Short Communication

The Crystal Structure of the Sodium Salt of 3-Hydroxy-2-propenal Sesquihydrate at −150 °C

P. Groth

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

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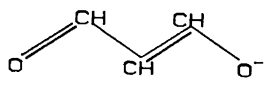
The anion of the title compound is the first member of the series of oxanol dyes studied by Malhotra and Whiting.[1] The main purpose of the present crystal structure investigation was to decide whether the anion has a "stretched-out" (**1**) or a "chelate" (**2**) configuration.



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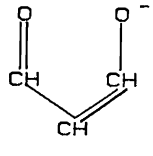
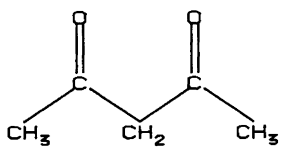


2

In the crystals of the (1:1) complex between 2,4-pentandione and lithium,[2] configuration **2** is preferred:



The crystals of $C_3H_3O_2^- \cdot Na^+ \cdot 1\frac{1}{2}H_2O$ belong to the orthorhombic system which cell dimensions a = 7.084(2), b = 17.716(4) and c = 9.387(2) Å; space group $P2_12_12$ with Z = 8 (D_x = 1.36 g cm^{-3}, D_m = 1.35 g cm^{-3}). A total of 1022 independent reflections [$I>2.5\sigma(I)$] were recorded on an automatic four circle diffractometer at ca. −150 °C using Mo$K\alpha$ radiation and with $2\theta_{max}$ = 50°. No corrections for absorption or secondary extinction were applied (crystal size 0.4 × 0.4 × 0.2 mm). The structure was solved by direct methods[3] and refined by the full matrix least-squares technique. Anisotropic temperature factors were introduced for non-hydrogen atoms. Weights in least-squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I) = [C_T + (0.02\ C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N the net count. Hydrogen atom positions were localized in a Fourier difference map and refined with isotropic temperature factors. The maximum r.m.s. amplitudes of thermal vibrations range from 0.16 to 0.20 Å. The R-value arrived at was 3.4% (R_W = 3.6%) for 1022 observed reflections. Final fractional coordinates with estimated standard deviations for non-hydrogen atoms are listed in Table 1. Bond distances and angles may be found in Table 2. Fig. 1 is a schematic drawing showing the numbering of atoms. A stereoscopic drawing of the unit cell contents is presented in Fig. 2.

The anion has the "stretched-out" configuration. Table 2 shows that the four C−C bonds, and also the four C−O bonds, of the two independent anions are of equal length within estimated limits of error. It should be pointed out that the C−C−O angles are large (ranging from 128.4° to 131.8°). The network of bonds between the anion oxygen atoms, the sodium cations and the water molecules is somewhat complicated: O1 is bonded to three cations, O2 and O3 are

Table 1. Final fractional coordinates and equivalent temperature factors, with estimated standard deviations, for non-hydrogen atoms.

Atom	*x*	*y*	*z*	U_{eq}[a]
Na1	0.4905(3)	0.2492(2)	0.9991	0.021
Na2	0.2494(3)	0.0692(1)	0.0172(1)	0.022
O1W	1.000	0.0000	0.8936(8)	0.020
O2W	0.5000	0.0000	0.8860(9)	0.028
O3W	0.2425(7)	0.2905(1)	1.1537(3)	0.024
O4W	0.5117(6)	0.3604(3)	0.8553(5)	0.026
O5W	0.4859(5)	0.1388(3)	0.1451(5)	0.020
O1	0.2438(7)	0.1845(1)	0.8682(2)	0.022
C1	0.1982(6)	0.1952(2)	0.7411(5)	0.027
C2	0.2912(6)	0.1775(2)	0.6170(4)	0.022
C3	0.2083(7)	0.1946(2)	0.4906(5)	0.030
O2	0.2581(7)	0.1829(1)	0.3644(3)	0.028
O3	0.7496(9)	0.0733(1)	0.7016(2)	0.030
C4	0.7532(13)	0.0378(2)	0.5857(4)	0.028
C5	0.7506(11)	0.0648(2)	0.4490(4)	0.024
C6	0.7508(11)	0.0137(2)	0.3371(4)	0.023
O4	0.7522(7)	0.0271(2)	0.2057(2)	0.022

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations.

Distance		Distance	
Na1–O1	2.424(5)	Na1–O1′	2.481(5)
Na1–O3W	2.393(5)	Na1–O3W′	2.395(5)
Na1–O4W	2.394(6)	Na1–O5W″	2.388(6)
Na2–O1‴	2.475(3)	Na2–O1W	2.444(4)
Na2–O2W‴	2.484(5)	Na2–O4W	2.414(5)
Na2–O5W	2.401(5)	Na2–O4⁗	2.458(2)
O2 –O3W‴	2.749(4)	O2 –O4W	2.808(6)
O2 –O5W	2.730(6)	O3 –O1W	2.843(7)
O3 –O2W	2.794(7)	O3 –O3W′	2.770(4)
O4 –O4‴	2.771(7)	O4 –O5W	2.792(5)
O1 –C1	1.251(5)	C1 –C2	1.374(6)
C2 –C3	1.359(6)	C3 –O2	1.254(6)
O3 –C4	1.257(5)	C4 –C5	1.370(5)
C5 –C6	1.386(5)	C6 –O4	1.256(4)

