The Crystal and Molecular Structure of 1,4-Anhydroerythritol.NaClO₄

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Crystalline complexes of 1,4-anhydroerythritol (*cis*-3,4-dihydroxytetrahydrofuran) of the formulae $(C_4H_8O_3)_2.NaI$, $C_4H_8O_3.NaClO_4$ and $C_4H_8O_3.NaSCN$ have been prepared. The $NaClO_4$ complex is orthorhombic, space group $P2_12_12_1$ with $a = 12·77$, $b = 7·28$, $c = 17·69$ Å, $Z = 8$. There are two crystallographically distinct molecules in the structure but they are approximately alike and both furanoid rings have the same near-envelope conformation. About both sodium atoms there is a distorted octahedron of oxygen atoms comprising three from different ClO_4^- ions, one pair of hydroxyl oxygens from one carbohydrate molecule and the etheric oxygen from another.

Carbohydrates are known to form complexes with the alkali and alkaline earth salts (Rendleman, 1972; Angyal, 1972; Andrasko & Forsén, 1973) and this property is believed to be connected with the process of ion transport through cellular membranes. Certain antibiotics and the 'crown compounds' also form such complexes (Pedersen & Frensdorff, 1972). Complexes of sugars with metal ions involve metal to hydroxyl bonds (Beevers & Cochran, 1947; Craig, Stephenson & Stevens, 1972; Bugg, 1973): metal to ether and metal to carbonyl linkages are found in the 'cryptates' (Dobler, Dunitz & Kilbourn, 1969). The observation that compounds with two hydroxy, alkoxy or amino groups on adjacent carbon atoms have markedly superior complexing properties to those of compounds with other spacings between groups (Arnett, Chung Ko & Chao, 1972) led us to investigate 1,4-anhydroerythritol (Fig. 1) since this compound possesses three such spacings.

Experimental

Crystals of the complexes with $NaClO_4$ and $NaSCN$ were prepared from equimolar ethanolic solutions of the salt and carbohydrate by evaporation. Deliquescent, glassy, crystalline solids were obtained and recrystallized from propan-2-ol/ethyl acetate. Elementary analysis indicated a 1:1 stoichiometry. Analysis of the complex formed with NaI suggested the formula $(C_4H_8O_3)_2.NaI$ and it was found that preparation from the components in this ratio gave a better product.

A perchlorate crystal of maximum dimension ~0·1 cm in a Lindemann tube was mounted along **c**. With Cu $K\alpha$ radiation $(\lambda = 1·5418$ Å) oscillation and Weissenberg photographs at 22° showed that the crystal was orthorhombic with $a = 12·77(2)$, $b = 7·82(2)$. c= $17·69(2)$ Å. The density measured by flotation was 1·79 g cm⁻³; for eight $C_4H_8O_3.NaClO_4$ units per cell the calculated density is 1·83 g cm⁻³. The systematic absences $(h00, h = 2n+1;$ $0k0$, $k = 2n+1;$ $00l$, $l = 2n+1)$ indicated the space group $P2_12_12_1$. With the multifilm technique, equi-inclination Weissenberg photographs were obtained for $hk0–hk14$. Intensities were measured visually with a calibrated film strip. Precession data enabled layers to be scaled from common reflexions. The usual Lorentz and polarization corrections were made. No absorption correction was made, the value for μ being 46 cm⁻¹. The number of non-zero independent reflexions was 1474. Atomic scattering factors were taken from Cromer & Waber (1965).

Solution and refinement of the structure

The structure was solved by direct methods. 367 E values lying between 3·102 and 1·2 were employed to obtain an E map in which the positions of the Na and Cl atoms were evident; tentative positions for the O atoms were also derived. After six cycles of refinement the value of R was 0·354. A difference map enabled corrections to be made for some misplaced O atoms. A further six cycles of refinement with anisotropic temperature factors for the heavy atoms gave $R = 0·129$ and refinement of the interlayer scaling factors gave a final $R = 0·112$. The positional and thermal parameters are given in Table 1.*
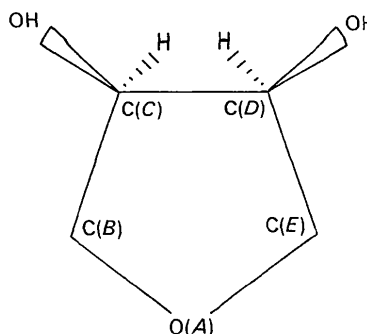

Fig. 1. Molecular structure of 1,4-anhydroerythritol.

