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Potassium trihydrogen 1,2,4,5-benzenetetracarboxylate trihydrate

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Key indicators

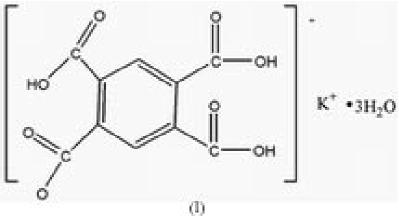
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.084
Data-to-parameter ratio = 12.7

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

Colourless crystal of the title compound, $K^+\cdot C_{10}H_5O_8^-\cdot 3H_2O$, were isolated under hydrothermal conditions (423 K, 72 h). The structure consists of trihydrogen 1,2,4,5-benzenetetracarboxylate (H_3btec$^-$) anions, potassium cations and water of crystallization. Each K^+ cation is seven-coordinated by four carboxylate O atoms and three water O atoms. In turn, each H_3btec$^-$ anion connects to four K^+ cations and so an undulating layer forms. Adjacent layers are held together by hydrogen bonds to form a three-dimensional network. A short intramolecular hydrogen bond is found to exist in the H_3btec$^-$ anions.

Comment

Considerable attention has been paid to the investigation 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. In the long list of compounds containing btec reported so far, most are complexes of transition metal ions, examples being 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 earths were reported (Cao, Sun *et al.*, 2002; Daiguebonne *et al.*, 2003). Salts of group 1 metals with 1,2,4,5-benzenetetracarboxylate are rare.



(I)

In the title compound, (I), the 1,2,4,5-benzenetetracarboxylate ligand exists as the H_3btec$^-$ anion, *i.e.* with one CO_2^- and three CO_2H groups. In the anion, a short intramolecular hydrogen bond forms between a pair of adjacent CO_2^- and CO_2H groups (O2—H2···O4, Table 2). Owing to the small difference in bond lengths of O2—H2 and O4—H2,

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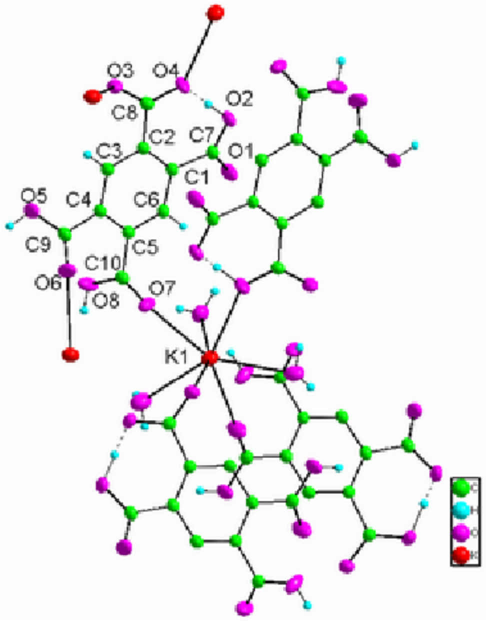

Figure 1
A segment of a layer in the title compound, showing atom labels and 50% probability displacement ellipsoids.

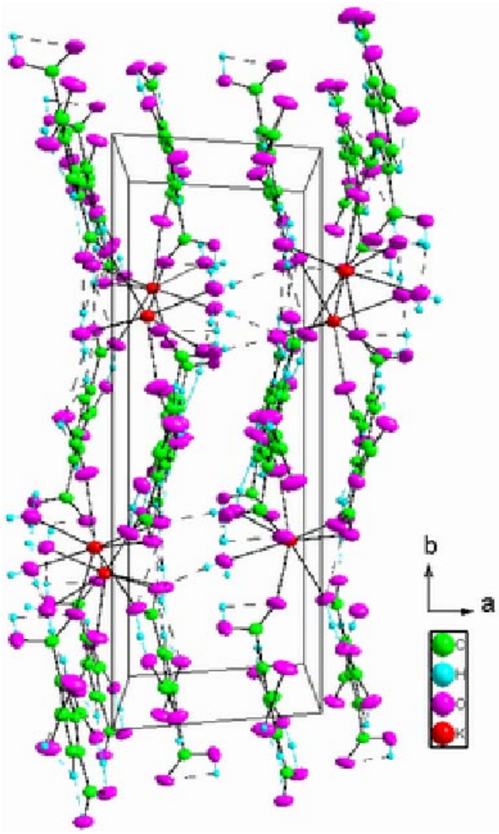

Figure 2
Packing of the structure, viewed along the *c* axis.

