oxygen refined poorly. Refinement of the thermal and occupancy parameters for Cl^- gave an occupancy of 0·67. The refined occpancy factor in excess of 0·5 for Cl^- implied the presence of water as well as Cl^- at this position. The refinement of the oxygen O(*w*) of water and a Cl^- (with occupancy fixed at 0·5) in alternating cycles resulted in an occupancy factor of 0·39 for O(*w*). As the sites for Cl^- and O(*w*) could not be resolved, we employed in refinement for the final model a single atom of type 0·5 of Cl^- + 0·39 of O(*w*) with occupancy fixed at 1·0. The final model, $R = 0{\cdot}044$, $wR = 0{\cdot}048$, $S = 2{\cdot}33$, $(\Delta/\sigma)_{\max} = 0{\cdot}002$, $\Delta\rho_{\max} = 0{\cdot}76$ and $\Delta\rho_{\min} = -0{\cdot}58$ e Å^{-3}, appears in Table 1.*

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

The occupancy of Na is 0·5. Occupancies for H′(O4), H(O*w*) and H′(O*w*) are 0·39. The occupancy for H(O4) is 0·61. Cl/O(*w*) is a single atom of composition $0{\cdot}5Cl^- + 0{\cdot}39O(w)$ with an occupancy of 1·0. See text for explanation.

$$U_{\text{eq}} = 1000/3\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
C(1)	0·3723 (6)	−0·0598 (7)	0·1939 (3)	33 (3)
C(2)	0·3742 (6)	0·0884 (6)	0·1633 (3)	29 (2)
C(3)	0·2365 (6)	0·0474 (6)	0·1067 (3)	29 (2)
C(4)	0·2305 (6)	−0·0647 (7)	0·0432 (3)	29 (2)
C(5)	0·2300 (7)	−0·2082 (7)	0·0796 (3)	31 (3)
C(6)	0·2345 (8)	−0·3219 (8)	0·0203 (3)	47 (3)
O(1)	0·2422 (5)	−0·1417 (4)	0·2425 (2)	39 (2)
O(2)	0·3609 (5)	0·1729 (4)	0·2296 (2)	33 (2)
O(3)	0·2611 (5)	0·1915 (5)	0·0726 (2)	44 (2)
O(4)	0·0912 (4)	−0·1130 (5)	−0·0026 (2)	41 (2)
O(5)	0·3702 (4)	−0·1533 (5)	0·1285 (2)	36 (2)
O(6)	0·3595 (6)	−0·2458 (6)	−0·0353 (2)	59 (3)
Na	0·1770 (3)	0·0000	0·3333	31 (1)
Cl/O(*w*)	0·2077 (3)	−0·1797 (3)	−0·1605 (1)	53 (1)

Table 2. *Comparison of the refined model with chemical analysis*

D_x (g cm^{-3})	1·544
D_m (g cm^{-3})	1·54 (1)
%NaCl (*w*/*w*) from refinement	13·503 (4)
%NaCl (*w*/*w*) by assay	13·5 (2)
%H_2O (*w*/*w*) from refinement	3·24 (3)
%H_2O (*w*/*w*) by assay	3·21 (1)

In order to confirm the results of the refinement we assayed for Cl^- and water in crystals. Results of the Cl^- determination are based on five titrations using the method of Mohr (Skoog & West, 1982). The water content was measured gravimetrically. A sample was ground to a powder, weighed initially and then heated at 343 K in a vacuum oven until a constant weight had been achieved. Density measurements were made by introducing crystals into mixtures of CCl_4 and $CHCl_3$. The results of density measurements and assays as compared to the refined model appear in Table 2.

