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

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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)
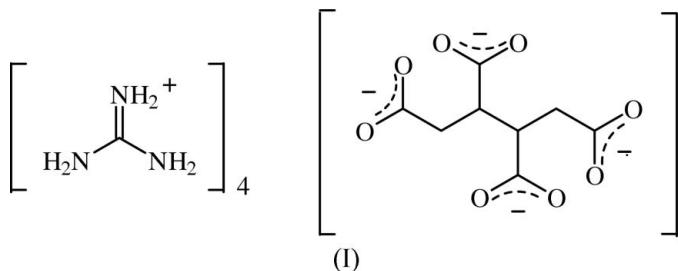
The structure of (I) is shown in Fig. 1. The anion lies on a centre of symmetry so that the asymmetric unit contains half a $[C_8H_6O_8]^{4-}$ anion and two independent $[CH_6N_3]^+$ cations. The anion conformation is very similar to that observed in the previously reported ammonium salt (Barnes & Barnes, 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 guanidinium cations so that there is a total of three hydrogen bonds to each O atom
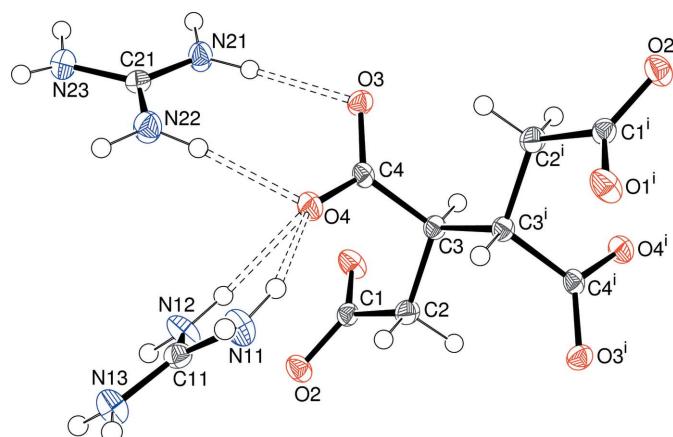
Figure 1
A view of the molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for H atoms). Hydrogen bonds are shown as double dashed lines. [Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.]
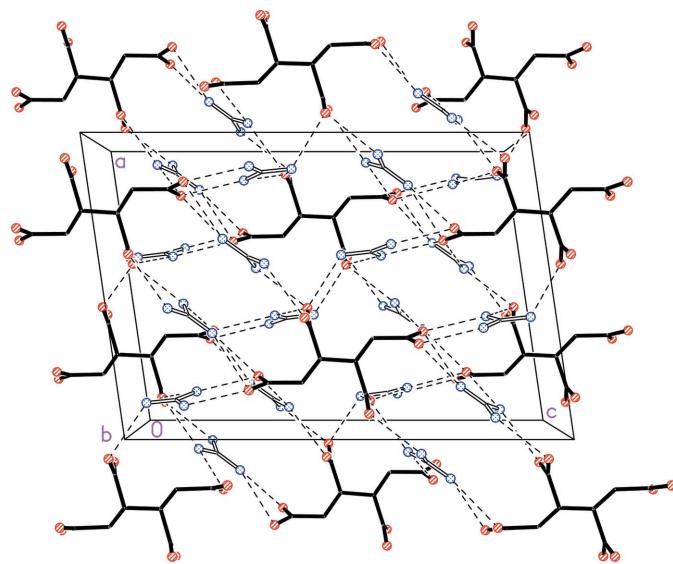

Figure 2
A packing diagram for (I), viewed perpendicular to *b*. Guanidinium ions are shown with white bonds and anions with black bonds, and H atoms have been omitted for clarity. The N···O contacts for the hydrogen bonds are shown as dashed lines.