Table 1. *Positional and thermal parameters* ($\times 10^4$)

Anisotropic temperature factors are defined as exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2)]$. The numbering scheme used is that of Fig. 3. Significant figures of standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}
Cl(1)	2303 (2)	9532 (4)	4174 (2)	38 (1)	40 (2)	13 (2)
Cl(2)	2225 (2)	5159 (4)	1648 (2)	35 (1)	39 (2)	16 (2)
Na(1)	2768 (4)	4555 (9)	4648 (3)	32 (2)	58 (3)	25 (4)
Na(2)	2265 (4)	9967 (9)	2181 (3)	33 (2)	63 (4)	24 (4)

|	x	y	z	B
O(1)	2598 (11)	7931 (19)	4535 (9)	69 (4)
O(2)	2792 (11)	9738 (21)	3465 (9)	77 (4)
O(3)	1205 (9)	9521 (17)	4067 (7)	59 (3)
O(4)	2588 (9)	11070 (16)	4612 (7)	54 (3)
O(5)	2767 (11)	5366 (20)	980 (8)	74 (4)
O(6)	1130 (8)	5156 (15)	1552 (7)	48 (3)
O(7)	2520 (9)	3473 (17)	2016 (7)	56 (3)
O(8)	2516 (10)	6604 (12)	2129 (8)	63 (3)
O(9)	4562 (4)	4316 (15)	4803 (6)	43 (3)
O(10)	3588 (4)	4275 (14)	3500 (6)	41 (2)
O(11)	5929 (17)	5278 (14)	3070 (6)	39 (2)
O(12)	8552 (17)	4905 (14)	3998 (6)	43 (2)
O(13)	9503 (8)	5324 (7)	2681 (7)	49 (3)
O(14)	979 (7)	4217 (14)	4371 (6)	40 (2)
C(1)	5643 (10)	5757 (20)	3837 (9)	39 (3)
C(2)	5199 (10)	4054 (20)	4151 (9)	37 (3)
C(3)	4550 (10)	3317 (20)	3489 (9)	37 (3)
C(4)	5199 (11)	3846 (21)	2800 (9)	38 (3)
C(5)	163 (10)	5330 (20)	4681 (9)	37 (3)
C(6)	−539 (10)	5980 (20)	4018 (9)	37 (3)
C(7)	132 (10)	5555 (20)	3339 (9)	39 (3)
C(8)	704 (11)	3863 (22)	3593 (9)	42 (3)
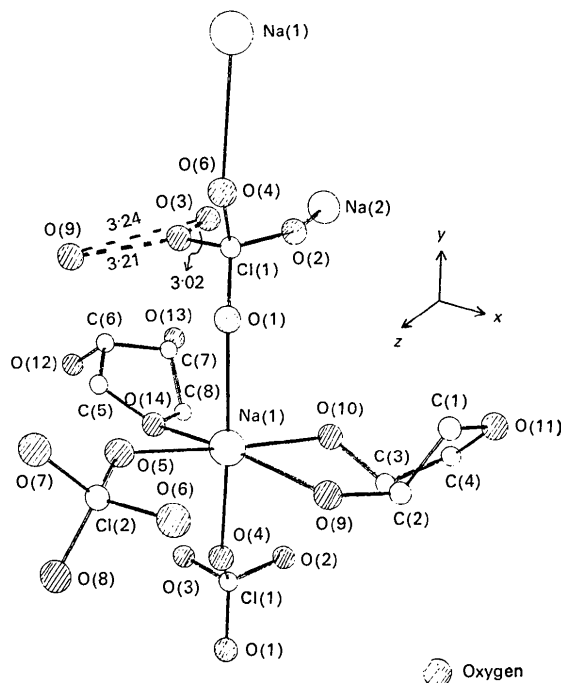
Fig. 3. Part of the infinite net showing the coordination about one of the two kinds of Na atoms. The sets of atoms differ only slightly in their coordination geometry. In every ClO$_4^-$ ion one of the O atoms is bound only to Cl and two such atoms are depicted together with a neighbouring hydroxyl O, the packing distances (dashed lines) being indicated numerically.

