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Sodium Acetate Trihydrate: A Redetermination

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$C_2H_3NaO_2.3H_2O$, monoclinic, $C2/c$; $a = 12{\cdot}353\,(5)$, $b = 10{\cdot}466\,(6)$, $c = 10{\cdot}401\,(6)$ Å, $\beta = 111{\cdot}69\,(4)^\circ$, 23 °C; $M_r = 136{\cdot}08$; $Z = 8$, $D_x = 1{\cdot}447$ g cm^{-3}; the material was recrystallized from aqueous solutions. The final R was 0·038 (2279 unique diffractometer data, Mo $K\alpha$, $2\theta \leq 65^\circ$, isotropic H, anisotropic non-H). The Na^+ ion is coordinated by six O atoms in a distorted octahedral arrangement at distances of 2·349 to 2·512 Å. The C—O distances are 1·253 and 1·257 Å. Extensive hydrogen bonding in two dimensions, involving both carboxyl O atoms and the waters of hydration joins the acetate ions and waters of hydration into sheets parallel to (001); chains of O polyhedra coordinating the Na^+ ions connect the sheets to complete the three-dimensional structure.

Introduction

Crystals of the title compound are currently being used in a study of the ESR of methyl radicals in crystals (Rogers, 1975). The crystal and molecular structure determination of the title compound was undertaken to further elucidate the results of the ESR studies and to reveal the hydrogen-bonding network in the crystal.

A single crystal of approximate dimensions 0·25 × 0·29 × 0·89 mm [μ(Mo $K\alpha$) = 1·477 cm^{-1}] was sealed in a glass capillary tube with a drop of saturated aqueous solution to prevent loss of water from the crystal. The diffraction conditions hkl: $h + k = 2n$, $h0l$: $l = 2n$ ($h = 2n$), the absence of other non-related conditions, and the monoclinic symmetry indicate the space groups $C2/c$ and Cc. Diffraction data were measured at 23 °C with a Picker FACS-I automatic diffractometer and Zr-filtered Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings (2θ, ω, χ, φ) of 12 reflections in the range $35 \leq 2\theta \leq 39^\circ$, for which the α_1, α_2 doublet was clearly resolved [λ(Mo $K\alpha_1$) = 0·70926 Å]. The 2279 unique reflections (including 352 'unobserved') in the $+h + k \pm l$ region were collected for $2\theta \leq 65^\circ$ with the θ–2θ scan method: a scan speed of 1° (2θ) min^{-1}; 10 s backgrounds; and scan ranges of 1·2° (2θ) plus the α_1,α_2 divergences. Three standard reflections measured after every 50 data were used to scale the data.

The data were reduced and standard deviations calculated as a function of counting statistics, as reported previously (Wei & Ward, 1976); the least-squares refinement weights were calculated from the standard deviations of the structure factors by weight (w) = $1/[\sigma^2 + (0{\cdot}02F)^2]$; an extinction correction was applied (EF = 0·32 × 10^{-6}) and an absorption correction (Templeton & Templeton, 1973) giving corrections to F ranging from 1·031 to 1·047 was also applied.

Structure solution and refinement

The crystal structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study include *ORTEP* (Johnson, 1965), the entire system of Allan Zalkin's programs (Zalkin, 1974), *ABSOR* (Templeton & Templeton, 1973), and programs written and/or modified locally. A CDC 6500 computer was used.

The structure was refined by full-matrix least squares to $R_1 = (\Sigma\,|F_o - F_c|)/\Sigma F_o = 0{\cdot}038$, $R_2 = [\Sigma\, w(F_o - F_c)^2/\Sigma\, w(F_o)^2]^{1/2} = 0{\cdot}034$; $R_1 = 0{\cdot}047$ including the 352 zero-weighted data for which $I \leq \sigma(I)$, the standard deviation of an observation of unit weight (1·529), and the atomic parameters listed in Table 1. The maximum shift-to-error ratio for the last cycle of least-squares refinement was 0·000. The final difference map showed densities ranging from +0·22 to −0·13 e Å^{-3}, with no indication of incorrectly placed or missing atoms. The scattering factors of Doyle & Turner (1968) were used for the non-H atoms, those of Stewart, Davidson & Simpson (1965) for H; the anomalous scattering factors of Cromer & Liberman (1970) were used for the non-H atoms, and anomalous scattering factors of zero were assumed for H. Interatomic distances and angles are listed in Table 2.*

The structure and hydrogen bonding

The Na^+ and acetate ions lie in general positions and the waters of hydration (whose O atoms are labelled *W* to distinguish them from acetate O atoms) consist of two molecules in general positions and two in special positions along the twofold axes; the molecular formula is $Na^+(C_2H_3O_2)^-.3H_2O$.