it is better to describe the pair of CO_2^- and CO_2H groups as two CO_2^-groups trapping one H atom between them. Each H_3btec^- anion connects to four K^+ cations (Fig. 1), with different carboxylate–metal coordination modes. The C7/O1/O2 carboxylic acid group is uncoordinated and the C8/O3/O4 carboxylate group is linked to two K^+ cations (Table 1). Groups C9/O5/O6 and C10/O7/O8 are carboxylic acid groups, with atoms O5 and O8 being the OH groups. Both are linked to one K^+ cation in a monodentate fashion. In turn, each K^+ cation is coordinated by four carboxylate O atoms and three water O atoms in an irregular geometry (Fig. 1). The distances of the K^+ cation to water O atoms O9, O10 and O11 are longer than those from the K^+ cation to carboxylate O atoms (Table 1). The connectivity mentioned above results in a polymerized structure. The polymers extend parallel to the *bc* plane in a wave-like double-layer fashion (Fig. 2). There are numerous intra- and interlayer hydrogen bonds between water–water, water–carboxyl and carboxyl–carboxyl in the structure. These contribute to the stabilization of the structure. Adjacent layers are held together by hydrogen bonds to form a three-dimensional network.

Experimental

The title compound was prepared hydrothermally. A mixture of 1,2,4,5-benzenetetracarboxylic anhydride (1.0 mmol), KOH (5.0 mmol) and water (5 ml) was stirred with a magnetic bar for 1 h, then the pH value was adjusted to 1.5 with HNO_3. The mixture was transferred to a sealed stainless-steel Teflon-lined autoclave and heated at 423 K for 3 d, then slowly cooled to room temperature. Colourless crystals of (I) were obtained in about 80% yield.

Crystal data

$K^+\cdot C_{10}H_5O_8^-\cdot 3H_2O$
$M_r = 346.29$
Monoclinic, $P2_1/c$
$a = 7.5703$ (3) Å
$b = 19.5133$ (13) Å
$c = 9.7623$ (7) Å
$\beta = 111.273$ (4)°
$V = 1343.84$ (14) Å^3
$Z = 4$
$D_x = 1.712$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5478 reflections
$\theta = 3.0$–27.5°
$\mu = 0.46$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colourless
0.40 × 0.40 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω–2θ scans
Absorption correction: multi-scan (*RAPID-AUTO*; Rigaku, 1998)
$T_{min} = 0.834$, $T_{max} = 0.872$
5932 measured reflections
3079 independent reflections
2495 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -25 \rightarrow 25$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.02$
3079 reflections
243 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.3628P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

K1—O6^i	2.6953 (12)	O2—C7	1.2763 (18)
K1—O7^{ii}	2.7174 (13)	O3—C8	1.2396 (18)
K1—O4^{iii}	2.8313 (12)	O4—C8	1.2770 (18)
K1—O3	2.8717 (13)	O5—C9	1.3059 (18)
K1—O11	2.8789 (16)	O6—C9	1.2032 (19)
K1—O10	2.9067 (17)	O7—C10	1.2045 (19)
K1—O9	2.9241 (16)	O8—C10	1.3129 (19)
O1—C7	1.2347 (18)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O11—H11$B\cdots$O10$^{\rm iii}$	0.85 (3)	1.83 (3)	2.684 (2)	176 (3)
O9—H9$A\cdots$O3$^{\rm iii}$	0.85 (3)	2.02 (3)	2.8662 (18)	172 (2)
O8—H8$\cdots$O11$^{\rm i}$	0.85 (3)	1.77 (3)	2.6088 (19)	168 (2)
O11—H11$A\cdots$O3$^{\rm iv}$	0.77 (3)	2.13 (3)	2.890 (2)	170 (3)
O5—H5$\cdots$O1$^{\rm v}$	0.89 (3)	1.74 (3)	2.6368 (16)	176 (3)
O10—H10$A\cdots$O9$^{\rm vi}$	0.83 (3)	2.01 (3)	2.831 (2)	167 (3)
O9—H9$B\cdots$O2$^{\rm v}$	0.86 (3)	2.16 (3)	2.9893 (17)	161 (3)
O10—H10$B\cdots$O1$^{\rm vii}$	0.80 (3)	2.15 (3)	2.935 (2)	170 (3)
O2—H2$\cdots$O4	1.15 (3)	1.25 (3)	2.3898 (16)	172 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iv) $1+x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $x, y, 1+z$; (vi) $1+x, y, z$; (vii) $-x, 1-y, -z$.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*97-2 (Sheldrick, 1997).

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