

Ammonium 2,4-dihydroxybenzoate monohydrate

Lin-Heng Wei

College of Environment and Planning, Henan
University, Kaifeng 475001, People's Republic
of ChinaCorrespondence e-mail:
linhengw@henu.edu.cn

Key indicators

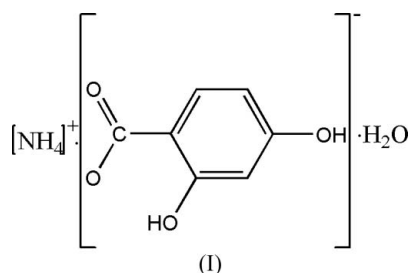
Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.038
 wR factor = 0.104
Data-to-parameter ratio = 11.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The two independent ammonium cations of the title compound, $\text{NH}_4^+\cdot\text{C}_7\text{H}_5\text{O}_4^-\cdot\text{H}_2\text{O}$, lie on twofold rotation axes. The ammonium cations, 2,4-dihydroxybenzoate anions and water molecules are linked into a three-dimensional structure via $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ interactions.

Received 12 October 2006
Accepted 24 October 2006

Comment

Various hydrogen bonds have recently been used in the design and construction of crystalline architectures due to their strength and directionality (Vishweshwar *et al.*, 2002). 2,4-Dihydroxybenzoic acid can build some salts or cocrystals with other organic molecules, acting as an excellent hydrogen-bond donor (Wang & Wei, 2006; Lin *et al.*, 2006). Ammonia is a weak base which can be protonated easily when it interacts with organic acids. Here, we report the crystal structure of the title compound, (I).



The asymmetric unit of (I) consists of half each of two ammonium cations, one 2,4-dihydroxybenzoate anion and one uncoordinated water molecule (Fig. 1). The ammonium cations lie on twofold rotation axes. The 2,4-dihydroxybenzoate anion shows an intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond (Table 1), forming an $S(6)$ ring. The cations, anions and water molecules are linked into a three-dimensional structure via $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, and $\pi-\pi$ interactions between dihydroxybenzoate anions (Fig. 2). The centroid-to-centroid distances between the benzene ring (C1–C6) and the symmetry-related rings at $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$ and $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ are 3.8305 (9) and 3.8512 (9) Å, respectively.

Experimental

All reagents were commercially available and of analytical grade. 2,4-Dihydroxybenzoic acid (0.31 g, 2.0 mmol) was slowly added to a vigorously stirred aqueous solution of ammonia (13 M, 1 ml). The solution was then stirred for 15 min at room temperature and filtered. Distilled water (10 ml) was then added to the filtrate to slow the rate

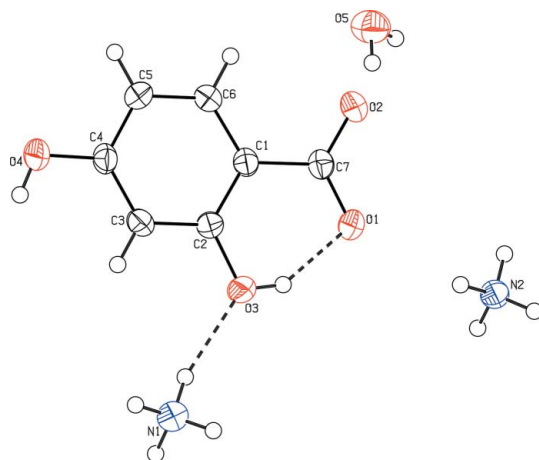


Figure 1
The asymmetric unit of (I), with symmetry-related H atoms of ammonium ions, showing 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonds.