The geometry of the acetate ion is very similar to that found in ammonium acetate (Nahringbauer, 1967) (whose values are listed in parentheses): C—C 1·505 (1·504), C—O(1) 1·253 (1·250), C—O(2) 1·257 (1·253 Å); O—C—O 123·7 (123·4), C—C—O(1) 118·7 (118·5), and C—C—O(2) 117·6 (118·0°). The acetate ion is relatively planar with the maximum deviation from the least-squares plane of C(1), C(2), O(1) and O(2) being less than 0·001 Å for C(1).

The hydrogen-bonding network, involving each water H atom in a normal hydrogen bond, consists of: bonds between carboxylate O atom O(1) and waters of hydration *W*(1) and *W*(2); bonds between carboxylate O atom O(2) and waters of hydration *W*(1), *W*(2) and *W*(4); and a bond between waters of hydration *W*(3) and *W*(1). This network of hydrogen bonds joins the acetate ions and the waters of hydration into sheets parallel to (001). A stereo drawing of the structure, indicating possible hydrogen bonds by fine solid lines, is shown in Fig. 1. The arrangement of atoms around O(1) is far from planar; that about O(2) and *W*(1) is considerably distorted from regular tetrahedral [assuming a lone pair of electrons of *W*(1) occupies the fourth position] and the angles across *W*(3) and *W*(4) are both opened to 132°. The hydrogen-bonding geometry, based on O coordinates, is not ideal and is probably a result of the molecular packing; however, an examination of Table 2 shows that the hydrogen bonds themselves are fairly uniform in length and are fairly linear.

Table 1. *Atomic parameters for sodium acetate trihydrate*

Fractional coordinates are ×10^5, for H × 10^3. Thermal parameters in Å^2. Anisotropic temperature factor in the form $\exp[-\frac{1}{4}\Sigma_i\Sigma_j(a_i^*a_j^*h_ih_jB_{ij})]$, where a_i^* is a reciprocal-cell edge and h_i is one of the Miller indices.

	x	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na	8803 (3)	42870 (3)	42131 (3)	2·24 (1)	2·16 (1)	2·05 (1)	−0·14 (1)	0·75 (1)	−0·13 (1)
C(1)	32590 (7)	56152 (8)	42150 (9)	1·73 (3)	1·85 (3)	2·25 (3)	0·05 (2)	0·68 (2)	0·12 (2)
C(2)	39423 (10)	56698 (14)	57491 (11)	3·26 (4)	4·68 (6)	2·31 (4)	−0·92 (4)	0·30 (3)	−0·01 (4)
O(1)	26225 (6)	46641 (6)	37289 (7)	2·54 (2)	1·97 (2)	2·73 (3)	−0·42 (2)	0·82 (2)	−0·15 (2)
O(2)	33646 (7)	65349 (7)	34929 (8)	3·39 (3)	2·45 (3)	3·19 (3)	−0·67 (2)	0·78 (2)	0·68 (2)
W(1)	35084 (7)	21112 (8)	38428 (9)	3·23 (3)	2·20 (3)	3·07 (3)	0·44 (2)	0·43 (2)	0·06 (2)
W(2)	88005 (6)	41728 (7)	40426 (7)	2·74 (3)	2·05 (3)	2·35 (3)	−0·12 (2)	0·74 (2)	−0·28 (2)
W(3)	0	59762 (10)	25000	3·15 (4)	2·21 (4)	3·23 (4)	0·0	1·65 (4)	0·0
W(3)	0	26258 (9)	25000	3·43 (4)	1·96 (3)	3·31 (4)	0·0	1·97 (4)	0·0

	x	*y*	*z*	B_{iso}		*x*	*y*	*z*	B_{iso}
H(1)	466 (2)	398 (3)	86 (2)	8·4 (5)	H(6)	166 (1)	774 (2)	100 (2)	4·7 (4)
H(2)	359 (2)	358 (3)	113 (3)	10·8 (8)	H(7)	205 (1)	683 (2)	178 (2)	4·5 (3)
H(3)	370 (2)	494 (2)	125 (2)	6·7 (4)	H(8)	130 (1)	339 (2)	95 (1)	3·5 (3)
H(4)	32 (1)	641 (2)	213 (2)	4·0 (3)	H(9)	168 (1)	438 (1)	178 (2)	3·8 (3)
H(5)	41 (1)	215 (2)	228 (2)	4·2 (3)					

