# metal-organic papers

# Disodium dihydrogen 1,2,4,5-benzene-tetracarboxylate dihydrate

**Mao-Lin Hu**[a]***** **and Seik Weng Ng**[b]

[a]Department of Chemistry and Material Science, Wenzhou Normal College, Wenzhou 325027, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: maolin_hu@yahoo.com

Each of the two acid H atoms in the centrosymmetric $[C_6H_2(CO_2H)_2(CO_2)_2]^{2-}$ dianion of disodium dihydrogen 1,2,4,5-benzenetetracarboxylate dihydrate, $2Na^+ \cdot C_{10}H_4O_8{}^{2-} \cdot 2H_2O$, holds together a pair of adjacent carboxyl groups so that all four groups are coplanar with the aromatic ring. The $Na^+$ cation has a distorted octahedral coordination made up of two *cis*-coordinated water molecules and the O atoms of four carboxyl groups belonging to four different dianions; the water molecule acts as a bridge between two $Na^+$ ions related by an inversion center.

## Comment

The dihydrogen 1,2,4,5-benzenetetracarboxylate dianion has been documented in a number of salts, such as the hydrated cobalt (Ward & Leuhrs, 1983), dilithium (Jessen & Küppers, 1990), disodium cobalt(II) (Karanović *et al.*, 1999) and disodium zinc (Wu *et al.*, 2001) derivatives. In these compounds, the dianion has two acid H atoms that are involved in hydrogen bonds, each linking two adjacent carboxyl groups, giving rise to a planar conformation of the dianion; each of the two H atoms lies in a position approximately midway between the two negatively charged O atoms.
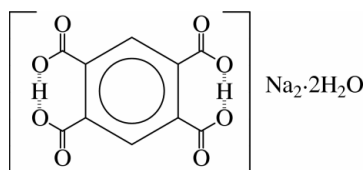


(I)

In the title compound, the dihydrated disodium salt (Fig. 1) of dihydrogen 1,2,4,5-benzenetetracarboxylate dianion, (I), the $Na^+$ ion is coordinated by two water molecules in *cis*-positions of the coordination octahedron. The coordination sites *trans* to the water molecules are occupied by the carbonyl O atoms of the carboxylate groups of two different 1,2,4,5-benzenetetracarboxylate(2−) anions. The coordination geometry of the $Na^+$ ion is distorted towards a pentagonal bipyramid, owing to the weak coordination of the atom O2 at 2.695 (2) Å. The remaining sites of the sodium coordination octahedron are occupied by the carboxyl O atoms of two bridging carboxyl groups (Fig. 2), so that an infinite three-dimensional framework is formed. The framework is further consolidated by hydrogen bonds involving water molecules.

The carboxyl groups show unambiguous differences in C—O single- and double-bond lengths. Two water molecules
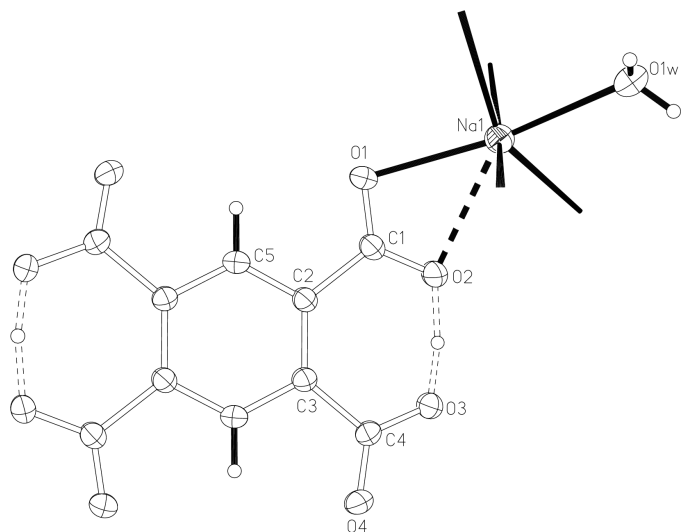
**Figure 1**
*ORTEP*II (Johnson, 1976) plot of a fragment of the structure of (I), showing the atom numbering and 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

bridge two Na$^+$ ions across an inversion center, to form a four-membered Na$_2$O$_2$ ring.

## Experimental

The title compound is the unexpected product of the reaction of sodium tungstate (0.58 g, 2 mmol), 1,1,1-trifluoro-4-(2-thienyl)butan-2,4-dione (0.22 g, 1 mmol) and 1,2,4,5-benzenetetracarboxylic acid (0.25 g, 1 mmol) in water (50 ml). The mixture was heated until the reagents dissolved; colorless crystals separated from the solution upon cooling.