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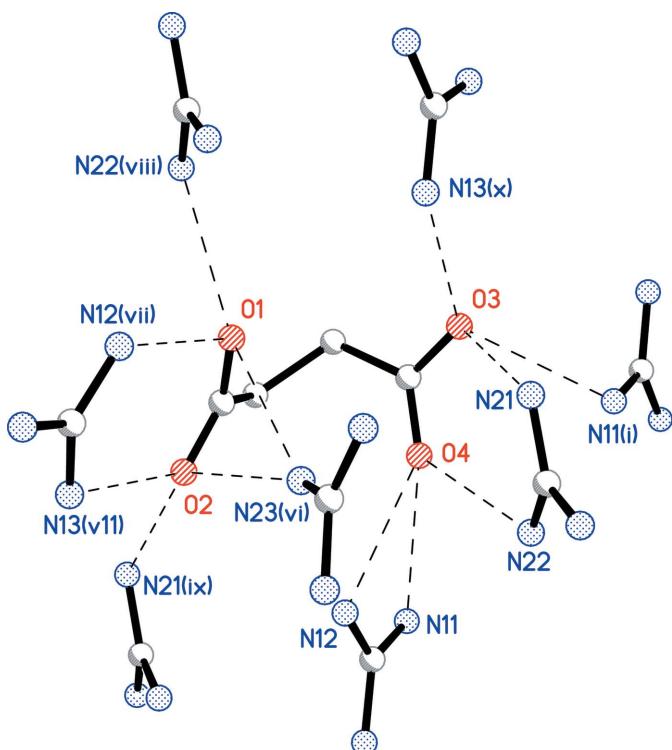
Figure 3
Detail of (I), showing the hydrogen bonding to one unique half of the anion. H atoms have been omitted for clarity and the N···O contacts for the hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (vi) $2 - x, y, \frac{1}{2} - z$; (vii) $\frac{3}{2} - x, -\frac{1}{2}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

Crystal data

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

Data collection

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

Refinement

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

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N11—H11A···O4	0.88 (2)	2.17 (2)	2.9591 (19)	150.1 (18)
N11—H11B···O3$^{\mathrm{i}}$	0.87 (2)	2.20 (2)	2.9854 (18)	148.8 (19)
N12—H12A···O1$^{\mathrm{ii}}$	0.88 (2)	1.99 (2)	2.8613 (18)	171 (2)
N12—H12B···O4	0.89 (2)	2.04 (2)	2.8495 (18)	151.3 (18)
N13—H13A···O3$^{\mathrm{iii}}$	0.86 (2)	1.95 (2)	2.8013 (18)	170 (2)
N13—H13B···O2$^{\mathrm{ii}}$	0.88 (2)	2.00 (2)	2.8788 (18)	175 (2)
N21—H21A···O2$^{\mathrm{iv}}$	0.85 (2)	2.00 (2)	2.8528 (18)	175 (2)
N21—H21B···O3	0.90 (2)	1.97 (2)	2.8712 (18)	177.0 (19)
N22—H22A···O4	0.89 (2)	2.02 (2)	2.8955 (19)	169.8 (19)
N22—H22B···O1$^{\mathrm{v}}$	0.89 (2)	2.14 (2)	2.9844 (19)	156.4 (18)
N23—H23A···O1$^{\mathrm{v}}$	0.89 (2)	2.39 (2)	3.170 (2)	147.0 (18)
N23—H23A···O2$^{\mathrm{vi}}$	0.89 (2)	2.52 (2)	3.0010 (18)	114.7 (16)
N23—H23B···O1$^{\mathrm{vi}}$	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 $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. H atoms bonded to N were located in difference maps and their coordinates refined with a common fixed U_{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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supporting information

