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Tetrasodium tetrahydrofuran-*trans*-*cis*-*trans*-tetracarboxylate pentahydrate

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In $Na_4[C_4H_4O(COO)_4]\cdot 5H_2O$ (or $4Na^+\cdot C_8H_4O_9^{4-}\cdot 5H_2O$), the anions are connected by hydrogen bonds to water molecules to form bilayers of open columns. Three of the sodium ions are located inside these columns. The final sodium ion interconnects the bilayers of anions. Three of the sodium ions have distorted octahedral coordination, the other has a trigonal pyramidal environment. The ligands are O atoms belonging to water, carboxylate groups or, in one case, the furan ring. The Na—O distances are between 2.303 (2) and 2.596 (3) Å.

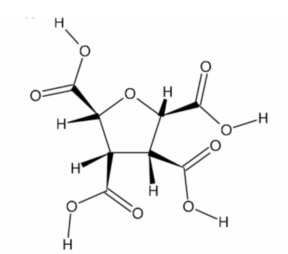
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.052
wR factor = 0.145
Data-to-parameter ratio = 13.6

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

Comment

There are relatively few published structures of tri- or tetracarboxylic acids or their salts. We have reported studies of hydrogen bonding in derivatives of tricarballylic acid, β-methyltricarballylic acid and 1,2,3,4-butanetetracarboxylic acid (Barnes & Barnes, 1996) and a range of salts of tetrahydrofuran *trans*-*cis*-*trans*-tetracarboxylic acid, (I), in which one (Barnes & Paton, 1982, 1984), two (Barnes & Paton, 1984, Barnes, 1997), three (Barnes, 1997) or all four carboxylate groups (Barnes & Paton, 1984) are deprotonated.



(I)

(I) Free acid
(II) Sodium salt, $Na_4C_4H_8O(COO)_4\cdot 5H_2O$

As with many polycarboxylic acids, a particular cation will only form crystals of a few (usually one) of its possible salts with (I). These must represent particularly low energy combinations of hydrogen bonding and packing. With sodium ions, the crystals proved to be $Na_4(C_4H_4O(COO)_4)\cdot 5H_2O$, (II), whereas the crystalline caesium salt is the anhydrous $Cs[C_4H_4O(COOH)_3(COO)]$ (Barnes & Paton, 1984).

In the isolated (4−) anion derived from (I), the carboxylate groups are able to twist relative to the tetrahydrofuran ring with little steric hindrance. Thus, the conformation in crystalline salts is determined by hydrogen bonding to water or to cations such as NH_4^+ and electrostatic interactions with cations. Partially protonated anions can, in addition, form intramolecular or inter-anion hydrogen bonds (Barnes, 1997).

In (II), Fig. 1 and the torsion angles in Table 1 show that the anion is far from the possible ideal mirror symmetry. Each of

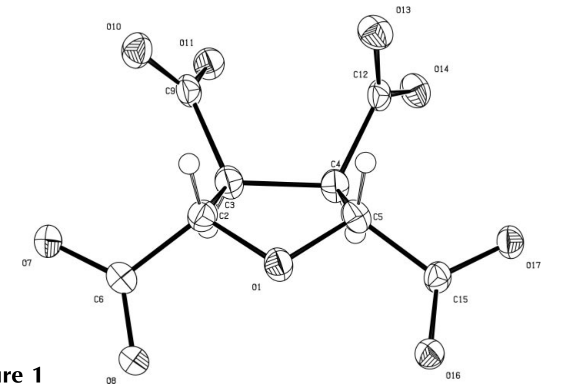


Figure 1
The structure of the anion in (II), showing 50% probability displacement ellipsoids.

the carboxylate O atoms, except for O16, takes part in hydrogen bonding to water molecules (Table 2). Atom O16 and furan atom O1 have short contacts only to sodium.