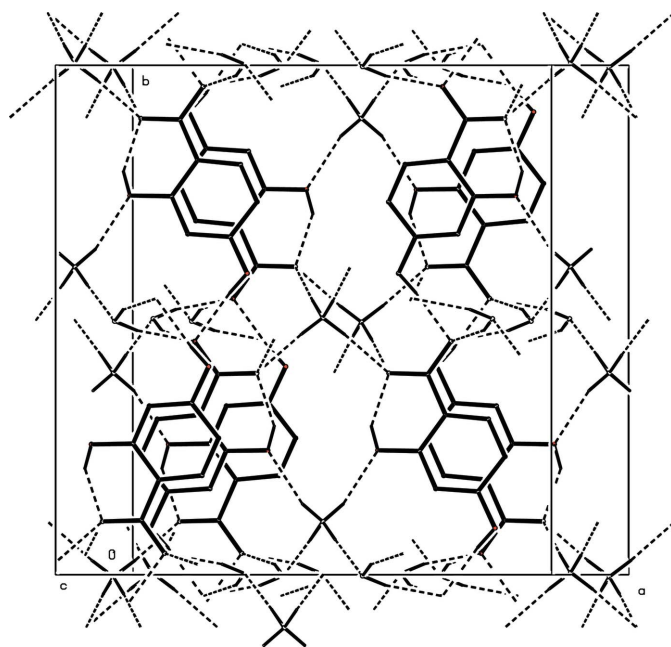


Figure 2
The crystal structure of (I). Hydrogen bonds are shown as dashed lines. Other H atoms have been omitted.

of evaporation. After 7 d, red crystals of (I) were obtained (yield 52%).

Crystal data

$\text{H}_4\text{N}^+\cdot\text{C}_7\text{H}_5\text{O}_4^-\cdot\text{H}_2\text{O}$
 $M_r = 189.17$
 Monoclinic, $C2/c$
 $a = 15.5715$ (17) Å
 $b = 15.9806$ (18) Å
 $c = 7.3688$ (8) Å
 $\beta = 109.186$ (2)°
 $V = 1731.8$ (3) Å³

$Z = 8$
 $D_x = 1.451$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 298$ (2) K
 Block, red
 $0.36 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.957$, $T_{\max} = 0.976$

5274 measured reflections
 1700 independent reflections
 1492 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.104$
 $S = 1.07$
 1700 reflections
 147 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.6723P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A ⁱ ···O1	0.82	1.80	2.5298 (13)	147
O4—H4 ⁱ ···O2 ⁱ	0.82	1.90	2.7151 (15)	174
O5—H51 ⁱ ···O2 ⁱ	0.843 (9)	1.960 (11)	2.7902 (16)	168 (2)
O5—H52 ⁱ ···O2 ⁱⁱ	0.847 (9)	2.041 (12)	2.8567 (16)	161 (2)
N1—H11 ⁱ ···O5	0.914 (9)	1.930 (10)	2.8432 (17)	177.8 (18)
N1—H12 ⁱ ···O3	0.900 (9)	2.020 (12)	2.8792 (18)	159.3 (19)
N2—H21 ⁱ ···O1 ⁱⁱⁱ	0.906 (9)	2.018 (10)	2.9193 (13)	173.2 (16)
N2—H22 ⁱ ···O1 ⁱⁱ	0.901 (9)	2.065 (10)	2.9606 (14)	172.9 (17)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x + \frac{1}{2}, y + \frac{1}{2}, z + 1$.

H atoms of the ammonium cations and water molecule were located in difference maps and refined with distance restraints [$N-H = 0.90$ (1), $O-H = 0.82$ (1) and $H\cdots H = 1.34$ Å]. Hydroxy H atoms were placed in calculated positions and treated as riding, with $O-H = 0.82$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. C-bound H atoms were positioned geometrically and treated as riding, with $C-H = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

References

- Bruker (2001). SAINT-Plus (Version 6.45) and SMART (Version 5.628). Bruker AXS Inc., Madison, Wisconsin, USA.
 Lin, D.-D., Liu, J.-G. & Xu, D.-J. (2006). *Acta Cryst.* E62, o451–o452.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Sheldrick, G. M. (2001). SADABS. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
 Spek, A. L. (2003). *J. Appl. Cryst.* 36, 7–13.
 Vishweshwar, P., Nangia, A. & Lynch, V. M. (2002). *J. Org. Chem.* 67, 556–565.
 Wang, Z. L., Wei, L. H. & Li, M.-X. (2006). *Acta Cryst.* E62, o3031–o3032.