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Crystal data
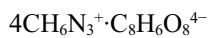
$4CH_6N_3^+ \cdot C_8H_6O_8^{4-}$	$F(000) = 1000$
$M_r = 470.48$	$D_x = 1.439$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 3043 reflections
$a = 13.0411$ (13) Å	$\theta = 2.2–23.4°$
$b = 8.9177$ (9) Å	$\mu = 0.12$ mm^{-1}
$c = 18.8692$ (19) Å	$T = 150$ K
$\beta = 98.289$ (2)°	Plate, colourless
$V = 2171.5$ (4) Å^3	$0.35 \times 0.15 \times 0.05$ mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	8107 measured reflections
Radiation source: normal-focus sealed tube	2136 independent reflections
Graphite monochromator	1741 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.026$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.2°$
	$h = -16\rightarrow16$
	$k = -11\rightarrow11$
$T_{min} = 0.876$, $T_{max} = 1.00$	$l = -23\rightarrow23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: difmap and geom
$wR(F^2) = 0.089$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.11$	
2136 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 1.6442P]$ where $P = (F_o^2 + 2F_c^2)/3$
181 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.27$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
O1	0.69273 (9)	0.17756 (12)	0.31000 (6)	0.0242 (3)
O2	0.65689 (9)	0.41895 (12)	0.28976 (5)	0.0223 (3)
C1	0.67633 (11)	0.30840 (17)	0.33106 (8)	0.0164 (3)
C2	0.67789 (12)	0.33449 (18)	0.41112 (8)	0.0191 (3)
H2A	0.6072	0.3180	0.4228	0.023*
H2B	0.6963	0.4406	0.4220	0.023*
C3	0.75332 (11)	0.23416 (17)	0.45963 (7)	0.0154 (3)
H3	0.7347	0.1269	0.4490	0.019*
C4	0.86530 (12)	0.26014 (16)	0.44669 (8)	0.0152 (3)
O3	0.92444 (8)	0.14777 (12)	0.44635 (6)	0.0186 (3)
O4	0.89455 (8)	0.39294 (12)	0.43873 (6)	0.0217 (3)
C11	0.88420 (12)	0.74996 (17)	0.38683 (8)	0.0184 (3)
N11	0.89593 (12)	0.72249 (18)	0.45713 (8)	0.0250 (3)
N12	0.86122 (12)	0.63807 (16)	0.34127 (8)	0.0242 (3)
N13	0.89573 (11)	0.88714 (16)	0.36297 (8)	0.0229 (3)
C21	1.09697 (12)	0.31126 (17)	0.32844 (8)	0.0189 (3)
N21	1.06074 (12)	0.17722 (16)	0.34047 (8)	0.0235 (3)
N22	1.07380 (12)	0.42887 (16)	0.36587 (8)	0.0254 (3)
N23	1.15688 (12)	0.33132 (19)	0.27746 (8)	0.0277 (3)
H11A	0.8953 (16)	0.627 (3)	0.4689 (11)	0.040*
H11B	0.9314 (17)	0.789 (2)	0.4842 (12)	0.040*
H12A	0.8474 (16)	0.660 (2)	0.2957 (12)	0.040*
H12B	0.8585 (15)	0.546 (2)	0.3588 (11)	0.040*
H13A	0.9007 (15)	0.961 (2)	0.3922 (11)	0.040*
H13B	0.8822 (16)	0.901 (2)	0.3163 (12)	0.040*
H21A	1.0868 (16)	0.100 (2)	0.3232 (11)	0.040*
H21B	1.0202 (17)	0.168 (2)	0.3748 (11)	0.040*
H22A	1.0241 (17)	0.420 (2)	0.3933 (11)	0.040*
H22B	1.0961 (15)	0.520 (3)	0.3547 (11)	0.040*
H23A	1.1890 (16)	0.419 (3)	0.2769 (11)	0.040*
H23B	1.1784 (17)	0.251 (2)	0.2602 (12)	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0386 (7)	0.0178 (6)	0.0160 (6)	0.0017 (5)	0.0032 (5)	−0.0005 (4)
O2	0.0327 (7)	0.0192 (6)	0.0157 (5)	0.0032 (5)	0.0055 (5)	0.0016 (4)
C1	0.0139 (7)	0.0189 (8)	0.0164 (7)	−0.0013 (6)	0.0025 (6)	0.0010 (6)
C2	0.0196 (8)	0.0235 (8)	0.0145 (7)	0.0036 (6)	0.0035 (6)	−0.0001 (6)
C3	0.0176 (8)	0.0163 (7)	0.0127 (8)	0.0006 (6)	0.0034 (6)	−0.0011 (6)