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31988 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

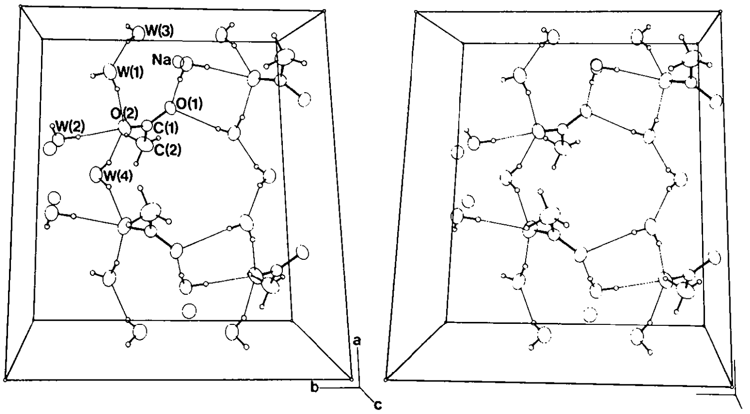

Fig. 1. Hydrogen bonding, showing one sheet of acetate ions and waters of hydration (*ORTEP*, Johnson, 1965).

Six O atoms lie in a distorted octahedral arrangement around the Na$^+$ ion at distances of 2·349 to 2·512 Å, with an average of 2·427 Å. The angles that would be 90° in a regular octahedral arrangement range from 75·30 to 104·47° with an average of 89·83°; those ideally 180° are 162·91, 163·60, and 166·71°. The O polyhedra form chains in the z direction by the hydrogen bond between atoms *W*(1) and *W*(3) and by sharing edges; one edge consists of atoms *W*(3) and *W*(4) and the other consists of centrosymmetrically related *W*(2) atoms. The distances between adjacent Na$^+$ ions are 3·421 and 3·503 Å; the shorter distance is that across the twofold axis. Fig. 2 illustrates the environment of the Na$^+$ ions and the chain of O polyhedra along the line $0, \frac{1}{2}, z$; twofold axes lie approximately normal to the paper, passing through *W*(3) and *W*(4), and the centers of symmetry are indicated. The coordination distances and angles around the Na$^+$ ion are given in Table 2. It is these chains which connect the two-dimensional hydrogen-bonded sheets of acetate ions and waters of hydration to form the rigid three-dimensional structure.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in sodium acetate trihydrate*

Bond distances and angles	
C(1)–C(2)	1·505 (1)
C(1)–O(1)	1·253 (1)
C(1)–O(2)	1·257 (1)
C(2)–H(1)^j	0·93 (3)
C(2)–H(2)^j	1·05 (3)
C(2)–H(3)^j	0·94 (2)
W(1)–H(6)^d	0·73 (2)
W(1)–H(7)^d	0·81 (2)
W(2)–H(8)^f	0·83 (2)
W(2)–H(9)^f	0·87 (2)
W(3)–H(4)	0·79 (2)
W(4)–H(5)	0·80 (2)
O(1)–C(1)–O(2)	123·7 (1)
O(1)–C(1)–C(2)	118·7 (1)
O(2)–C(1)–C(2)	117·6 (1)
C(1)–C(2)–H(1)^j	106 (1)
C(1)–C(2)–H(2)^j	106 (1)
C(1)–C(2)–H(3)^j	113 (1)
H(6)^d–*W*(1)–H(7)^d	106 (2)
H(8)^f–*W*(2)–H(9)^f	102 (2)
H(4)–*W*(3)–H(4)^e	109 (1)
H(5)–*W*(4)–H(5)^e	103 (1)
Coordination of Na$^+$ ion	
Na–O(1)	2·417 (1)
Na–*W*(1)^a	2·382 (1)
Na–*W*(2)^b	2·512 (1)
Na–*W*(2)^c	2·349 (1)
Na–*W*(3)	2·460 (1)
Na–*W*(4)	2·439 (1)
O(1)–Na–*W*(1)^a	104·47 (3)
O(1)–Na–*W*(2)^b	163·60 (3)
O(1)–Na–*W*(2)^c	98·09 (3)
O(1)–Na–*W*(3)	85·47 (2)
O(1)–Na–*W*(4)	98·92 (3)
W(1)^a–Na–*W*(2)^b	91·48 (3)
W(1)^a–Na–*W*(2)^c	81·71 (3)
W(1)^a–Na–*W*(3)	166·71 (4)
W(1)^a–Na–*W*(4)	95·63 (4)
W(2)^b–Na–*W*(2)^c	87·85 (4)
W(2)^b–Na–*W*(3)	79·42 (2)
W(2)^b–Na–*W*(4)	75·30 (2)
W(2)^c–Na–*W*(3)	88·24 (3)
W(2)^c–Na–*W*(4)	162·91 (3)
W(3)–Na–*W*(4)	91·42 (2)