Discussion of the structure

A view down **b** showing half the contents of the unit cell is given in Fig. 2. The coordination about both types of Na atom comprises six O atoms in a distorted octahedral geometry (Fig. 3). The pair of hydroxyl O's from one ring plus the ether O from another make up the carbohydrate contribution to the coordination of Na and the remainder consists of the O atoms from three different perchlorate ions. The range of Na–O distances given (Kennard, 1968) for sixfold coordination is 2·25–2·78 Å and all the separations found lie within this range (Table 2). In sucrose.NaBr the Na–OH distances range from 2·32–2·62 Å (Beevers & Cochran, 1974) and here we find 2·29–2·33. The Na–O
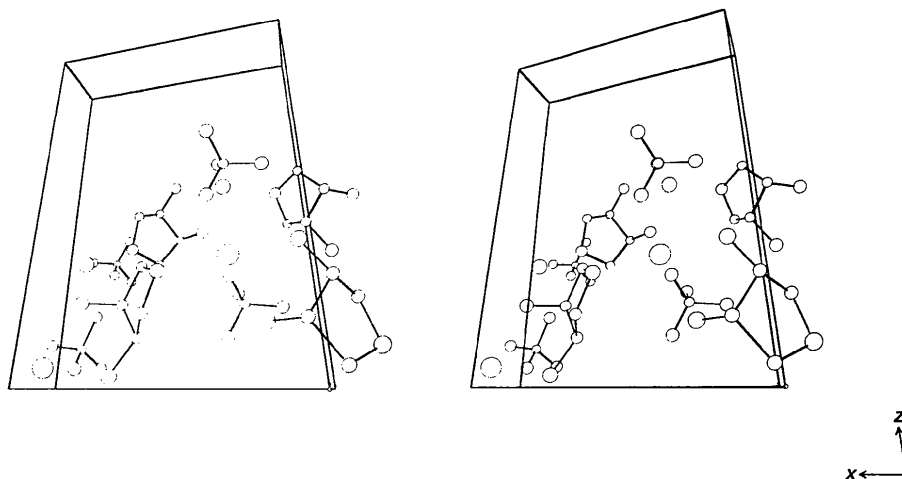

Fig. 2. Stereodrawing showing the crystal packing of half a cell viewed down b.

(ether) distances are 2.36 and 2·35 Å; Na–O (perchlorate) distances are found to be in the range 2·37-2·59 Å.

A planarity analysis (Sundaralingam, 1965) shows that the furanoid rings are twisted so that one of the hydroxyl-bearing carbon atoms is more out of the plane of the ring than the other ring atoms (Tables 3 and 4). Since we have chosen a particular chirality the rings all appear to be approximately of the E_c conformation (Schwarz, 1973),* *i.e.* the atom labelled C(C) (Fig. 1) is displaced to the side of the plane of the ring from

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* The lettering scheme of Fig. 1 is used here and in Table 3 only to designate the conformation; elsewhere the numbering scheme of Table 1 is used.

Table 3. *R.m.s. deviations (Å) from the best planes through four atoms of the furanoid rings*

The atom omitted from each calculation is the one designated in the central column.

Lettering as in Fig. 1	Numbering as in the tables	R.m.s. deviation (Å)
O(A)	O(11)	0·1691
C(B)	C(1)	0·0855
C(C)	C(2)	0·0304
C(D)	C(3)	0·1319
C(E)	C(4)	0·1847
O(A)	O(14)	0·1647
C(B)	C(8)	0·0747
C(C)	C(7)	0·0413
C(D)	C(6)	0·1377
C(E)	C(5)	0·1865