Fig. 2 shows that the structure can be visualized as bilayers of anions parallel to *bc*, separated by layers of Na3 ions close to $x = 0$ and $x = 0.5$. Anions are joined into pairs in the *a* direction by hydrogen bonds to pairs of water molecules O25 centred at $x = 0.25$ and $z = 0.25$. The outer edges of these anion pairs (at about $x = 0.06$, 0.44) are connected to adjacent pairs in the *c* direction by water molecules O22, O23 and O24 to complete the bilayer of open columnar cells which enclose Na1, Na2 and Na4 (Fig. 3). The water molecule O21 connects anions in the *b* direction.

Na1, Na2 and Na3 each have six O-atom neighbours (assortments of carboxylate O atoms and water molecules and, for Na1, the furan atom O1) at distances between 2.303 (2) and 2.596 (3) Å. There is no correlation between the environment of the O atom and the Na—O distance. Table 1 and Fig. 3 show that these coordination environments are very irregular octahedra. Na4 has only five O-atom neighbours, at similar distances, which form a distorted trigonal pyramid.

The water molecules O21, O22, O24 and O25 coordinate to two Na atoms and act as H-atom donors in two hydrogen bonds (Table 2). Atom O23 acts as a ligand to Na3 only, as H-atom donor in hydrogen bonds to O10 and O8′ (x, $2-y$, $z-0.5$), and as H-atom acceptor from H22*A*′ (x, $1+y$, z).

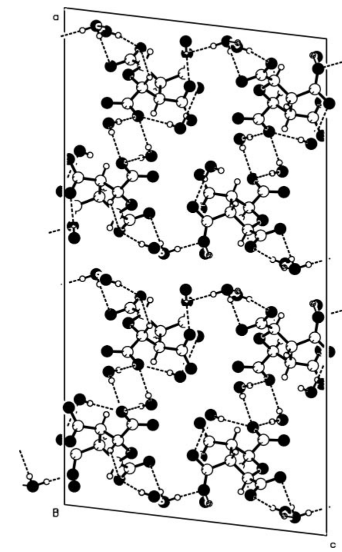


Figure 2
The unit cell of (II), viewed down the *b* axis, showing anions and water molecules only.

Experimental

An aqueous solution of (I) was neutralized by adding four equivalents of aqueous sodium hydroxide. The solution was allowed to crystallize in air and the resulting crystalline mass recrystallized from water. The same product was obtained from other ratios of (I) to NaOH.

Crystal data

$4Na^+\cdot C_8H_4O_9^{4-}\cdot 5H_2O$
$M_r = 426.15$
Monoclinic, $C2/c$
$a = 30.1575$ (13) Å
$b = 6.3341$ (3) Å
$c = 15.9844$ (9) Å
$\beta = 96.772$ (2)°
$V = 3032.0$ (3) Å^3
$Z = 8$
$D_x = 1.867$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10138 reflections
$\theta = 2.9$–33.7°
$\mu = 0.27$ mm^{-1}
$T = 150$ (2) K
Plate, colourless
$0.10 \times 0.05 \times 0.02$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.940$, $T_{max} = 0.976$
12544 measured reflections
3594 independent reflections
2389 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 28.0°$
$h = -39 \to 39$
$k = -7 \to 8$
$l = -20 \to 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.145$
$S = 1.02$
3594 reflections
265 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.1007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.82$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