Comparison

The crystal structure of $C_2H_3NaO_2.3H_2O$ has been reported previously by Cameron, Mannan & Rahman (1976) (hereafter CMR). The study by CMR obtained 475 observed and 81 unobserved diffraction data from Weissenberg photographs with Cu $K\alpha$ radiation at 30°C; absorption [μ(Cu $K\alpha$) = 16·8 cm^{-1}] corrections were not applied to the data; anisotropic refinement of the non-H atoms by block-diagonal least squares (H atoms held as fixed contributors with coordinates from a difference map and isotropic temperature factors set to 4·0 Å^2) led to R = 11%. The atomic parameters in the present study have been labeled and chosen from among the possible equivalent positions to correspond directly to those of CMR.

Table 2 (*cont.*)

Hydrogen bonding

	O···H	O···O	O···H–O
O(1)–H(6)^d–W(1)	2·17 (2)	2·873 (1)	161
O(1)–H(9)–W(2)^f	1·95 (2)	2·814 (1)	172
O(2)–H(5)^h–W(4)^g	2·06 (2)	2·827 (1)	159
O(2)–H(7)–W(1)^h	1·94 (2)	2·732 (1)	166
O(2)–H(8)^h–W(2)^i	2·03 (2)	2·830 (1)	163
W(1)–H(4)^d–W(3)^d	2·18 (2)	2·943 (1)	163

C(1)–O(1)–W(1)	123·32 (6)	W(1)^i–W(3)–W(1)^h	132·38 (3)
C(1)–O(1)–W(2)^f	128·29 (6)	O(2)^d–W(4)–O(2)^k	132·37 (2)
W(1)–O(1)–W(2)^f	87·51 (3)	C(1)–O(2)–W(1)^h	117·36 (6)
Sum around O(1)	339·12	C(1)–O(2)–W(2)^i	132·86 (6)
O(1)–W(1)–O(2)^d	89·09 (3)	C(1)–O(2)–W(4)^g	140·66 (6)
O(1)–W(1)–W(3)^d	130·66 (3)	W(1)^h–O(2)–W(2)^i	89·98 (3)
O(2)^d–W(1)–W(3)^d	87·81 (3)	W(1)^h–O(2)–W(4)^g	94·05 (3)
O(1)^f–W(2)–O(2)^i	88·35 (3)	W(2)^i–O(2)–W(4)^g	64·64 (3)

Symmetry code

(*a*)	$\frac{1}{2}-x$,	$\frac{1}{2}-y$,	$1-z$	(*g*)	$\frac{1}{2}+x$,	$\frac{1}{2}+y$,	z
(*b*)	$-1+x$,	y,	z	(*h*)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
(*c*)	$1-x$,	$1-y$,	$1-z$	(*i*)	$-\frac{1}{2}+x$,	$\frac{1}{2}+y$,	z
(*d*)	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	(*j*)	x,	$1-y$,	$\frac{1}{2}+z$
(*e*)	$-x$,	y,	$\frac{1}{2}-z$	(*k*)	$-\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	z
(*f*)	$1-x$,	y,	$\frac{1}{2}-z$	(*l*)	$\frac{1}{2}+x$,	$-\frac{1}{2}+y$,	z