Discussion. Bond distances and three-center angles are in Table 3. The numbering scheme for atoms is in Fig. 1 and the crystal packing arrangement in Fig. 2. The Na ion sits on the twofold axis. Each Na atom has six hydroxyl groups in its immediate vicinity (Fig. 3). Distances between Na^+ and the O atoms of the first coordination sphere lie between 2·359 (4) and 2·480 (3) Å (Table 4). These distances are generally much shorter than the sum of ionic radii of Na^+ and O (2·66 Å), and, in fact, are similar to those distances between Na^+ and O atoms in sodium hydroxide heptahydrate [2·29–2·46 Å (Wyckoff, 1965)] and in sucrose sodium bromide dihydrate [2·32–2·62 Å (Beevers & Cochran, 1947)]. The

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52410 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1. 2HU, England.

Table 3. *Bond lengths* (Å) *and angles* (°) *in* α-D-*glucose*.1/2NaCl.0·39H_2O *with e.s.d.'s in parentheses*

C(1)—C(2)	1·524 (6)	C(3)—O(3)	1·422 (6)
C(1)—O(1)	1·383 (6)	C(4)—C(5)	1·524 (6)
C(1)—O(5)	1·433 (6)	C(4)—O(4)	1·424 (6)
C(2)—C(3)	1·533 (6)	C(5)—C(6)	1·515 (7)
C(2)—O(2)	1·441 (5)	C(5)—O(5)	1·453 (6)
C(3)—C(4)	1·517 (6)	C(6)—O(6)	1·423 (7)
C(2)—C(1)—O(1)	109·0 (4)	C(3)—C(4)—C(5)	110·4 (4)
C(2)—C(1)—O(5)	108·8 (4)	C(3)—C(4)—O(4)	108·5 (4)
O(1)—C(1)—O(5)	112·5 (4)	C(5)—C(4)—O(4)	110·7 (4)
C(1)—C(2)—C(3)	111·9 (4)	C(4)—C(5)—C(6)	114·1 (4)
C(1)—C(2)—O(2)	107·9 (3)	C(4)—C(5)—O(5)	108·9 (4)
C(3)—C(2)—O(2)	109·1 (3)	C(6)—C(5)—O(5)	106·7 (4)
C(2)—C(3)—C(4)	110·6 (4)	C(5)—C(6)—O(6)	113·2 (4)
C(2)—C(3)—O(3)	107·8 (4)	C(1)—O(5)—C(5)	113·2 (3)
C(4)—C(3)—O(3)	110·1 (4)		

Table 4. *Distances* (Å) *and angles* (°) *involving the sodium ion in* α-D-*glucose*.1/2NaCl.0·39H_2O *with e.s.d.'s in parentheses*

O(1)—Na	2·361 (4)	O(2^{i})—Na	2·480 (3)
O(2)—Na	2·480 (3)	O(4^{ii})—Na	2·359 (4)
O(1^{i})*—Na	2·361 (4)	O(4^{iii})—Na	2·359 (4)
O(1)—Na—O(2)	67·3 (2)	O(2)—Na—O(4^{iii})	134·6 (2)
O(1)—Na—O(2^{i})	87·6 (2)	O(1^{i})—Na—O(2^{i})	67·3 (2)
O(1)—Na—O(1^{i})	111·9 (2)	O(1^{i})—Na—O(4^{iii})	137·7 (3)
O(1)—Na—O(4^{ii})	137·7 (3)	O(1^{i})—Na—O(4^{ii})	91·5 (2)
O(1)—Na—O(4^{iii})	91·5 (2)	O(2^{i})—Na—O(4^{ii})	134·6 (2)
O(2)—Na—O(1^{i})	87·6 (2)	O(2^{i})—Na—O(4^{iii})	79·7 (2)
O(2)—Na—O(2^{i})	135·1 (3)	O(4^{ii})—Na—O(4^{iii})	93·6 (2)
O(2)—Na—O(4^{ii})	79·7 (2)		

* Symmetry operations: (i) $x - y,\ -y,\ \frac{2}{3} - z$; (ii) $-y,\ x - y,\ \frac{1}{3} + z$; (iii) $-x,\ y - x,\ \frac{1}{3} - z$.