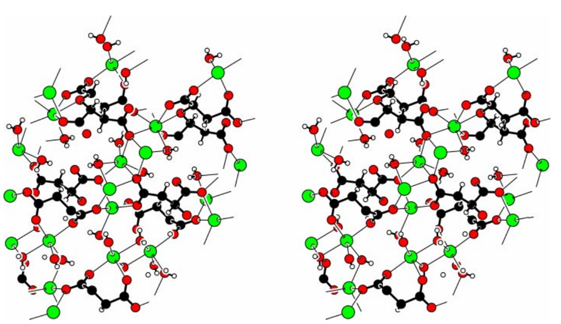


Figure 3
Stereopair of half the unit cell, in the same orientation as Fig. 2. This shows the environment of the sodium ions. At the centre of the diagram, Na2 is seen in two positions related by the screw axis at 1/4, *y*, 1/2. Na1 and Na4 are close to the (vertical) line $z = 1/2$ at $x = 0.16$ and 0.11, respectively. Four symmetry-related Na3 atoms can be seen at the bottom of the diagram, close to the horizontal line $x = 0$. Hydrogen bonds have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Na1—O25	2.305 (2)	Na3—O7^{i}	2.295 (2)
Na1—O8^{i}	2.342 (2)	Na3—O24^{iii}	2.365 (2)
Na1—O11	2.357 (2)	Na3—O22^{vi}	2.397 (2)
Na1—O1^{i}	2.463 (2)	Na3—O10^{i}	2.409 (2)
Na1—O14	2.551 (2)	Na3—O24^{vi}	2.429 (2)
Na1—O16^{i}	2.588 (2)	Na3—O23^{vi}	2.480 (2)
Na2—O14^{ii}	2.391 (2)	Na4—O8^{i}	2.303 (2)
Na2—O14	2.426 (2)	Na4—O11^{vii}	2.326 (2)
Na2—O16^{iii}	2.447 (2)	Na4—O13	2.332 (2)
Na2—O21^{iv}	2.481 (2)	Na4—O22	2.378 (2)
Na2—O21^{v}	2.503 (2)	Na4—O16^{iii}	2.483 (2)
Na2—O25	2.596 (3)		
O25—Na1—O8^{i}	97.89 (8)	O24^{iii}—Na3—O10^{i}	93.92 (8)
O25—Na1—O11	152.77 (9)	O22^{vi}—Na3—O10^{i}	177.68 (8)
O8^{i}—Na1—O11	104.02 (7)	O7^{i}—Na3—O24^{vi}	174.60 (8)
O25—Na1—O1^{i}	102.63 (8)	O24^{iii}—Na3—O24^{vi}	85.48 (8)
O8^{i}—Na1—O1^{i}	65.78 (7)	O22^{vi}—Na3—O24^{vi}	93.02 (8)
O11—Na1—O1^{i}	101.02 (7)	O10^{i}—Na3—O24^{vi}	88.90 (8)
O25—Na1—O14	80.96 (8)	O7^{i}—Na3—O23^{vi}	99.97 (8)
O8^{i}—Na1—O14	104.47 (7)	O24^{iii}—Na3—O23^{vi}	166.82 (9)
O11—Na1—O14	78.07 (7)	O22^{vi}—Na3—O23^{vi}	96.34 (8)
O1^{i}—Na1—O14	169.85 (8)	O10^{i}—Na3—O23^{vi}	85.23 (7)
O25—Na1—O16^{i}	95.85 (8)	O24^{vi}—Na3—O23^{vi}	81.36 (8)
O8^{i}—Na1—O16^{i}	128.01 (8)	O8^{i}—Na4—O11^{vii}	172.00 (8)
O11—Na1—O16^{i}	83.33 (7)	O8^{i}—Na4—O13	88.15 (7)
O1^{i}—Na1—O16^{i}	62.32 (6)	O11^{vii}—Na4—O13	87.19 (8)
O14—Na1—O16^{i}	127.16 (7)	O8^{i}—Na4—O22	81.02 (8)
O14^{ii}—Na2—O14	89.28 (7)	O11^{vii}—Na4—O22	106.93 (8)
O14^{ii}—Na2—O16^{iii}	150.92 (7)	O13—Na4—O22	118.62 (8)
O14—Na2—O16^{iii}	107.94 (7)	O8^{i}—Na4—O16^{iii}	89.47 (7)
O14^{ii}—Na2—O21^{iv}	112.17 (8)	O11^{vii}—Na4—O16^{iii}	86.32 (7)
O14—Na2—O21^{iv}	83.25 (7)	O13—Na4—O16^{iii}	112.66 (7)