Table 2. *Interatomic distances (Å) and bond angles (°)*

Cl(1)–O(4)	1·410 (12)		O(10)–Na(1)–O(9)	69·3 (4)
Cl(1)–O(3)	1·414 (12)		O(14)–Na(1)–O(1)	90·1 (5)
Cl(1)–O(1)	1·381 (14)		O(14)–Na(1)–O(4)	78·6 (4)
Cl(1)–O(2)	1·410 (15)		O(14)–Na(1)–O(9)	168·4 (5)
Cl(2)–O(7)	1·440 (13)		O(14)–Na(1)–O(10)	104·5 (4)
Cl(2)–O(8)	1·402 (14)		O(7)—Na(2)–O(2)	98·1 (5)
Cl(2)–O(5)	1·378 (15)		O(8)—Na(2)–O(2)	86·0 (5)
Cl(2)–O(6)	1·410 (10)		O(8)—Na(2)–O(7)	163·0 (4)
Na(1)–O(1)	2·475 (15)		Na(1)–O(1)—Cl(1)	154·1 (9)
Na(1)–O(4)	2·548 (13)		Na(2)–O(2)—Cl(1)	137·2 (8)
Na(1)–O(5)	2·452 (13)		Na(1)–O(4)—Cl(1)	145·9 (8)
Na(1)–O(9)	2·314 (11)		Na(2)–O(7)—Cl(2)	149·2 (8)
Na(1)–O(10)	2·294 (12)		Na(2)–O(8)—Cl(2)	137·0 (8)
Na(1)–O(14)	2·350 (10)		C(2)—O(9)—Na(1)	118·7 (8)
Na(2)–O(2)	2·374 (16)		C(3)—O(10)–Na(1)	116·9 (9)
Na(2)–O(7)	2·590 (14)		C(4)—O(11)–C(1)	108·2 (10)
Na(2)–O(8)	2·472 (15)		C(5)—O(14)–Na(1)	124·7 (8)
Na(2)–O(11)	2·359 (16)		C(8)—O(14)–Na(1)	117·0 (8)
Na(2)–O(12)	2·332 (16)		C(8)—O(14)–C(5)	106·8 (11)
Na(2)–O(13)	2·285 (16)		C(2)—C(1)—O(11)	104·4 (12)
O(9)—C(2)	1·424 (18)		C(1)—C(2)—O(9)	114·3 (12)
O(10)–C(3)	1·413 (16)		C(3)—C(2)—O(9)	110·9 (11)
O(11)–C(1)	1·449 (19)		C(3)—C(2)—C(1)	102·4 (13)
O(11)–C(4)	1·477 (17)		C(2)—C(3)—O(10)	106·6 (12)
O(12)–C(6)	1·400 (16)		C(4)—C(3)—O(10)	111·1 (12)
O(13)–C(7)	1·427 (19)		C(4)—C(3)—C(2)	103·2 (11)
O(14)–C(5)	1·429 (16)		C(3)—C(4)—O(11)	105·3 (12)
O(14)–C(8)	1·444 (19)		C(6)—C(5)—O(14)	107·8 (12)
C(1)—C(2)	1·472 (20)		C(5)—C(6)—O(12)	109·2 (12)
C(2)—C(3)	1·532 (21)		C(7)—C(6)—O(12)	109·6 (12)
C(3)—C(4)	1·523 (21)		C(7)—C(6)—C(5)	102·2 (11)
C(5)—C(6)	1·550 (21)		C(6)—C(7)—O(13)	110·7 (11)
C(6)—C(7)	1·508 (22)		C(8)—C(7)—O(13)	115·0 (13)
C(7)—C(8)	1·499 (20)		C(8)—C(7)—C(6)	102·0 (13)
			C(7)—C(8)—O(14)	105·0 (12)
O(2)—Cl(1) –O(1)	112·3 (9)		O(2)—Na(1)–O(5)	91·7 (5)
O(3)—Cl(1) –O(2)	108·7 (8)		O(4)—Na(1)–O(5)	91·3 (5)
O(3)—Cl(1) –O)1	109·2 (8)		O(5)—Na(1)–O)9)	99·4 (5)
O(4)—Cl(1) –O(3)	109·5 (7)		O(5)—Na(1)–O(10)	168·3 (5)
O(4)—Cl(1) –O(2)	106·8 (8)		O(5)—Na(1)–O(14)	86·1 (5)
O(4)—Cl(1) –O(1)	110·3 (7)		O(2)—Na(2)–O(11)	84·9 (5)
O(6)—Cl(2) –O(5)	113·2 (8)		O(7)—Na(2)–O(11)	76·2 (5)
O(7)—Cl(2) –O(5)	110·5 (8)		O(8)—Na(2)–O(11)	87·8 (5)
O(7)—Cl(2) –O(6)	108·2 (7)		O(2)—Na(2)–O(12)	168·7 (5)
O(8)—Cl(2) –O(5)	107·9 (8)		O(7)—Na(2)–O(12)	88·5 (5)
O(8)—Cl(2) –O(6)	109·8 (7)		O(8)—Na(2)–O(12)	90·3 (5)
O(8)—Cl(2) –O(7)	107·1 (7)		O(11)–Na(2)–O(12)	105·7 (5)
O(4)—Na(1) –O(1)	168·1 (5)		O(2)—Na(2)–O(13)	100·7 (5)
O(9)—Na(1)–O(1)	99·8 (5)		O(7)—Na(2)–O(13)	91·3 (5)
O(9)—Na(1)–O(4)	91·0 (4)		O(8)—Na(2)–O(13)	104·18 (5)
O(10)–Na(1)–O(1)	93·2 (5)		O(11)–Na(2)–O(13)	167·0 (5)
O(10)–Na(1)–O(4)	86·0 (4)		O(12)–Na(2)–O(13)	69·8 (5)

which the lettering in alphabetical order appears to be anti-clockwise. The other choice of enantiomer gives E_D rings. Torsional angles of the ring are given in Table 5.

