Notes

Crystal Structure of Sodium Dihydrogen Triacetate

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In the crystal structure of $NaH_2[O_2CCH_3]_3$ the residues CH_3CO_2H and $CH_3CO_2^-$ are crystallographically distinct; they are co-ordinated to the Na^+ ions forming chains parallel to the *c* axis, which are strengthened by short asymmetric hydrogen bonds. Intermolecular interactions hold together these parallel chains. The crystals are tetragonal, space group $P4_1$, with $a = 8.266(1)$, $c = 14.794(2)$ Å, $Z = 4$, and $R = 0.050$ for 609 ' observed ' reflections

THE hydrogen diacetates of ammonium,[1] sodium,[2] and potassium [3] have been fully investigated, whereas there are only few, inconclusive reports on the dihydrogen triacetates,[4] and nothing at all is known about their structural properties. Therefore we report here the preparation and *X*-ray crystal structure of the title compound, the first example of a dihydrogen triacetate.

EXPERIMENTAL

The crystals have been obtained as a by-product in the preparation of acetato-borate complexes of sodium: acetic anhydride (20 cm^3) was added to a suspension of orthoboric acid (3.05 g, 0.05 mol) in acetic acid (10 cm^3) and the mixture was heated until all the solid had dissolved. After cooling, anhydrous sodium carbonate (2.65 g, 0.025 mol) was added and the mixture heated again until a clear solution was obtained. From this solution a few colourless crystalline needles, elongated along the *c* axis, were obtained after some months. They immediately decompose in air; therefore a crystal with dimensions *ca.* 0.2 × 0.3 × 0.6 mm was mounted in a capillary, which was sealed after addition of mother-liquor. From the above solution, sodium tetraacetatoborate, $Na[B(O_2CMe)_4]$, was obtained after several months.

Crystal Data.—$C_6H_{11}NaO_6$, $M = 202.14$, Tetragonal, $a = 8.266(1)$, $c = 14.794(2)$ Å, $U = 1\,010.8$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}, $F(000) = 380.06$, space group $P4_1$, (Mo-K_α) radiation, $\lambda = 0.710\,7$ Å, graphite crystal monochromator, μ(Mo-K_α) = 1.61 cm^{-1}. Intensity data were collected with a Philips PW computer-controlled automatic diffractometer, with a scan width = 2°, scan speed 0.1° s^{-1}, in the range $2 \leqslant \theta \leqslant 30°$, maximum $(\sin \theta)/\lambda = 0.7035$ Å^{-1}. Of 1 530 independent reflections (from 3 236 collected), 609 having $I \geqslant 3\sigma(I)$ were processed. Intensities were corrected for Lorentz and polarisation factors; absorption was assumed to be negligible. Cell dimensions were determined by the least-squares method from 20 high-angle reflections. The structure was solved by direct methods [5] and anistropically refined by least squares to $R = 0.050$ for the 609 ' observed ' reflections. No significant electron density was found in the ΔF map where hydrogen atoms were expected. The final atomic parameters are listed in Table 1, and bond lengths and angles in Table 2. Tables of structure factors, anisotropic thermal parameters, and isotropic temperature factors are listed in Supplementary Publication No. SUP 23045 (14 pp.).*

TABLE 1

Final atomic co-ordinates with their standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Na	0.008 5(2)	0.048 5(2)	0.101 4(3)
C(1)	0.159 7(7)	0.644 2(7)	0.109 0(3)
C(2)	0.616 4(8)	0.879 0(7)	0.095 4(4)
C(3)	0.806 8(5)	0.319 1(4)	0.226 8(4)
C(4)	0.687 5(6)	0.877 7(5)	0.189 6(3)
C(5)	0.705 5(5)	0.470 3(5)	0.228 4(4)
C(6)	0.142 0(6)	0.714 4(6)	0.014 0(3)
O(1)	0.584 4(4)	0.850 6(4)	0.254 1(2)
O(2)	0.832 4(4)	0.895 1(3)	0.203 2(2)
O(3)	0.056 2(4)	0.826 3(4)	−0.003 5(2)
O(4)	0.831 1(4)	0.245 6(4)	0.299 9(2)
O(5)	0.862 2(4)	0.269 5(4)	0.152 1(2)
O(6)	0.224 3(4)	0.634 8(5)	−0.047 4(2)

TABLE 2

Interatomic distances (Å) and bond angles (°), with standard deviations in parentheses

