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Ethylenediammonium bis(trihydrogen 1,2,4,5-benzenetetracarboxylate) dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.055
wR factor = 0.200
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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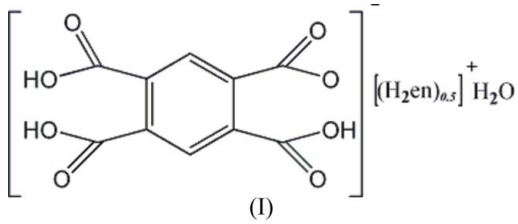
Colourless crystals of the title compound, $C_2H_{10}N_2^{2+}\cdot 2C_{10}H_5O_8^{-}\cdot 2H_2O$, were isolated from an aqueous solution. The basic structural unit consists of two trihydrogen 1,2,4,5-benzenetetracarboxylate (H_3btec^{-}) anions, an ethylenediammonium cation and two solvent water molecules. The ethylenediammonium cation is centrosymmetric. The anion has a short intramolecular hydrogen bond of 2.427 (4) Å involving a deprotonated carboxylate group as acceptor. A three-dimensional hydrogen-bonding network defines the crystal packing, and solvent water molecules and the cations occupy voids in the crystal structure.

Comment

Considerable attention has been paid to the exploration of the structures and properties of complexes or salts containing benzenepolycarboxylate ligands, due to their potential technological importance. In the case of 1,2,4,5-benzenetetracarboxylate (btec), the coordination chemistry is well represented, although there are not as many structures as have been reported for 1,3,5-benzenetricarboxylate. Among many reported compounds containing btec, most are complexes of transition metal ions, including manganese (Rochon & Massarweh, 2000; Hu *et al.*, 2001), iron (Chu *et al.*, 2001), cobalt (Murugavel *et al.*, 2002; Kumagai *et al.*, 2002; Poleti & Karanovic, 1989; Cheng *et al.*, 2002), nickel (Murugavel *et al.*, 2002; Rochon & Massarweh, 2000; Poleti *et al.*, 1988), copper (Zou *et al.*, 1998; Cheng *et al.*, 2001; Cao, Shi *et al.*, 2002), silver (Jaber *et al.*, 1997) and zinc (Robl, 1987; Rochon & Massarweh, 2000). However, examples of compounds with main group metals such as calcium (Robl, 1988) and thallium (Day & Luehrs, 1988) also exist. Recently, compounds of the rare earth elements were reported (Cao, Sun *et al.*, 2002; Daiguebonne *et al.*, 2003). The salts of 1,2,4,5-benzenetetracarboxylate containing organic ammonium cations are rare and may have interesting supramolecular chemistry.



(I)

In the title compound, (I), the 1,2,4,5-benzenetetracarboxylate exists as the H_3btec^{-} anion, *i.e.* with one CO_2^{-} and three CO_2H groups (Fig. 1, Table 1). The anion has a short intramolecular hydrogen bond between adjacent CO_2^{-} and

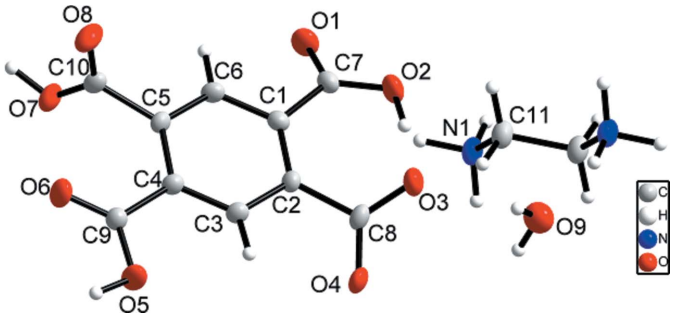


Figure 1
A view of the asymmetric unit of (I) plus the symmetry-related half of the cation, with atom labels and 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operator $(2-x, -1-y, 1-z)$.

CO_2H groups (Table 2). The value observed is longer than those in $K(H_3btec)\cdot 3H_2O$ (Wang *et al.*, 2004) and $Na_2[Co(H_2O)](H_2btec)_2\cdot 4H_2O$ (Karanovic *et al.*, 1999). In $K(H_3btec)\cdot 3H_2O$, the O···O distance of the intramolecular hydrogen bond is 2.39 (2) Å and the angle between the two planes of adjacent carboxylate groups is 24.4 (3)°. In $Na_2[Co(H_2O)](H_2btec)_2\cdot 4H_2O$, the corresponding O···O distance is 2.384 (3) Å. Generally, one or more strong intramolecular hydrogen bonds can occur in H_3btec^- or H_2btec^- anions.