*Crystal data*

| | |
|---|---|
| 2Na$^+$·C$_{10}$H$_4$O$_8$$^{2-}$·2H$_2$O | $Z = 1$ |
| $M_r = 334.14$ | $D_x = 1.888$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 5.490$ (1) Å | Cell parameters from 722 |
| $b = 6.799$ (2) Å | reflections |
| $c = 8.716$ (2) Å | $\theta = 2.4$–28.1° |
| $\alpha = 79.742$ (4)° | $\mu = 0.23$ mm$^{-1}$ |
| $\beta = 75.852$ (3)° | $T = 298$ (2) K |
| $\gamma = 69.517$ (3)° | Block, colorless |
| $V = 294.0$ (1) Å$^3$ | 0.31 × 0.15 × 0.11 mm |

*Data collection*

| | |
|---|---|
| Bruker AXS SMART diffractometer | 962 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.018$ |
| Absorption correction: none | $\theta_{max} = 28.1°$ |
| 1893 measured reflections | $h = -6 \rightarrow 7$ |
| 1311 independent reflections | $k = -8 \rightarrow 8$ |
| | $l = -6 \rightarrow 11$ |

*Refinement*

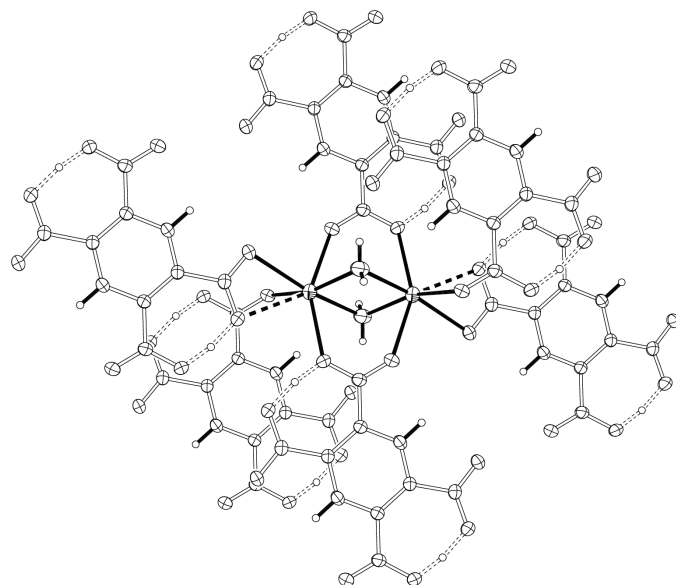| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0621P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.107$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 0.94$ | $\Delta\rho_{max} = 0.24$ e Å$^{-3}$ |
| 1311 reflections | $\Delta\rho_{min} = -0.32$ e Å$^{-3}$ |
| 117 parameters | Extinction correction: *SHELXL*97 |
| All H-atom parameters refined | Extinction coefficient: 0.28 (3) |



**Figure 2**
Fragment of the crystal packing of the title compound, showing the interaction between the Na$_2$(H$_2$O)$_2$ fragments and the dihydrogen 1,2,4,5-benzenetetracarboxylate dianions. H atoms are drawn as spheres of arbitrary radii.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Na1—O1 | 2.491 (2) | Na1—O1$w$ | 2.501 (2) |
| Na1—O2 | 2.695 (2) | Na1—O1$w^{iv}$ | 2.337 (2) |
| Na1—O3$^i$ | 2.463 (2) | O2—H1$o$ | 1.25 (3) |
| Na1—O4$^{ii}$ | 2.482 (2) | O3—H1$o$ | 1.15 (3) |
| Na1—O4$^{iii}$ | 2.439 (2) | | |
| | | | |
| O1—Na1—O2 | 49.6 (1) | O3$^i$—Na1—O4$^{ii}$ | 151.6 (1) |
| O1—Na1—O3$^i$ | 118.6 (1) | O3$^i$—Na1—O4$^{iii}$ | 111.6 (1) |
| O1—Na1—O4$^{ii}$ | 87.2 (1) | O3$^i$—Na1—O1$w$ | 78.6 (1) |
| O1—Na1—O4$^{iii}$ | 81.2 (1) | O3$^i$—Na1—O1$w^{iv}$ | 84.8 (1) |
| O1—Na1—O1$w$ | 160.8 (1) | O4$^{ii}$—Na1—O4$^{iii}$ | 82.6 (1) |
| O1—Na1—O1$w^{iv}$ | 98.6 (1) | O4$^{ii}$—Na1—O1$w$ | 78.4 (1) |
| O2—Na1—O3$^i$ | 73.2 (1) | O4$^{ii}$—Na1—O1$w^{iv}$ | 79.1 (1) |
| O2—Na1—O4$^{ii}$ | 135.0 (1) | O4$^{iii}$—Na1—O1$w$ | 84.5 (1) |
| O2—Na1—O4$^{iii}$ | 79.2 (1) | O4$^{iii}$—Na1—O1$w^{iv}$ | 161.6 (1) |
| O2—Na1—O1$w$ | 139.2 (1) | O1$w$—Na1—O1$w^{iv}$ | 91.0 (1) |
| O2—Na1—O1$w^{iv}$ | 114.8 (1) | | |

Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $x, y, z-1$; (iii) $2-x, 1-y, 2-z$; (iv) $1-x, 1-y, 1-z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1$w$—H1$w$1⋯O1$^v$ | 0.81 (3) | 2.06 (3) | 2.868 (2) | 174 (3) |
| O1$w$—H1$w$2⋯O1$^{vi}$ | 0.89 (3) | 2.02 (3) | 2.888 (2) | 166 (3) |
| O3—H1$o$⋯O2 | 1.15 (3) | 1.25 (3) | 2.390 (2) | 169 (3) |

Symmetry codes: (v) $2-x, 1-y, 1-z$; (vi) $x, y-1, z$.

H atoms were located in a difference map and included in the refinement in isotropic approximation [O—H = 1.15 (3) and 1.25 (3) Å for the H-atom forming the short hydrogen bond in the dianion; C—H in the dianion = 0.94 (2) Å; O—H in water molecule = 0.81 (3) and 0.89 (3) Å].

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