(*a*) $CH_3CO_2^-$	
C(5)–C(3)	1.505(5)
C(3)–O(4)	1.256(5)
C(3)–O(5)	1.265(5)
O(4)–C(3)–O(5)	122.51(34)
C(5)–C(3)–O(4)	118.54(43)
C(5)–C(3)–O(5)	118.94(43)
(*b*) CH_3CO_2H (I)	
C(1)–C(6)	1.517(6)
C(6)–O(3)	1.213(5)
C(6)–O(6)	1.300(5)
O(6)–C(6)–O(3)	122.46(41)
C(1)–C(6)–O(6)	114.75(44)
C(1)–C(6)–O(3)	112.79(44)
(*c*) CH_3CO_2H (II)	
C(2)–C(4)	1.512(7)
C(4)–O(2)	1.223(5)
C(4)–O(1)	1.299(5)
O(1)–C(4)–O(2)	122.84(40)
C(2)–C(4)–O(1)	114.99(43)
C(2)–C(4)–O(2)	122.12(46)
(*d*) Hydrogen bonds	
O(6)–O(4)	2.509(4)
O(1)–O(5)	2.503(4)
(*e*) Na polyhedron	
Na–O(2)	2.448(3)
Na–O(2′)	2.580(4)
Na–O(3)	2.437(3)
Na–O(3′)	2.544(4)
Na–O(4)	2.326(3)
Na–O(5)	2.316(4)
O(2)–Na–O(2′)	120.27(9)
O(2)–Na–O(3)	95.61(10)
O(2)–Na–O(3′)	79.25(11)
O(2)–Na–O(4)	157.53(14)
O(2)–Na–O(5)	84.18(12)
O(2′)–Na–O(3)	78.75(11)
O(2′)–Na–O(3′)	154.45(11)
O(2′)–Na–O(4)	82.20(11)
O(2′)–Na–O(5)	77.54(11)
O(3)–Na–O(3′)	118.01(10)
O(3)–Na–O(4)	88.72(12)
O(3)–Na–O(5)	152.27(14)
O(3′)–Na–O(4)	79.26(11)
O(3′)–Na–O(5)	89.28(12)
O(4)–Na–O(5)	102.05(14)
(*f*) Shortest intermolecular contacts	
O(1)–C(1)	3.537(6)
O(1)–O(6)	3.661(6)

DISCUSSION

As in Type B (asymmetric [6]) hydrogen diacetate salts,[1,3] two kinds of non-equivalent residues are present in the anionic unit of sodium dihydrogen triacetate (see C–O distances in Table 2); namely a symmetrical $CH_3CO_2^-$ anion C(5),C(3),O(4),O(5) and two neutral asymmetrical CH$_3$-

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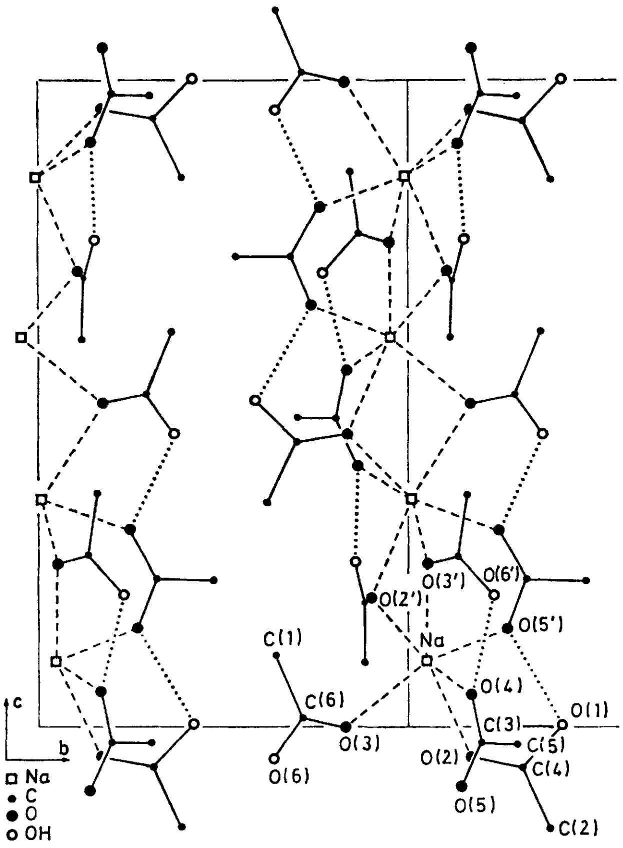
* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

CO_2H molecules, C(1),C(6),O(3),O(6) and C(2),C(4),O(2),O(1). In these last two, O(1) and O(6) can be identified as hydroxyls; they have indeed the longest C–O distances [1.299(5) and 1.300(5) Å respectively]. Neither O(1) nor O(6) belongs to the Na co-ordination polyhedron [Na–O(1) = 3.604(4), Na–O(6) = 3.611(4) Å]; they are linked to O(4) and O(5) of the $CH_3CO_2^-$ anion by two strong[6] asymmetrical hydrogen bonds, whose lengths [2.503(4) and 2.509(4) Å respectively] are intermediate between the Type B (asymmetric[6]) hydrogen bonds found in potassium hydrogen diacetate[3] (2.476 Å) and the Type B hydrogen bonds in the ammonium salt[1] (2.517 Å). The O(4) and O(5) atoms of the acetate ions, even if they are involved in these hydrogen bonds, have nevertheless the shortest Na–O distances, according to the remarkable electrostatic attraction between the Na^+ and $CH_3CO_2^-$ ions. These distances are furthermore significantly shorter than the corresponding ones found in sodium hydrogen diacetate.[2] The main structural feature of the title compound (Figure) is the chains of Na co-ordination polyhedra generated by repetition along the 4_1 axis of the asymmetric unit $NaH_2[O_2CCH_3]_3$ ($= Na^+ + CH_3CO_2^- + 2\ CH_3CO_2H$); the Na polyhedra are distorted octahedra directly tied along the chain direction by the shared O(2)–O(3) edges and further bridged by $CH_3CO_2^-$. The chain is strengthened by the hydrogen bonds O(1)–O(5) and O(6)–O(4). Only intermolecular interactions bind the parallel chains in the framework, the shortest intermolecular distances being O(1)–C(1) [3.537(6) Å] and O(1)–O(6) [3.661(6) Å].



View of the packing down the *a* axis

The C–C bond length in $CH_3CO_2^-$ is exactly the expected one for a single bond between sp^3 and sp^2 carbon atoms[7] [1.505(5) Å]; in both the CH_3CO_2H units this distance does not significantly differ from the preceding one. All the acetate groups are planar within the standard deviations.

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