lengths of O–H$\cdots$O bonds range from 2·621(4) to 3·056(4)Å and N–H$\cdots$O from 2·828(4) to 3·379(5)Å.

Table 10. *Hydrogen-bonding parameters*

Symmetry code

(I)	x,	y,	z;
(II)	$-x$,	$-y$,	$-z$;
(III)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;
(IV)	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$;
(V)	$x-1$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$;
(VI)	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$;
(VII)	$-x+1$,	$-y$,	$-z+1$;
(VIII)	$-x$,	$-y$,	$-z+1$;
(IX)	x,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$;
(X)	$-x+1$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;

	Distance between bonded atoms (Å)
N(1$^{\mathrm{I}}$)—H(1$^{\mathrm{I}}$)—O(4$^{\mathrm{V}}$)	2·828 (4)
N(1$^{\mathrm{I}}$)—H(2$^{\mathrm{I}}$)—O(5$^{\mathrm{VI}}$)	2·886 (4)
N(1$^{\mathrm{I}}$)—H(4$^{\mathrm{I}}$)—O(8$^{\mathrm{I}}$)	2·979 (5)
N(1$^{\mathrm{I}}$)—H(4$^{\mathrm{I}}$)—O(9$^{\mathrm{I}}$)	2·887 (5)
N(1$^{\mathrm{I}}$)—H(3$^{\mathrm{I}}$)—O(10$^{\mathrm{III}}$)	3·087 (4)
N(1$^{\mathrm{I}}$)—H(3$^{\mathrm{I}}$)—O(11$^{\mathrm{I}}$)	3·097 (4)
N(2$^{\mathrm{I}}$)—H(6$^{\mathrm{I}}$)—O(9$^{\mathrm{I}}$)	3·096 (5)
N(2$^{\mathrm{I}}$)—H(6$^{\mathrm{I}}$)—O(9$^{\mathrm{III}}$)	3·379 (5)
N(2$^{\mathrm{I}}$)—H(5$^{\mathrm{I}}$)—O(11$^{\mathrm{I}}$)	3·016 (5)
N(2$^{\mathrm{I}}$)—H(7$^{\mathrm{I}}$)—O(4$^{\mathrm{VII}}$)	3·003 (6)
N(2$^{\mathrm{I}}$)—H(8$^{\mathrm{I}}$)—O(7$^{\mathrm{IV}}$)	2·893 (5)
N(2$^{\mathrm{I}}$)—H(8$^{\mathrm{I}}$)—O(11$^{\mathrm{VIII}}$)	3·104 (5)
O(2$^{\mathrm{I}}$)—H(11$^{\mathrm{I}}$)—O(5$^{\mathrm{IX}}$)	2·685 (4)
O(2$^{\mathrm{I}}$)—H(12$^{\mathrm{I}}$)—O(3$^{\mathrm{X}}$)	2·621 (4)
O(11$^{\mathrm{I}}$)-H(9$^{\mathrm{I}}$)—O(1$^{\mathrm{III}}$)	3·056 (4)
O(11$^{\mathrm{I}}$)-H(10$^{\mathrm{I}}$)—O(6$^{\mathrm{VI}}$)	2·955 (4)

References

BEAGLEY, B. & SMALL, R. W. H. (1964). *Acta Cryst.* **17**, 783–788.

BERSTED, B., BELFORD, R. L. & PAUL, J. C. (1968). *Inorg. Chem.* **7**, 1557–1562.

DREW, R. E., EINSTEIN, F. W. B. & GRANSDEN, S. E. (1974). *Canad. J. Chem.* **52**, 2184–2189.

FORM, G. R., RAPER, E. S., OUGHTRED, R. E. & SHEARER, H. M. M. (1972). *Chem. Commun.* pp. 945–946.

GLEN, G. L., SILVERTON, J. W. & HOARD, J. L. (1963). *Inorg. Chem.* **2**, 250–256.

HAZELL, A. C. (1963). *J. Chem. Soc.* 5745–5752.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KIERKEGAARD, P. & LONGO, J. M. (1965). *Acta Chem. Scand.* **19**, 1906–1914.

KOJIĆ-PRODIĆ, B., LIMINGA, R. & ŠĆAVNIČAR, S. (1973). *Acta Cryst.* **B29**, 864–869.