Table 5. *Details of the hydrogen bonding in* α-D-*glucose*.1/2NaCl.0·39H_2O *with e.s.d.'s in parentheses*

Bond	Symmetry transformation*	Distances (Å)			Angle (°)
D—H···A		D—H†	H···A	D···A	D—H···A‡
O(1)—H(O1)···O(6)	3,0$\bar{1}$0	0·99	1·67	2·652 (5)	174
O(2)—H(O2)···O(5)	4,110	0·99	1·87	2·829 (4)	163
O(3)—H(O3)···Cl/O(w)	3,000	1·09	1·87	2·946 (9)	167
O(6)—H(O6)···Cl/O(w)	1,000	1·12	1·81	2·847 (9)	152
O(w)—H(Ow)···O(4)	1,000	0·97	2·21	3·114 (4)	154
O(4)—H(O4)···Cl	1,000	0·99	2·15	3·114 (4)	162
O(w)—H′(Ow)···Cl	6,00$\bar{1}$	1·05	2·01	3·030 (5)	163

* The symmetry transformations generate the coordinates of the acceptor atoms from the basic coordinates in Table 1. The first digit represents a position equivalent to x, y, z as follows: (1) x, y, z; (2) $y, x, -z$; (3) $-y,\ x - y,\ \frac{1}{3} + z$; (4) $-x,\ y - x,\ \frac{1}{3} - z$; (5) $y - x,\ -x,\ \frac{2}{3} + z$; (6) $x - y,\ -y,\ \frac{2}{3} - z$.

† The e.s.d. in D—H and H···A bond lengths is 0·07 Å.

‡ The e.s.d. in D—H···A angles is 6°.

coordination shell of Na^+ deviates significantly from a regular octahedron. Interestingly Na^+ and Cl^- are far apart from each other (4·646 Å), whereas the Na^+ and the Br^- ions are linked (2·94 Å) in sucrose sodium bromide dihydrate. A symmetry operation ($x - y,\ -y,\ -z - 1/3$) brings the Cl^- site to within approximately 3 Å of itself. We believe these sites are mutually exclusive in regard to Cl^- occupancy with a statistical average of 1/2. However the site not occupied by Cl^- can be occupied by H_2O at a statistical level of 0·39. Our interpretation in regard

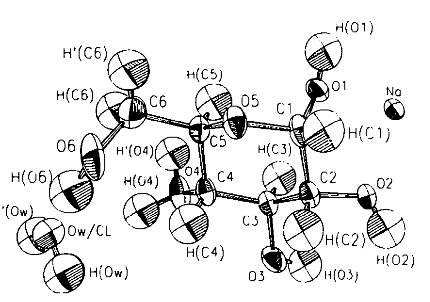

Fig. 1. *ORTEP* (Johnson, 1970) plot showing the labeling scheme for atoms. Ellipsoids represent a 50% probability level.

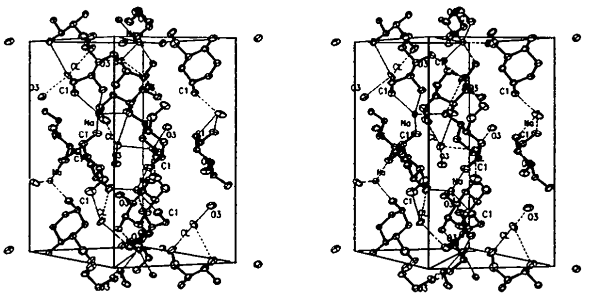

Fig. 2. Stereoscopic drawing of the molecular packing. Interactions between the Na^+ and glucose molecules and between the Cl^- and glucose molecules are indicated by dashed lines. Atoms are represented by their 50% probability ellipsoids. H atoms have been omitted for clarity. The positions of O(w) are the same as those of Cl^-.