The crystal packing of (I) is determined by a three-dimensional hydrogen-bond network (Table 2, Fig. 2). Intermolecular hydrogen bonds connect ions as follows: anion···anion (O5—H···O1 and O7—H···O4), cation···anion (N1—H···O6 and N1—H···O8), water···anion (O9—H···O4 and O9—H···O3) and cation···water (N1—H···O9). Anions are interconnected by medium to strong hydrogen bonds (Table 2). The angle between the two planes of adjacent carboxylate groups (O1/C7/O2 and O3/C8/O4) is 39.5 (4)°. The ethylenediammonium cation is centrosymmetric.

Experimental

1,2,4,5-Benzenetetracarboxylic dianhydride (0.5 mmol) and $CuCl_2\cdot 2H_2O$ (0.5 mmol) were dissolved in water (15 ml). To this solution, ethylenediamine (0.5 mmol) was added dropwise with stirring, and the pH was adjusted to 3.0 with 2 *M* NaOH solution. Colourless crystals of (I) were obtained after several days at room temperature.

Crystal data

$C_2H_{10}N_2^{2+}\cdot 2C_{10}H_5O_8^-\cdot 2H_2O$
$M_r = 604.44$
Triclinic, $P\overline{1}$
$a = 8.118$ (2) Å
$b = 8.2266$ (17) Å
$c = 9.596$ (3) Å
$\alpha = 83.50$ (1)°
$\beta = 77.178$ (13)°
$\gamma = 72.395$ (10)°
$V = 594.9$ (2) Å^3
$Z = 1$
$D_x = 1.687$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2246 reflections
$\theta = 2.6$–27.4°
$\mu = 0.15$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.35 × 0.35 × 0.32 mm

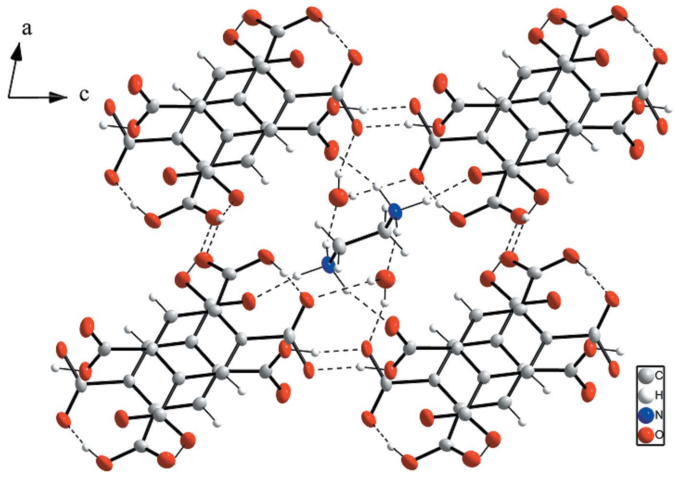


Figure 2
The crystal packing of (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

Data collection

Rigaku R-AXIS RAPID diffractometer
$\omega/2\theta$ scans
4366 measured reflections
2484 independent reflections
2074 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.200$
$S = 1.01$
2484 reflections
238 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 2.3708P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected bond lengths (Å).

O5—C9	1.292 (4)	C1—C6	1.394 (5)
O4—C8	1.241 (4)	C1—C7	1.505 (4)
O7—C10	1.302 (4)	C2—C3	1.385 (4)
O1—C7	1.221 (4)	C2—C8	1.513 (4)
O6—C9	1.201 (4)	C3—C4	1.378 (4)
O3—C8	1.254 (4)	C4—C5	1.379 (4)
O2—C7	1.279 (4)	C4—C9	1.484 (4)
O2—H101	1.03 (5)	C5—C6	1.383 (4)
O8—C10	1.215 (4)	C5—C10	1.499 (4)
N1—C11	1.484 (5)	C11—C11^{i}	1.501 (7)
C1—C2	1.386 (4)		

Symmetry code: (i) $-x+2, -y-1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H301···O4^{ii}	0.92 (6)	1.94 (6)	2.837 (5)	164 (5)
O2—H101···O3	1.03 (5)	1.40 (5)	2.427 (4)	171 (5)
O7—H107···O4^{iii}	0.95 (5)	1.62 (5)	2.554 (3)	169 (4)
O5—H105···O1^{iv}	0.92 (7)	1.71 (7)	2.610 (3)	165 (7)
N1—H201···O6^{v}	1.04 (6)	1.74 (6)	2.759 (4)	166 (5)
N1—H203···O8^{vi}	0.99 (6)	1.87 (6)	2.831 (4)	165 (5)
N1—H202···O9	0.99 (6)	1.80 (6)	2.743 (5)	156 (5)
O9—H302···O3	0.73 (8)	2.20 (8)	2.825 (4)	145 (9)

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

The positions of all H atoms were found in difference Fourier maps and refined.

Data collection: *RAPID AUTO* (Rigaku, 1998); cell refinement: *RAPID AUTO*; data reduction: *RAPID AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97-2* (Sheldrick,1997).

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