PALMER, W. G. (1954). *Experimental Inorganic Chemistry.* Cambridge Univ. Press.

SATHYANARAYANA, D. N. & PATEL, C. C. (1965). *J. Inorg. Nucl. Chem.* **27**, 297–302.

SCHEIDT, W. R., TSAI C.-C. & HOARD, J. L. (1971). *J. Amer. Chem. Soc.* **93**, 3867–3872.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1966). *J. Chem. Phys.* **42**, 3175–3187.

STOMBERG, R. (1970). *Acta Chem. Scand.* **24**, 2024–2036.

SUTTON, L. E. (1965). *Interatomic Distances and Configuration in Molecules and Ions, Supplement,* Spec. Publ. No. 18. London: The Chemical Society.

TEMPLETON, D. H. (1962). *International Tables for X-ray Crystallography,* Vol. III, p. 213. Birmingham: Kynoch Press.

VISWAMITRA, M. A. (1962). *J. Chem. Phys.* **37**, 1408–1414.

The Crystal Structure of Sodium Acetate Trihydrate

BY T. STANLEY CAMERON

University of Ulster, Coleraine, N. Ireland

AND KH. M. MANNAN* AND MD. OBAIDUR RAHMAN

Physics Department, Dacca University, Bangladesh

The molecular structure of the title compound has been determined by direct methods from photographic data. $Na^+(CH_3COO)^-.3H_2O$, monoclinic, $a=12\cdot475$, $b=10\cdot407$, $c=10\cdot449$ Å, $\beta=112\cdot65°$, space group $C2/c$, 475 reflexions, $R=0\cdot11$. The Na^+ ion has distorted octahedral coordination with six oxygen atoms. Adjacent octahedra share an edge and form a continuous chain along the z axis. Along the chain the separations between the Na^+ ions are 3·39 and 3·56 Å and the Na^+–O distances are in the range 2·35–2·56 Å. The C–O bond lengths are 1·23 and 1·31 Å and both oxygen atoms are hydrogen bonded to two water molecules.

Sodium acetate trihydrate is one of the better known salts of one of the simple organic acids; as such its crystal structure has been determined.

---

* On sabbatical leave as Nuffield Fellow, New University of Ulster.

Experimental

Crystals of sodium acetate trihydrate, grown by slow evaporation from aqueous solution, are small hexagons. Weissenberg and oscillation photographs established that the crystals were monoclinic in space

group $C2/c$ (Mannan & Rahman, 1972) and not $C2/m$ as was reported by Padmanabhan (1952). The choice of space group $C2/c$ rather than Cc was borne out by the analysis and independently by the goniometric finding of the prismatic class (Groth, 1910). In this context the reported $a:b:c$ ratios are $1\cdot1809:1:0\cdot9962$ with $\beta=111\cdot71°$, while the ratios from the crystal data (below) are $1\cdot1987:1:1\cdot0040$ with $\beta=112\cdot65°$. The discrepancy may in part be due to the different conditions in which the two sets of data were obtained (Groth gives no details but the X-ray data were determined in Dacca at 30°C and high humidity). However the X-ray cell parameters may be less accurate than their e.s.d.'s suggest.

Crystal data

$C_2H_3NaO_2.3H_2O$, $M=136\cdot08$, monoclinic, $a=12\cdot475$ (2), $b=10\cdot407$ (3), $c=10\cdot449$ (3) Å, $\beta=112\cdot65$ (5)°. $U=1251\cdot94$ Å^3, systematic extinctions hkl: $h+k=2n+1$, $h0l$: $l=2n+1$; space group $C2/c$ (C_{2h}^6, No. 15), $D_m=1\cdot45$ (by flotation), $D_c=1\cdot45$ g cm^{-3} (for $Z=8$), $F(000)=576$, Cu $K\alpha$ ($\lambda=1\cdot54178$ Å) radiation, $\mu=18\cdot3$ cm^{-1}, Weissenberg photographic data layers $0kl$ to $11kl$, 475 reflexions significantly above the background intensity; an additional 81 reflexions too weak to measure were assigned half the value of the local minimum observable intensity. Lorentz and polarization but not absorption corrections were applied.

