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# Poly[sodium(I)-$\mu_6$-hydrogen benzene-1,4-dicarboxylato]

**Sophie H. Dale and Mark R. J. Elsegood***

Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England
Correspondence e-mail: m.r.j.elsegood@lboro.ac.uk

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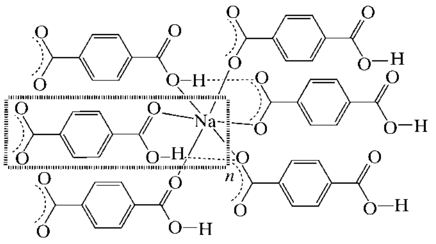
Alkali metal salts of terephthalic acid are common reagents in the preparation of metal–ligand coordination complexes containing terephthalate anions. In the title compound, sodium hydrogen terephthalate, $[Na(C_8H_5O_4)]_n$, the cations occupy crystallographic inversion centres, and each bridging anion coordinates to six octahedral cations and *vice versa*. As seen in the known potassium derivative [Kaduk (2000). *Acta Cryst.* B**56**, 474–485; Miyakubo, Takeda & Nakamura (1994). *Bull. Chem. Soc. Jpn*, **67**, 2301–2303], sodium hydrogen terephthalate contains short O—H⋯O hydrogen bonds between anions [O⋯O = 2.4734 (17) Å]. The structure is centrosymmetric and exhibits disorder of the H-atom position in the hydrogen bond and of the non-bridging ring C atoms in the terephthalate ion.

## Comment

While it bears desirable *para*-distributed carboxylic acid groups, the insolubility of terephthalic acid (benzene-1,4-dicarboxylic acid, hereinafter $H_2TA$) in many organic solvents could limit its use in coordination chemistry. However, many chemists employ its alkali metal salts in the preparation of complexes of other metals, for example, $TA^{2-}$ anions are often utilized as bridging anions, linking metal centres together in the solid state to produce functional magnetic materials (Kurmoo *et al.*, 2001). The use of coordinating anions such as $TA^{2-}$ aids the creation of supramolecular arrays, as the neutral networks no longer need to be interrupted by uncoordinated anions (Groeneman & Atwood, 1999), and such networks have been shown to have both solvent inclusion (Li, Davis *et al.*, 1998) and gas sorption (Li, Eddaoudi *et al.*, 1998) properties.



(I)

A search of the Cambridge Structural Database (Version 5.24, July 2003 update; Allen, 2002) highlights a paper by Kaduk (2000), which studies the $Li^+$, $Na^+$ and $K^+$ salts of $H_2TA$ (all three having the stoichiometry $M_2TA$) and gives an additional redetermination of the $K^+$ salt of the mono-deprotonated hydrogen terephthalate ($HTA^-$) anion, KHTA [previously studied by Miyakubo *et al.* (1994)]. We have now

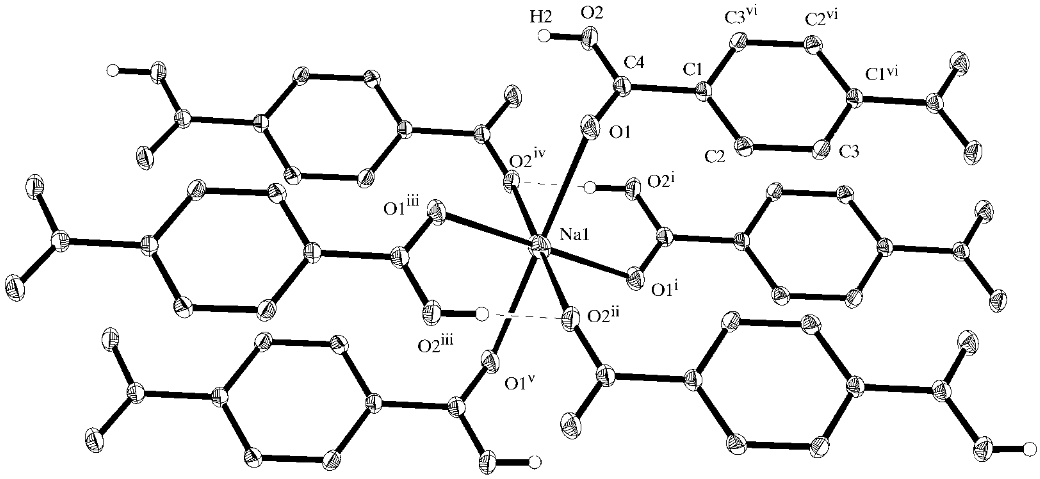


**Figure 1**
A view of (I), showing the atom-labelling scheme, the completed $Na^+$ coordination sphere and the hydrogen bonding. Displacement ellipsoids are drawn at the 50% probability level. Aromatic H atoms and one disorder component have been omitted for clarity, and O-bound H atoms are drawn as small spheres of arbitrary radii. The hydrogen bonding is shown by dashed lines [symmetry codes: (i) $x + 1, y, z$; (ii) $x + 1, 1 + y, z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, -y, 1 - z$; (v) $2 - x, 1 - y, 1 - z$; (vi) $1 - x, -y, -z$].