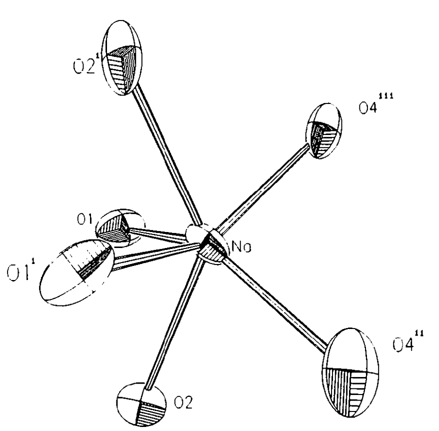

Fig. 3. Distorted octahedral coordination of the Na^+. Ellipsoids are at a 50% probability level. Symmetry operators are those of Table 4.

to the chloride site maintains charge balance in the crystal and is supported by crystallographic data in refinement, chemical analyses and density measurements. The chloride ion participates in four hydrogen bonds contributed by two molecules of glucose and the water molecule (Table 5). However, when water is present instead of Cl^-, the atom H(O4) occupies an alternative site H′(O4), permitting O(4) to serve as an acceptor in a donor–acceptor link with O(*w*). Two hydrogen bonds between the glucose molecules and three hydrogen bonds between the glucose and water molecules also participate in stabilizing the crystal (Table 5). The Cremer & Pople (1975) ring-puckering parameters for the pyranose ring of glucose are $q_2 = 0{\cdot}052$ Å, $q_3 = 0{\cdot}570$ Å, $Q = 0{\cdot}573$ Å, $\theta = 5{\cdot}23°$ and $\varphi_2 = -31{\cdot}3°$. The torsion angle O(6)—C(6)—C(5)—O(5) is −68·5 (6)°.

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Structure of the Square-Planar Complex Bis(dimethyl tetrathiomalonato)nickel(II)

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Abstract. $[Ni(C_5H_7S_4)_2]$, $M_r = 449{\cdot}43$, triclinic, $P\bar{1}$, $a = 4{\cdot}0633\ (5)$, $b = 9{\cdot}091\ (1)$, $c = 11{\cdot}532\ (1)$ Å, $\alpha = 80{\cdot}632\ (4)$, $\beta = 84{\cdot}083\ (3)$, $\gamma = 86{\cdot}290\ (4)°$, $V = 417{\cdot}6$ Å^3, $Z = 1$, $D_m = 1{\cdot}76$, $D_x = 1{\cdot}79$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 21{\cdot}12$ cm^{-1}, $F(000) = 230$, $T = 296$ K, $R = 0{\cdot}041$ for 1582 observed reflections. The structure consists of discrete molecular units of composition $Ni(ligand)_2$. The molecules stack along the **a** direction with a short Ni—Ni distance of 4·0633 (5) Å. The coordination around Ni^{II} is distorted square-planar with an S—Ni—S angle of 98·47 (3)°, and Ni—S distances of 2·1749 (9)–2·1764 (9) Å.

Introduction. Square-planar transition metal complexes have been considered as possible components of molecular metals (Wudl, 1975; Miller, 1982) and, more recently, superconductors (Brossard, Ribault, Bousseau, Valade & Cassoux, 1986; Kobayashi, *et al.* 1987). While metal dithiolene complexes (McCleverty, 1968; Schrauzer & Maymeg 1965), where the metal is part of a five-membered chelate ring, have been extensively studied, the corresponding dithioacetylacetonate complexes, where the metal is part of a six-membered ring, have received little attention. This may be due to the fact that they are not as easily prepared in high yield as their five-ring counterparts. A number of complexes of the ligand dithioacetylacetone (sacsac, pentane-2,4-dithione) with both divalent and trivalent transition metals have been reported (Bowden, Holloway & Geiger, 1978; Bowmaker, Boyd, Zvagulis, Cavell & Masters, 1985; Boyd, Hope & Martin, 1986; Heath & Leslie, 1983; Herman, Kirchner, Loew, Mueller-Westerhoff, Nazzal & Zerner, 1982; Lockyer & Martin, 1980). The syntheses of these complexes were carried out

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