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Tetrakis(guanidinium) butane-1,2,3,4-tetracarboxylate

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Key indicators

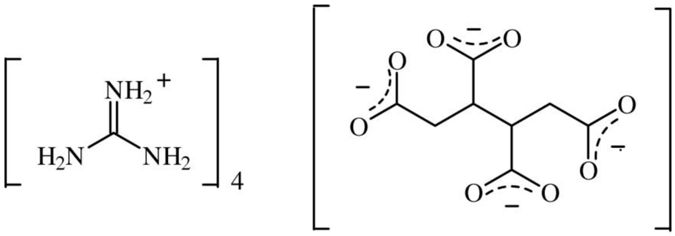
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.089
Data-to-parameter ratio = 11.8

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

The title compound, $4CH_6N_3^+\cdot C_8H_6O_8^{4-}$, forms a hydrogen-bonded network, in which each O atom is an acceptor for three hydrogen bonds and each guadinium H atom contributes to a single hydrogen bond. The complete anion is generated by inversion symmetry.

Comment

Guanidinium ions have long been utilized in modelling Arg–Glu or Arg–Asp side-chain interactions in proteins (see, for example, Melo *et al.*, 1999; Fülscher & Mehler, 1988; Singh *et al.*, 1987). More recently, the same types of interaction have been utilized in host–guest and sensor chemistry (see, for example, Houk *et al.*, 2005) and in crystal engineering (see, for example, Holman *et al.*, 2001; Burrows *et al.*, 2003). In this paper, we report the structure of the title compound, (I), the guanidinium salt of 1,2,3,4-butanetetracarboxylic acid. A search of the Cambridge Structural Database (Version 5.27; Allen, 2002; Fletcher *et al.*, 1996) showed that, to date, the only other structurally characterized 1,2,3,4-butanetetracarboxylate salt is $[NH_4]_4[C_8H_6O_8]\cdot H_2O$ (Barnes & Barnes, 1996).



(I)

The structure of (I) is shown in Fig. 1. The anion lies on a centre of symmetry so that the asymmetric unit contains half a $[C_8H_6O_8]^{4-}$ anion and two independent $[CH_6N_3]^+$ cations. The anion conformation is very similar to that observed in the previously reported ammonium salt (Barnes & Barnes, 1996), having an extended essentially planar C_6 chain. The anions are arranged in parallel stacks perpendicular to b and interact with each other only through hydrogen bonding *via* the guanidinium cations.

Each carboxylate group is paired with a guanidinium ion to form a conventional $R_2^2(9)$ ring (Etter *et al.*, 1990). There is also one $R_1^2(6)$ ring involving atoms O4, N11 and N12, and one $R_2^2(7)$ ring involving atoms N23, O1^{vi} and O2^{vi} [symmetry code: (vi) $2-x, y, \frac{1}{2}-z$]. Each O atom accepts further hydrogen bonds from neighbouring guanadinium cations so that there is a total of three hydrogen bonds to each O atom

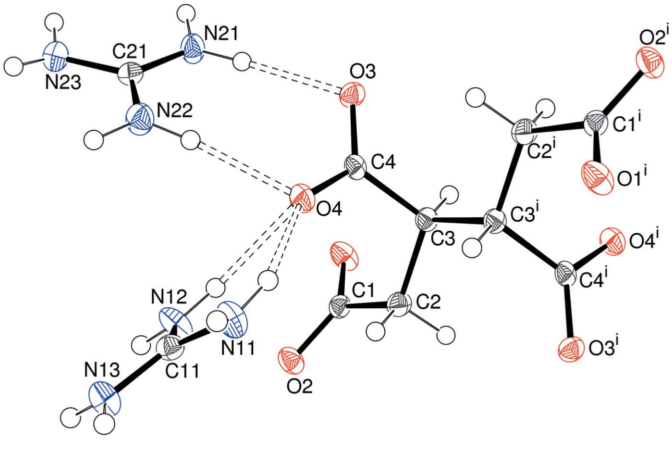


Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for H atoms). Hydrogen bonds are shown as double dashed lines. [Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.]

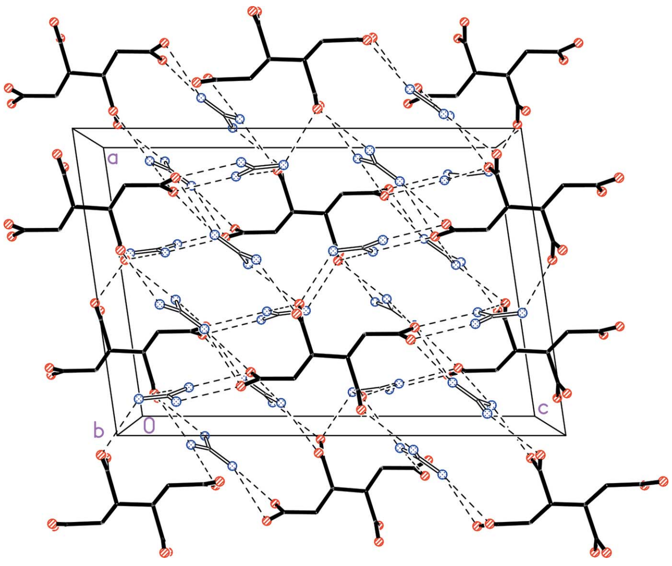


Figure 2
A packing diagram for (I), viewed perpendicular to *b*. Guanidinium ions are shown with white bonds and anions with black bonds, and H atoms have been omitted for clarity. The N$\cdots$O contacts for the hydrogen bonds are shown as dashed lines.