Attempts to solve the structure from Patterson functions in projection were unsuccessful and it was thought that several of the atoms were in special positions. The phases of 76 out of the 80 reflexions with the largest E's were determined by direct methods with the symbolic addition procedure. The resultant E map showed the position of the Na$^+$ ion, the acetate group and two water molecules; also there were two peaks in the E map on the twofold axis which were in chemically sensible positions to complete the coordination sphere about the Na$^+$ ion. An F_o map was calculated for the trial structure without the two atoms in special positions from which the position of the two remaining atoms was confirmed.

The structure was refined by block-diagonal least-squares calculations with the weighting scheme $w=1$ for $|F_o|_{abs}<30\cdot0$ and $w=(30\cdot0/F_{oabs})^2$ for the remaining reflexions. After four cycles with individual isotropic

temperature factors on all atoms R was $0\cdot19$ and this reduced to $0\cdot15$ after three cycles with anisotropic temperature factors for all the atoms in general positions. An electron density difference map calculated at this stage clearly indicated the position of all the nine hydrogen atoms and when these atoms were included (with $B=4$ Å^2) but not refined in the structure-factor
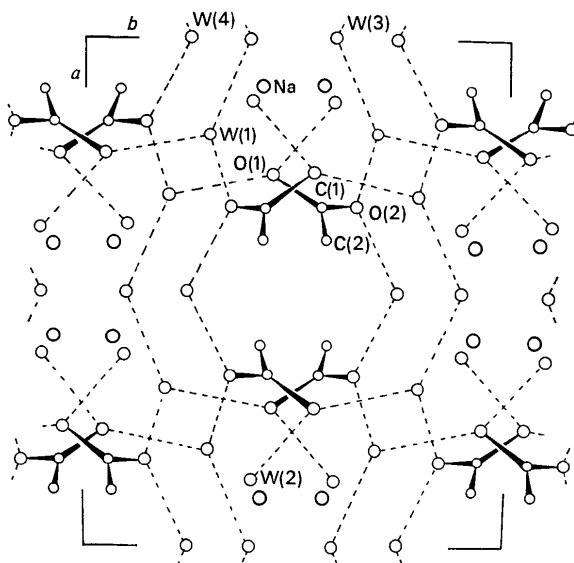

Fig. 1. A projection of the structure viewed along c. Hydrogen bonds are shown as broken lines. All the labelled atoms are in equivalent position [1] (Table 2).
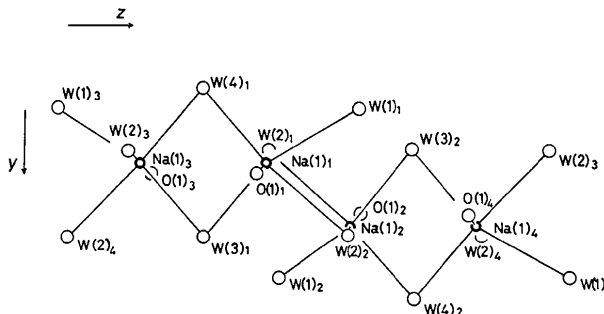

Fig. 2. The sodium ion environment as seen down a. The subscript numbers refer to the equivalent positions in Table 2.

Table 1. *Final atomic parameters* ($\times 10^4$)

U's are in Å^2. The temperature factor $T=\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*)\right]$, and W refers to the oxygen atom of a water molecule.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	883 (4)	4287 (4)	4201 (5)	41	21	45	−15	16	−21
O(1)	2645 (9)	4652 (8)	3732 (9)	60	18	58	−15	34	−51
O(2)	3368 (10)	6539 (9)	3464 (10)	92	38	75	−23	50	56
C(1)	3254 (11)	5597 (11)	4231 (13)	37	24	50	−54	29	−10
C2(2)	3939 (14)	5684 (14)	5760 (15)	98	50	31	16	−31	34
W(1)	3493 (10)	2113 (8)	3821 (10)	86	22	56	8	−26	13
W(2)	8789 (7)	4171 (7)	4048 (8)	17	22	29	7	−9	14

Table 1 (cont.)

	x	y	z	B_{iso}*
$W(3)$	0	6002 (8)	2500	2·553
$W(4)$	0	2608 (9)	2500	2·102
H(1)	4650	3800	800	4·0
H(2)	3300	4000	1200	4·0
H(3)	4000	5250	1000	4·0
H(4)	630	6500	2500	4·0
H(5)	730	2000	2500	4·0
H(6)	1870	8000	1250	4·0
H(7)	2300	6800	1750	4·0
H(8)	625	3250	250	4·0
H(9)	1867	4250	250	4·0

* These values are not $\times 10^4$.