Table 4. *Planarity analysis of the furanoid rings*

The equation of the plane through the remaining four atoms of the ring when $C(C)$ of Fig. 1 is excluded is given by,*

$$m(1)x + m(2)y + m(3)z = d .$$

Atom excluded = C(2)		Deviation from plane (Å)	
$m(1) =$	0·6809	O(11) =	0·0369
$m(2) =$	-0·6669	C(1) =	-0·0232
$m(3) =$	0·3027	C(2) =	0·5669
$d =$	4·2011	C(3) =	0·0223
		C(4) =	-0·0359

Atom excluded = C(7)			
$m(1) =$	0·5987	O(14) =	0·0507
$m(2) =$	0·7705	C(8) =	-0·0312
$m(3) =$	-0·2186	C(7) =	0·5666
$d =$	1·3558	C(6) =	0·0295
		C(5) =	-0·0490

* In one furanoid ring $C(C)$ of Fig. 1 is equivalent to C(2) and in the other, to C(7).

Three of the ClO_4 oxygen atoms are coordinated both to Na and Cl (Fig. 3) but one oxygen of every ion is not bound to Na and these atoms with only one bond pack together but at distances too great to imply a chemical linkage.

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References

ANDRASKO, J. & FORSÉN, S. (1973). *Biochem. Biophys. Res. Commun.* **52**, 233–239.

ANGYAL, S. J. (1972). *Aust. J. Chem.* **25**, 1957–1966.

ARNETT, E. M., CHUNG KO, H. & CHAO, C. C. (1972). *J. Amer. Chem. Soc.* **94**, 4776–4777.

BEEVERS, C. A. & COCHRAN, W. (1947). *Proc. Roy Soc.* A **190**, 257–272.

BUGG, C. E. (1973). *J. Amer. Chem. Soc.* **95**, 908–913.

CRAIG, D. C., STEPHENSON, N. C. & STEVENS, J. D. (1972). *Carbohydr. Res.* **22**, 494–495.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DOBLER, M., DUNITZ, J. D. & KILBOURN, B. T. (1969). *Helv. Chim. Acta*, **52**, 2573–2583.

KENNARD, O. (1968). *International Tables for X-ray Crystallography*. Vol. III, pp. 257–258. Birmingham: Kynoch Press.

PEDERSEN, C. J. & FRENSDORFF, H. K. (1972). *Angew. Chem. Int. Ed.* **11**, 16–25.

RENDLEMAN, J. A. (1972). *Carbohydr. Res.* **21**, 235–247.

SCHWARTZ, J. C. P. (1973). *Chem. Commun.* pp. 505–508.

SUNDARALINGAM, M. (1965). *J. Amer. Chem. Soc.* **87**, 599–606.

Table 5. *Torsional angles of the furanoid rings*

The e.s.d. is about 1·2°.

C(4)—O(11)-C(1)-C(2)	28·9°
C(1)—O(11)-C(4)-C(3)	-6·6
O(11)-C(1)—C(2)-O(9)	-161·4
O(11)-C(1)—C(2)-C(3)	-40·0
O(9)—C(2)—C(3)-O(10)	41·0
O(9)—C(2)—C(3)-C(4)	158·2
C(1)—C(2)—C(3)-O(10)	-82·0
C(1)—C(2)—C(3)-C(4)	35·2
O(10)-C(3)—C(4)-O(11)	96·5
C(2)—C(3)—C(4)-O(11)	-17·8
C(8)—O(14)-C(5)-C(6)	-9·1
C(5)—O(14)-C(8)-C(7)	30·5
O(14)-C(5)—C(6)-O(12)	100·3
O(14)-C(5)—C(6)-C(7)	-15·7
O(12)-C(6)—C(7)-O(13)	40·2
O(12)-C(6)—C(7)-C(8)	-83·1
C(5)—C(6)—C(7)-O(13)	156·3
C(5)—C(6)—C(7)-C(8)	33·0
O(13)-C(7)—C(8)-O(14)	-160·5
C(6)—C(7)—C(8)-O(14)	-40·0