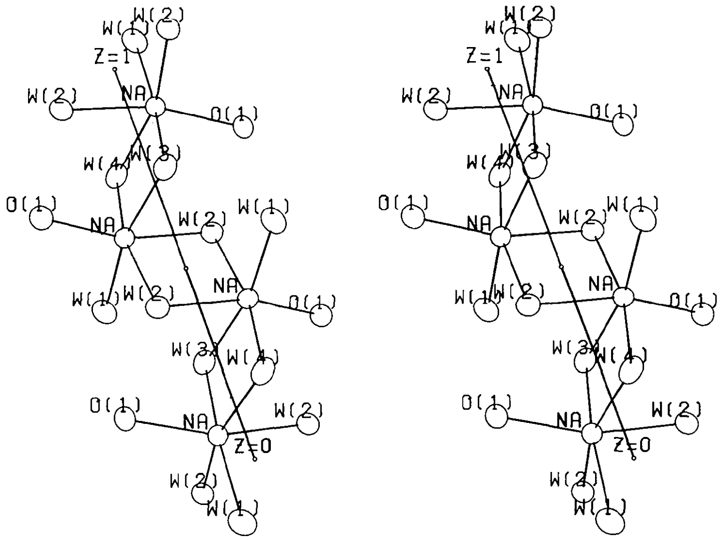

Fig. 2. Sodium-ion environment, viewed approximately along **b** and showing the line 0, $\frac{1}{2}$, z (*ORTEP*, Johnson, 1965).

The unit-cell parameters of $C_2H_3NaO_2.3H_2O$ have been reported by several authors and the results are summarized in Table 3. Of the five reported determinations of the axial ratios $a:b$ and $b:c$, four agree rather well and those of CMR are different. The unit-cell parameters reported by CMR (especially a, c and β) differ significantly from those of the other determinations. Considering the high degree of precision reported for their cell parameters, one may conclude that these differences are real and significant and may possibly be due (as suggested by CMR) to the humidity and high temperature of Dacca.

The structure determined by CMR is essentially the same as that found in the present study; the differences

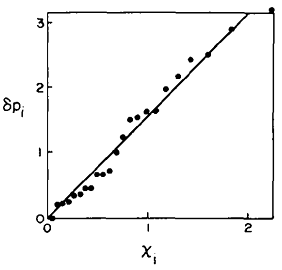

Fig. 3. Half-normal probability plot of 23 δp_i derived from the comparison of the refined atomic positional parameters reported by Cameron, Mannan & Rahman (1976) and those of the present study.

Table 3. *Comparison of unit-cell parameters determined for sodium acetate trihydrate*

	Groth (1910)	Padmanabhan (1952)	Kálmán (1965)	CMR	Present study
a (Å)	–	12·4	12·321 (10)	12·475 (2)	12·353 (5)
b	–	10·5	10·425 (10)	10·407 (3)	10·466 (6)
c	–	10·3	10·380 (10)	10·499 (3)	10·401 (6)
β(°)	111·72*	112·1	111·71 (15)	112·65 (5)	111·69 (4)
a:*b*	1·1809	1·18	1·1818	1·1987	1·1803
b:*c*	0·9962	0·99	0·9957	1·0040	0·9938
V (Å^3)	–	1243†	1238·7†	1251·94	1249·49
T (°C)	–	–	–	30	23
Space group	–	*C*2/*m*	*C*2/*c*	*C*2/*c*	*C*2/*c*

* Converted from the reported value of 111°43′.
† Calculated by the present authors.

are primarily due to the greater precision in the present study arising from the expanded and more precise data set. A half-normal probability plot (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) is shown in Fig. 3 for the comparison of the refined positional parameters and their estimated errors for the non-H atoms of the present study and those of CMR. The plot shows little deviation from a straight line of zero intercept and slope of 1·58. From this it may be concluded that there are no systematic differences between the non-H atom positional parameters of the two studies. As the estimated errors for the positional parameters in the present study are typically less than 1/10 those of CMR, they are insignificant in calculating the weighted parameter differences and the slope of 1·58 indicates that the estimated errors in the study by CMR are underestimated by approximately that factor.

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