Table 2. Key to the labelling of atoms

Equivalent position	Label	Equivalent position	Label
$x, y,\ \ z$	[1]	$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$	[5]
$\bar{x}, \bar{y},\ \ \bar{z}$	[2]	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$	[6]
$\bar{x}, y, \frac{1}{2}-z$	[3]	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	[7]
$x, \bar{y}, \frac{1}{2}+z$	[4]	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$	[8]

calculation the refinement converged at $R=0·11$ after five more cycles. Throughout the refinement with anisotropic temperature factors to avoid 'yawing' and the consequent false minima, the parameters were altered by 0·3 of the calculated shift.

The form factors used were those in *International Tables for X-ray Crystallography* (1962). The observed structure amplitudes and structure factors calculated from the atomic parameters in Table 1 are available.*

---

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31123 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England. Copies are also available from the Libraries of the University of Ulster, Coleraine, N. Ireland and the University of Dacca. Catalogue No. QD 921 C. 35. Copies may be obtained on application to the Librarian for Science.

A key to the labelling of the atoms produced by different symmetry operations is given in Table 2 and the interatomic distances and interbond angles are given in Table 3; water oxygens are labelled W to distinguish them from acetate oxygen atoms. Fig. 1 shows a projection of the unit cell along the c axis and Fig. 2 is a detail of the chain of coordination polyhedra viewed down the a axis.

Results and discussion

The structure contains four distinct water molecules, two in general positions which with two in special positions on the twofold axis produce the molecular formula $3H_2O$. The coordination of the six closest oxygen atoms about the Na^+ ion is approximately octahedral (Table 3). It consists of one acetate oxygen atom and the four water molecules $W(1-4)$ with the final position occupied by a water molecule $\{W(2)[2]\}$ centrosymmetically related to that already used. Adjacent oxygen polyhedra share an edge through the atoms in special positions [$W(3)$ and $W(4)$] on one side and through the centrosymmetically related pair of atoms $\{W(2)$ and $W(2)[2]\}$ on the other (Fig. 2). In the centre of the unit cell there is a tube of apparent free space but this is efficiently filled by the methyl groups of the acetate ion (Fig. 1), with several short carbon–carbon contact distances in the range 3·6–3·8 Å.

Acetate ion

The two C–O bond lengths are 1·23 (013) and 1·31 (014) Å for atoms O(1) and O(2) respectively, so they are only just significantly different. In ammonium acetate the corresponding distances are 1·250 and 1·253 Å (Nahringbauer, 1967), while in lithium acetate dihydrate these distances are equivalent by symmetry with a length of 1·245 Å (Galigné, Mouvet & Falgueirettes, 1970). The disparity in the C–O bond

Table 3. Interatomic distances (Å) and interbond angles (°)

E.s.d.'s are in parentheses. Numbers in square brackets indicate the symmetry (see Table 2) and W refers to the oxygen atom of a water molecule.

Na——O(1)	2·458 (7)		O(1)[1]–Na[1]–W(2)[2]	98·5 (3)	
Na——W(1)	2·401 (8)		O(1)——Na——W(1)	104·2 (3)	
Na——W(2)[2]	2·349 (7)		O(1)——Na——W(2)	164·7 (3)	
Na——W(3)	2·460 (7)		O(1)——Na——W(3)	86·0 (3)	
Na——W(4)	2·433 (7)		O(1)——Na——W(4)	98·8 (3)	
Na——W(2)[1]	2·557 (7)		W(1)——Na——W(2)	90·6 (3)	
O(1)——C(1)	1·23 (1)		W(1)[1]–Na[1]–W(2)[2]	80·9 (3)	
O(2)——C(1)	1·31 (1)		W(1)——Na——W(3)	165·7 (3)	
C(1)——C(2)	1·50 (1)		W(1)——Na——W(4)	95·7 (3)	
			W(2)——Na——W(3)	80·0 (3)	
W(1)[4]–H(7)[4]· · ·O(2)[1]	2·68 (2)		W(2)——Na——W(4)	75·9 (3)	
W(1)[4]–H(6)[4]· · ·O(1)[7]	2·83 (2)		W(2)[1]–Na[1]–W(2)[2]	87·1 (3)	
W(2)[3]–H(9)[3]· · ·O(1)[4]	2·81 (2)		W(2)[2]–Na[1]–W(3)[1]	87·9 (3)	
W(3)[1]–H(4)[1]· · ·W(1)[4]	2·96 (2)		W(2)[2]–Na[1]–W(4)[1]	162·6 (3)	
W(4)[5]–H(5)[7]· · ·O(2)[7]	2·82 (2)		W(3)——Na——W(4)	92·4 (3)	
Na—O(1)–C(1)	119·6 (3)				
O(1)–C(1)–C(2)	120·5 (5)				
O(2)–C(1)–C(2)	117·1 (5)				
O(1)–C(1)–O(2)	122·3 (5)				

