Refinement of the crystal structure of sodium hydrogen maleate trihydrate, $NaH(C_4H_2O_4) \cdot 3H_2O$, *at room temperature*

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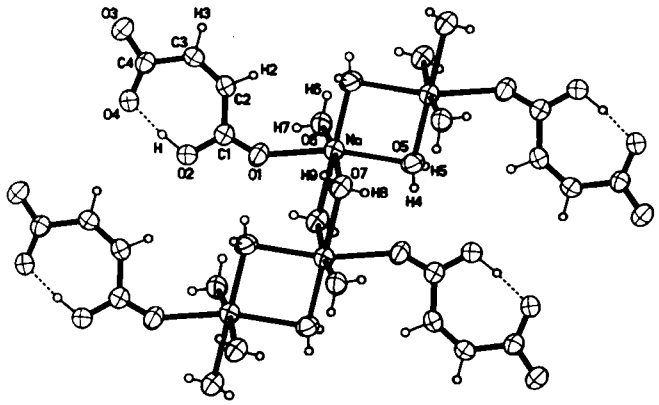

Abstract

$C_4H_9NaO_7$, triclinic, $P\bar{1}$ (No. 2), $a = 5.956(1)$ Å, $b = 6.392(1)$ Å, $c = 11.230(1)$ Å, $\alpha = 104.17(1)°$, $\beta = 91.55(1)°$, $\gamma = 100.20(1)°$, $V = 406.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.035$, $wR_{ref}(F^2) = 0.092$, $T = 293$ K.

Source of material

0.42 g (3.60 mmol) maleic acid was dissolved in 10 ml CH_3OH/H_2O (1:1 v/v) and then 1.0 ml (1 M) Na_2CO_3 was added dropwise. The resulting solution (pH = 2.3) was allowed to stand at room temperature. Colorless needle-like crystals were grown by slow evaporation for several weeks.

Discussion

Nearly three decades ago, the crystal structure of sodium hydrogen maleate trihydrate was partially established by Gupta and coworkers using the photographic X-ray diffraction data collected at room temperature, but unfortunately hydrogen atoms were not located [1]. The structure was later refined at 120 K by Olovsson et al. [2]. In order to gain further insight into the nature of the possible intramolecular asymmetric hydrogen bonds, it was necessary to redetermine the crystal structure of $Na(C_4H_3O_4) \cdot 3H_2O$ by using accurate X-ray diffraction data at room temperature.

In the crystal structure of the title compound, the hydrogen maleate ($HOO(CH)_2COO^-$) anions exhibit strong intramolecular asymmetric hydrogen bonds between two crystallographically distinct O atoms, namely O2 and O4, with $d(O2\cdots O4) = 2.442(2)$ Å, $\angle O2–H\cdots O4 = 173°$. Such asymmetric hydrogen bonds are considerably shorter than those reported for symmetric hydrogen bonds, which are in general shorter than asymmetric ones [3, 4]. In comparison with the respective U_{iso} values of 0.0376(6) Å^2 and 0.0369(3) Å^2 for the associated O2 and O4 atoms, the reasonable U_{iso} values of 0.067(7) Å^2 for the H atom suggests that the present asymmetric hydrogen bonds are dynamically ordered. The shortest C1—O1 bond (1.218(2) Å) and longest C1—O2 bond (1.300(2) Å) indicate the double and single bond characters, respectively. The hydrogen atom is covalently bonded to the O2 atom (d(O—H) = 1.00(2) Å), which implies that the terminal containing C1 atom belongs to the carboxylic group. For the carboxylate terminal, the C4—O3 bond of 1.245(2) Å is slightly shorter than that of 1.266(2) Å to the O4 atom involved in the intramolecular hydrogen bond. The center C2—C3 bond of 1.329(2) Å is significantly shorter than the remaining ones averaged at 1.494 Å, indicating more double bond character. Owing to the fixation effect of the intramolecular hydrogen bonds, all atoms of the hydrogen maleate anion lie in a common plane. The Na^+ cations in the crystal structure are surrounded by six O atoms from five H_2O molecules and one hydrogen maleate anion to form distorted NaO_6 octahedra with d(Na—O) = 2.380 Å – 2.476 Å. Through two pairs of crystallographically equivalent bidentate bridging water O atoms, namely O5 and O7, the NaO_6 octahedra are edge shared resulting in one-dimensional (1D) $^1_\infty[Na(H_2O)(\mu\text{-}H_2O)_{4/2}(HOO(CH)_2COO)]$ chains along the [100] direction. Each Na atom has two close Na neighbors at 3.490(1) Å and 3.497(1) Å, respectively.