(Figs. 1 and 3, Table 1). Each H atom in the guanidinium ions is involved in a single hydrogen bond. The resulting three-dimensional hydrogen-bonding network contains a number of large rings, but graph-set analysis of these is not particularly helpful in understanding the structure.

Experimental

1,2,3,4-Butanetetracarboxylic acid (Merck; 1 mmol, 0.23 g) was added to an aqueous solution (12 ml) of guanidinum carbonate (Merck; 4.1 mmol, 0.74 g). This solution yielded colourless crystals of (I) after 6 d.

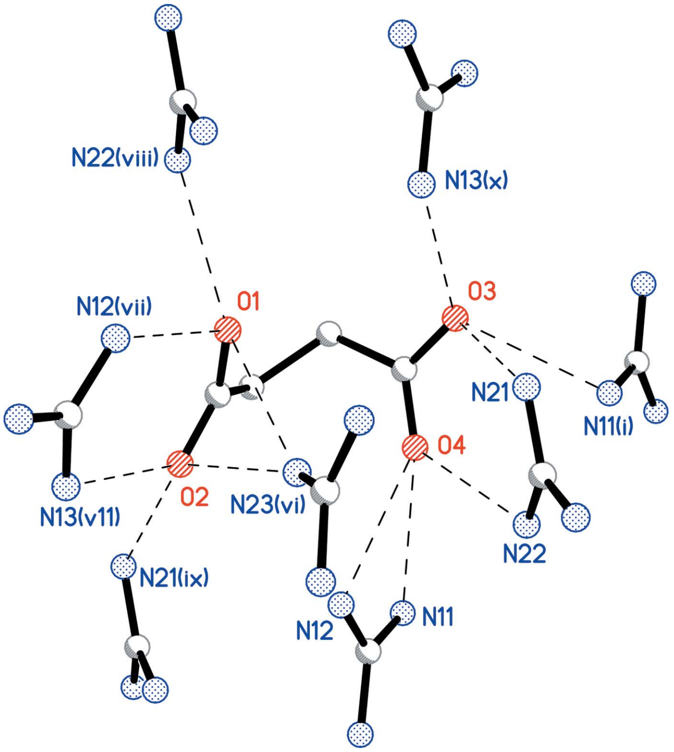


Figure 3
Detail of (I), showing the hydrogen bonding to one unique half of the anion. H atoms have been omitted for clarity and the N$\cdots$O contacts for the hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (vi) $2 - x, y, \frac{1}{2} - z$; (vii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (viii) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (ix)-1/2, $1 - y, -1z$; (*x*) $x, -1 + y, z$.]

Crystal data

$4CH_6N_3^+ \cdot C_8H_6O_8^{4-}$
$M_r = 470.48$
Monoclinic, $C2/c$
$a = 13.0411\ (13)$ Å
$b = 8.9177\ (9)$ Å
$c = 18.8692\ (19)$ Å
$\beta = 98.289\ (2)^\circ$
$V = 2171.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.439$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 150\ (2)$ K
Plate, colourless
0.35 × 0.15 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.876$, $T_{\max} = 1.00$
8107 measured reflections
2136 independent reflections
1741 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.089$
$S = 1.11$
2136 reflections
181 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 1.6442P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···O4	0.88 (2)	2.17 (2)	2.9591 (19)	150.1 (18)
N11—H11*B*···O3$^{\rm i}$	0.87 (2)	2.20 (2)	2.9854 (18)	148.8 (19)
N12—H12*A*···O1$^{\rm ii}$	0.88 (2)	1.99 (2)	2.8613 (18)	171 (2)
N12—H12*B*···O4	0.89 (2)	2.04 (2)	2.8495 (18)	151.3 (18)
N13—H13*A*···O3$^{\rm iii}$	0.86 (2)	1.95 (2)	2.8013 (18)	170 (2)
N13—H13*B*···O2$^{\rm ii}$	0.88 (2)	2.00 (2)	2.8788 (18)	175 (2)
N21—H21*A*···O2$^{\rm iv}$	0.85 (2)	2.00 (2)	2.8528 (18)	175 (2)
N21—H21*B*···O3	0.90 (2)	1.97 (2)	2.8712 (18)	177.0 (19)
N22—H22*A*···O4	0.89 (2)	2.02 (2)	2.8955 (19)	169.8 (19)
N22—H22*B*···O1$^{\rm v}$	0.89 (2)	2.14 (2)	2.9844 (19)	156.4 (18)
N23—H23*A*···O1$^{\rm v}$	0.89 (2)	2.39 (2)	3.170 (2)	147.0 (18)
N23—H23*A*···O2$^{\rm vi}$	0.89 (2)	2.52 (2)	3.0010 (18)	114.7 (16)
N23—H23*B*···O1$^{\rm vi}$	0.85 (2)	2.38 (2)	3.0632 (19)	138.1 (19)

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

Carbon-bound H atoms were placed in calculated positions, with C—H = 0.99–1.00 Å, and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. H atoms bonded to N were located in difference maps and their coordinates refined with a common fixed $U_{\rm iso}$ value. N—H distances are given in Table 1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

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