lengths in this compound is probably caused by hydrogen bonding, since each oxygen atom forms two hydrogen bonds but one, $O(2)\cdots W(1)$, is somewhat stronger than the others. The conformation of methyl hydrogen atoms around the C–C axis is such that the hydrogen atoms of one group fit into the spaces between the hydrogen atoms of an adjacent group.

Na^+–O contacts

The Na^+–O are in the range 2·35 (1) to 2·56 (1) Å with the distance to the acetate oxygen atom in the middle of the range at 2·46 (1) Å. The O–Na^+–O interbond angles vary between 80·9 (3) and 104·2 (3)° for the angles which would be 90° in a regular octahedron and 162·6 (3)–165·7 (3)° for those angles that should be 180°. A similar distorted octahedron was found by Gupta & Sahu (1970) in sodium hydrogen fumarate, where the Na^+–O distances ranged from 2·38 to 2·64 Å, and by Young, Tollin & Wilson (1974) in disodium deoxyguanosine-5′-phosphate tetrahydrate, where the Na^+–O distances were between 2·354 (5) and 2·559 (5) Å and the angles 78·1 (3) to 100·1 (3)°.

The separations between adjacent Na^+ ions are 3·39 and 3·56 Å with the closer separation corresponding to the octahedra shared through atoms $W(3)$ and $W(4)$. In trisodium tetraaquooctacyanotungstate where there is a similar coordination arrangement with shared edges around the Na^+ ion the $Na^+\cdots Na^+$ separations are 3·67 and 3·50 Å (Bok, Leipoldt & Basson, 1970).

Hydrogen bonding

The dashed lines in Fig. 1 indicate the probable hydrogen-bonding scheme. The oxygen$\cdots$oxygen contact distances for the hydrogen bonds are listed in Table 3. They vary between 2·68 and 2·96 Å. The O–$H\cdots O$ angles are in the range 142–174°. The only hydrogen atom not involved in bonding is $H(8)$ which itself makes the closest contact to $O(2)$ of 2·3 Å. Each oxygen atom of the acetate ion forms two hydrogen bonds. The acetate ions related by the twofold screw axis are hydrogen bonded together through water molecule $W(1)$ and the system $\cdots W(1)[4]\cdots O(2)$–$C(1)$–$O(1)\cdots W(1)[6]\cdots O(2)[7]$– forms a helix about this axis. The helices are bonded together by hydrogen bonds involving $W(2)$, $W(3)$ and $W(4)$.

References

BOK, L. D. C., LEIPOLDT, J. G. & BASSON, S. S. (1970). Acta Cryst. B26, 684–692.
CAMERON, T. S. (1972). Internal report.
GALIGNÉ, J. L., MOUVET, M. & FALGUEIRETTES, L. (1970). Acta Cryst. B26, 368–372.
GROTH, P. (1910). Chemische Krystallographie, Vol. III, pp. 64–65. Leipzig: Engelmann.
GUPTA, M. P. & SAHU, R. G. (1970). Acta Cryst. B26, 1964–1973.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
MANNAN, K. M. & RAHMAN, M. O. (1972). Acta Cryst. B28, 320.
NAHRINGBAUER, I. (1967). Acta Cryst. 23, 956–960.
PADMANABHAN, V. M. (1952). Curr. Sci. 21, 97.
YOUNG, D. W., TOLLIN, P. & WILSON, H. R. (1974). Acta Cryst. B30, 2012–2018.