The formed 1D chains are held into 2D layers parallel to (010) by linear interchain hydrogen bonds (d(O6···O3 ($-x, -y, -z$)) = 2.754 Å, d(O6···O4 ($-x+1, -y, -z$)) = 2.806 Å, d(O7···O3 ($x, y, z+1$)) = 2.935 Å). The interlayer hydrogen bonds (d(O5···O3 ($x, y+1, z+1$)) = 2.903 Å, d(O7···O6 ($x, y-1, z$)) = 2.855 Å) are responsible for the formation of 3D networks with tunnels parallel to the [100] direction. Additionally, intrachain hydrogen bonds have been found between the bridging water O5 atom and carboxyl O1 atom bound to the Na atom with d(O5···O1 (1–x, –y, 1–z)) = 2.862 Å. More interesting is the observation that the neighboring coplanar hydrogen maleate anions orientate parallelly and face opposite directions with the C—H bonds outwards and, as a result, the seven-membered rings are partially covered with the interplanar distances alternatively of 3.12 Å and 3.19 Å. This fact indicates strong columnar π–π stacking interactions propagating in the [010] direction.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.089 × 0.200 × 0.467 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.94 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2387, 1853
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1432
$N(param)_{refined}$:	146
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H	2*i*	0.590(4)	–0.245(4)	–0.003(2)	0.067(7)
H(2)	2*i*	0.094(4)	–0.208(3)	0.125(2)	0.048(6)
H(3)	2*i*	0.007(4)	–0.278(3)	–0.071(2)	0.055(6)
H(4)	2*i*	0.231(5)	0.147(4)	0.674(2)	0.075(8)
H(5)	2*i*	0.134(4)	0.305(4)	0.657(2)	0.062(7)
H(6)	2*i*	0.083(6)	0.341(5)	0.308(2)	0.085(9)
H(7)	2*i*	0.306(4)	0.337(4)	0.285(2)	0.054(7)
H(8)	2*i*	0.312(5)	–0.267(4)	0.583(2)	0.069(8)
H(9)	2*i*	0.325(4)	–0.362(4)	0.462(2)	0.053(7)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	2*i*	0.2536(1)	0.0371(1)	0.42647(5)	0.0338(4)	0.0371(4)	0.0288(3)	0.0075(3)	0.0034(3)	0.0084(3)
O(1)	2*i*	0.4448(2)	–0.1399(2)	0.2584(1)	0.0462(7)	0.0512(7)	0.0241(6)	0.0149(6)	0.0026(5)	0.0063(5)
O(2)	2*i*	0.6207(2)	–0.2150(2)	0.0889(1)	0.0300(6)	0.0532(8)	0.0301(6)	0.0097(5)	0.0022(5)	0.0101(5)
C(1)	2*i*	0.4369(3)	–0.1890(2)	0.1463(1)	0.0334(8)	0.0265(7)	0.0280(8)	0.0051(6)	0.0026(6)	0.0075(6)
C(2)	2*i*	0.2143(3)	–0.2172(3)	0.0754(2)	0.0279(8)	0.0424(9)	0.0308(8)	0.0052(7)	0.0074(7)	0.0087(7)
C(3)	2*i*	0.1607(3)	–0.2661(3)	–0.0451(2)	0.0249(8)	0.0435(9)	0.0330(8)	0.0028(7)	0.0025(6)	0.0081(7)
C(4)	2*i*	0.3067(3)	–0.3107(2)	–0.1518(1)	0.0335(9)	0.0261(7)	0.0267(7)	0.0024(6)	0.0026(6)	0.0059(6)
O(3)	2*i*	0.2085(2)	–0.3593(2)	–0.2569(1)	0.0439(7)	0.0483(7)	0.0273(6)	0.0061(6)	–0.0011(5)	0.0055(5)
O(4)	2*i*	0.5195(2)	–0.2978(2)	–0.1320(1)	0.0315(6)	0.0496(7)	0.0294(6)	0.0086(5)	0.0066(5)	0.0088(5)
O(5)	2*i*	0.1292(2)	0.1718(2)	0.6299(1)	0.0371(7)	0.0391(7)	0.0357(7)	0.0089(6)	–0.0045(5)	0.0016(5)
O(6)	2*i*	0.2242(2)	0.3376(2)	0.3397(1)	0.0385(7)	0.0476(7)	0.0326(6)	0.0130(6)	0.0064(6)	0.0122(5)
O(7)	2*i*	0.3514(2)	–0.2468(2)	0.5149(1)	0.0449(7)	0.0355(7)	0.0299(6)	0.0042(6)	0.0013(5)	0.0082(5)

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