Angle		Angle	
O1–C1–C2	130.6(5)	C1–C2–C3	118.8(4)
O2–C3–C2	132.8(5)	O3–C4–C5	129.5(4)
C4–C5–C6	118.8(4)	C5–C6–O4	128.4(3)

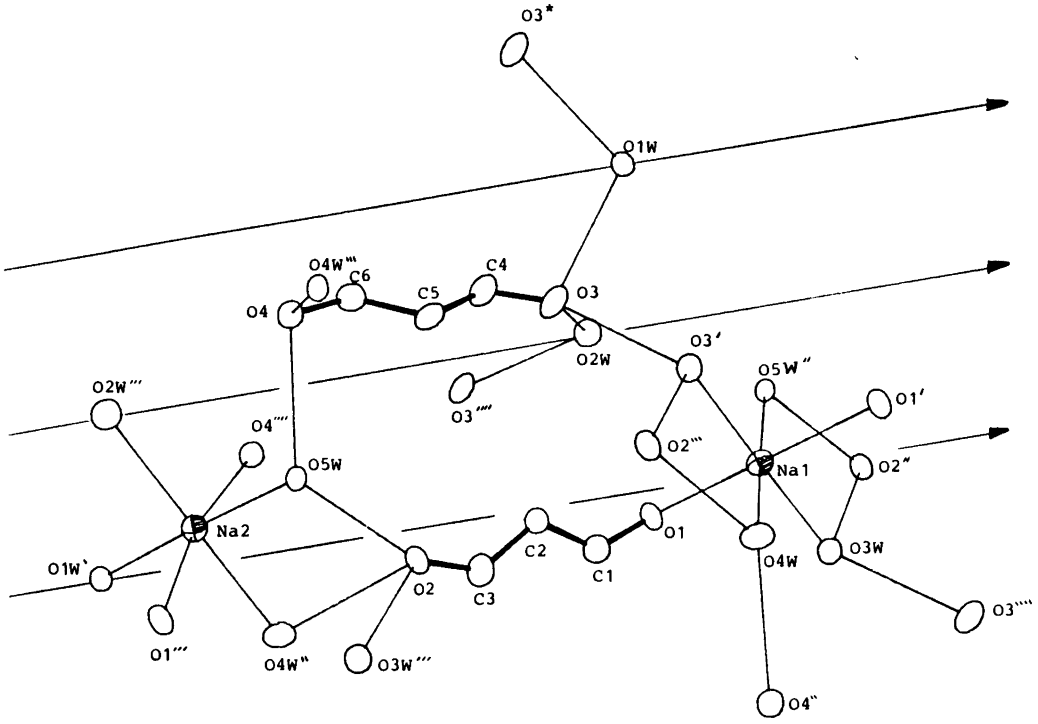


Fig. 1. Perspective drawing showing the numbering of atoms. The symmetry operators are: ': ½+*x*, ½−*y*, 2−*z*; '': *x*, *y*, 1+*z*; ''': *x*, *y*, *z*−1; '''': 1−*x*, −*y*, *z*; *: 2−*x*, −*y*, *z*; `: *x*−1, *y*, *z*−1; ``: *x*−½, ½−*y*, 1−*z*; ```: *x*, *y*, 1+*z*; ````: *x*−½, ½−*y*, 2−*z*.

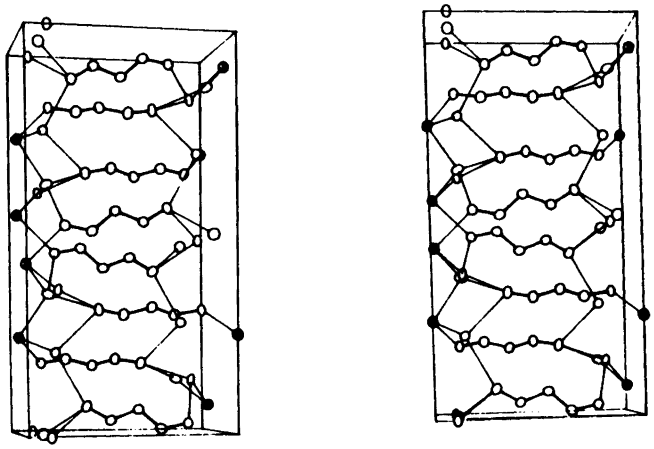


Fig. 2. Stereoscopic drawing of the unit cell contents.

both bonded to three water molecules, while O4 is bonded to one cation and two water molecules. As may be seen from Fig. 1, this leads to octahedral coordination for the sodium ions.

Lists of thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available from the author.

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References

1. Malhotra, S. S. and Whiting, M. C. *J. Chem. Soc.* (1960) 3812.
2. Schrøder, F. A. and Weber, H. P. *Acta Crystallogr., Sect. B 31* (1975) 1745.
3. Gilmore, C. J. *J. Appl. Crystallogr. 17* (1984) 42.

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