O16^{iii}—Na2—O21^{iv}	93.41 (7)	O22—Na4—O16^{iii}	127.30 (8)
O14^{ii}—Na2—O21^{v}	84.27 (7)	Na4^{viii}—O8—Na1^{viii}	105.73 (8)
O14—Na2—O21^{v}	152.37 (8)	Na4^{ix}—O11—Na1	91.74 (7)
O16^{iii}—Na2—O21^{v}	89.81 (7)	Na2^{ii}—O14—Na2	90.72 (7)
O21^{iv}—Na2—O21^{v}	74.50 (8)	Na2^{ii}—O14—Na1	103.17 (7)
O14^{ii}—Na2—O25	83.31 (7)	Na2—O14—Na1	95.62 (7)
O14—Na2—O25	77.85 (7)	Na2^{iv}—O16—Na4^{iv}	97.15 (7)
O16^{iii}—Na2—O25	77.91 (7)	Na2^{iv}—O16—Na1^{viii}	110.00 (8)
O21^{iv}—Na2—O25	155.47 (8)	Na4^{iv}—O16—Na1^{viii}	83.03 (6)
O21^{v}—Na2—O25	127.66 (7)	Na2^{iii}—O21—Na2^{x}	105.50 (8)
O7^{i}—Na3—O24^{iii}	93.08 (8)	Na4—O22—Na3^{vi}	111.48 (9)
O7^{i}—Na3—O22^{vi}	92.03 (8)	Na3^{iv}—O24—Na3^{vi}	94.52 (8)
O24^{iii}—Na3—O22^{vi}	84.94 (8)	Na1—O25—Na2	97.47 (8)
O7^{i}—Na3—O10^{i}	86.01 (7)		
O1—C2—C3—C4	20.1 (3)	C12—C4—C5—C15	92.5 (3)
C2—C3—C4—C5	3.0 (3)	O7—C6—C2—C3	73.7 (3)
C3—C4—C5—O1	−25.2 (3)	O17—C15—C5—C4	−60.1 (3)
C4—C5—O1—C2	39.7 (3)	O10—C9—C3—C2	1.3 (3)
C6—C2—C3—C9	−94.3 (3)	O13—C12—C4—C5	45.4 (3)
C9—C3—C4—C12	−1.5 (3)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21A···O11^{i}	0.87 (3)	1.94 (3)	2.805 (3)	176 (3)
O21—H21B···O17^{ii}	0.79 (3)	2.16 (3)	2.943 (3)	169 (3)
O22—H22A···O23^{iii}	0.83 (3)	2.08 (3)	2.845 (3)	154 (3)
O22—H22B···O7^{i}	0.82 (3)	1.96 (3)	2.730 (3)	157 (3)
O23—H23A···O10	0.96 (4)	1.74 (4)	2.702 (3)	174 (3)
O23—H23B···O8^{i}	0.68 (3)	2.28 (4)	2.948 (3)	169 (4)
O24—H24A···O10	0.78 (3)	2.36 (3)	3.010 (3)	142 (3)
O24—H24B···O13	0.81 (3)	1.93 (3)	2.740 (3)	176 (3)
O25—H25A···O17^{iv}	0.67 (3)	2.15 (3)	2.817 (3)	171 (4)
O25—H25B···O17^{ii}	0.88 (4)	1.82 (4)	2.699 (3)	175 (3)

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

H atoms attached to C1, C2, C3 and C4 were placed in calculated positions and allowed to ride on their attached C atom during refinement. Isotropic displacement parameters were constrained to be 1.3 times the U_{eq} value of the C atom. Water H atoms (O21–O25) were located on a difference synthesis. Their positional parameters were refined without constraint and their isotropic displacement parameters were fixed at 0.025 $Å^2$.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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