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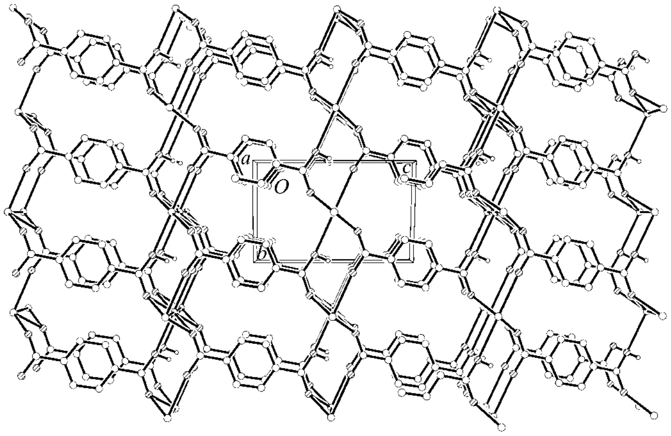

**Figure 2**
A packing plot of (I) viewed along the *a* axis. Aromatic H atoms, one disorder component and hydrogen bonds have been omitted for clarity. Open circles denote C atoms, shaded circles O atoms and dotted circles Na atoms.

synthesized and characterized the related title compound, NaHTA, (I), and report its structure here.

The asymmetric unit of (I) contains half a formula unit, with the octahedral $Na^+$ cation occupying a crystallographic inversion centre. The cation is six-coordinate and bonds to six different $HTA^-$ anions (Table 1 and Fig. 1), with each anion bonding to six cations through monodentate coordination in all cases.

The aromatic ring of the $HTA^-$ anion in (I) is disordered and has been modelled over two sets of positions (in a 50:50 ratio due to the centrosymmetric nature of the structure), with the substituted ring atoms coincident in the two alternative ring positions, which lie at 24.6 (2)° with respect to each other. The geometry of the anion is unsurprising (Miyakubo *et al.*, 1994).

The carboxyl group deviates from the planes of the two alternative aromatic ring positions by 8.2 (3) and 18.8 (3)°. Although an electron-density peak was clearly observed on an inversion centre in the difference Fourier map, displacing the H atom away from the centre of symmetry [as suggested by Miyakubo *et al.* (1994) and Kaduk (2000) in their characterizations of KHTA] resulted in a further lowering of the *R* factor. This produced more reasonable O—H and H···O bond lengths within the short O—H···O hydrogen bond (Table 2), and removed the electron-density peak from the inversion centre. The carboxyl H atom was therefore modelled as half-weight, having two equivalent positions disordered symmetrically across the inversion centre.

The combination of Na—O coordination bonds and O—H···O hydrogen bonds results in the formation of $R_1^1(6)$ graph-set motifs (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995), with each $Na^+$ centre being incorporated into two such rings, and this therefore leads to a three-dimensional structure (Fig. 2). While (I) and KHTA are not isostructural, the $K^+$ cations in KHTA also participate in two $R_1^1(6)$ motifs each. However, these motifs are distributed *cis* around the pseudo-octahedral $K^+$ cations in KHTA, while in (I) the two motifs are *trans* with respect to one another.

## Experimental

Terephthalic acid ($H_2TA$; 2 equivalents) was refluxed with $Na_2CO_3$ (1 equivalent) in water overnight, producing a colourless solution which was evaporated to dryness *in vacuo*. The resulting white solid was recrystallized from dimethylformamide and water (hot, 1:1), and slow cooling yielded colourless X-ray quality crystals of (I) in quantitative yield. Analysis calculated for $C_8H_5NaO_4$: C 51.08, H 2.68%; found: C 50.82, H 2.56%; IR (KBr, $\nu_{max}$, $cm^{-1}$): 3437 (*br*, OH), 2956 and 2924 (aromatic C—H), 1671 (C═O, acid), 1506 (asymmetric $CO_2^-$), 1370 (symmetric $CO_2^-$), 1297, 1207, 1145 and 1090 (C—O), 878, 778 and 740 (aromatic C—H), 509, 482.

*Crystal data*

$[Na(C_8H_5O_4)]$
$M_r = 188.11$
Triclinic, $P\overline{1}$
$a = 3.6204$ (11) Å
$b = 5.7446$ (17) Å
$c = 8.775$ (3) Å
$\alpha = 90.271$ (5)°
$\beta = 91.970$ (5)°
$\gamma = 105.776$ (5)°
$V = 175.50$ (10) Å$^3$
$Z = 1$
$D_x = 1.780$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1773 reflections
$\theta = 2.3$–28.6°
$\mu = 0.19$ mm$^{-1}$
$T = 150$ (2) K
Block, colourless
0.29 × 0.17 × 0.09 mm

*Data collection*

Bruker SMART 1000 CCD area-detector diffractometer
$\omega$ rotation scans with narrow frames
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.966$, $T_{max} = 0.983$
1532 measured reflections
807 independent reflections
747 reflections with $I > 2\sigma(I)$
$R_{int} = 0.009$
$\theta_{max} = 28.8°$
$h = -4 \rightarrow 4$
$k = -7 \rightarrow 7$
$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.085$
$S = 1.08$
807 reflections
82 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.0676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å$^{-3}$
$\Delta\rho_{min} = -0.17$ e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Na1—O1$^i$ | 2.4120 (9) | Na1—O2$^{ii}$ | 2.5745 (11) |
| Na1—O1 | 2.4359 (10) | | |
| O1$^{iii}$—Na1—O1 | 83.37 (4) | O1—Na1—O2$^{iv}$ | 84.09 (3) |
| O1$^{iii}$—Na1—O2$^{iv}$ | 103.71 (3) | | |

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

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O2$^i$ | 0.88 (3) | 1.59 (3) | 2.4734 (17) | 178 (4) |

Symmetry code: (i) $-x, -y, 1 - z$.

Aromatic H atoms were placed in geometric positions (C—H = 0.95 Å) using a riding model, while the coordinates of the O-bound H atom were freely refined. $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(C) for aryl H ($1.5U_{\rm eq}$ for OH). Restraints were applied to the anisotropic displacement parameters of all the C atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1544). Services for accessing these data are described at the back of the journal.

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