C4	0.0199 (8)	0.0171 (8)	0.0087 (7)	0.0001 (6)	0.0027 (6)	−0.0005 (5)
O3	0.0190 (5)	0.0178 (6)	0.0200 (6)	0.0018 (4)	0.0056 (4)	−0.0017 (4)
O4	0.0243 (6)	0.0165 (6)	0.0250 (6)	−0.0013 (5)	0.0064 (5)	0.0032 (5)
C11	0.0157 (8)	0.0189 (8)	0.0203 (8)	0.0005 (6)	0.0014 (6)	−0.0005 (6)
N11	0.0326 (8)	0.0230 (8)	0.0185 (7)	−0.0053 (6)	0.0003 (6)	0.0003 (6)
N12	0.0377 (9)	0.0153 (7)	0.0173 (7)	−0.0007 (6)	−0.0034 (6)	0.0012 (6)
N13	0.0338 (8)	0.0176 (7)	0.0165 (7)	−0.0040 (6)	0.0010 (6)	−0.0020 (6)
C21	0.0152 (7)	0.0213 (8)	0.0200 (8)	0.0021 (6)	0.0019 (6)	0.0030 (6)
N21	0.0296 (8)	0.0184 (7)	0.0254 (7)	0.0017 (6)	0.0140 (6)	0.0005 (6)
N22	0.0278 (8)	0.0187 (7)	0.0314 (8)	−0.0022 (6)	0.0097 (6)	−0.0004 (6)
N23	0.0251 (8)	0.0312 (9)	0.0289 (8)	0.0022 (7)	0.0110 (6)	0.0067 (7)

Geometric parameters (Å, º)

C1—O1	1.2608 (19)	N11—H11B	0.87 (2)
C1—O2	1.2596 (18)	N12—H12A	0.88 (2)
C1—C2	1.526 (2)	N12—H12B	0.89 (2)
C2—C3	1.532 (2)	N13—H13A	0.86 (2)
C2—H2A	0.9900	N13—H13B	0.88 (2)
C2—H2B	0.9900	C21—N21	1.317 (2)
C3—C4	1.533 (2)	C21—N22	1.324 (2)
C3—C3^i	1.564 (3)	C21—N23	1.336 (2)
C3—H3	1.0000	N21—H21A	0.85 (2)
C4—O4	1.2597 (18)	N21—H21B	0.90 (2)
C4—O3	1.2651 (18)	N22—H22A	0.89 (2)
C11—N13	1.320 (2)	N22—H22B	0.89 (2)
C11—N12	1.323 (2)	N23—H23A	0.89 (2)
C11—N11	1.336 (2)	N23—H23B	0.85 (2)
N11—H11A	0.88 (2)		
O2—C1—O1	123.88 (14)	C11—N11—H11A	115.1 (14)
O2—C1—C2	117.78 (13)	C11—N11—H11B	115.5 (14)
O1—C1—C2	118.33 (13)	H11A—N11—H11B	123 (2)
C1—C2—C3	114.73 (12)	C11—N12—H12A	117.5 (14)
C1—C2—H2A	108.6	C11—N12—H12B	118.2 (13)
C3—C2—H2A	108.6	H12A—N12—H12B	124.3 (19)
C1—C2—H2B	108.6	C11—N13—H13A	119.8 (14)
C3—C2—H2B	108.6	C11—N13—H13B	116.9 (14)
H2A—C2—H2B	107.6	H13A—N13—H13B	121.5 (19)
C4—C3—C2	111.16 (12)	N21—C21—N22	120.80 (15)
C4—C3—C3^i	108.41 (14)	N21—C21—N23	120.48 (15)
C2—C3—C3^i	110.83 (15)	N22—C21—N23	118.71 (15)
C4—C3—H3	108.8	C21—N21—H21A	119.7 (14)
C2—C3—H3	108.8	C21—N21—H21B	118.1 (13)
C3^i—C3—H3	108.8	H21A—N21—H21B	120.6 (19)
O4—C4—O3	123.28 (14)	C21—N22—H22A	118.6 (14)
O4—C4—C3	118.23 (13)	C21—N22—H22B	118.9 (13)
O3—C4—C3	118.46 (13)	H22A—N22—H22B	120.6 (19)

N13—C11—N12	120.25 (15)	C21—N23—H23A	116.9 (14)
N13—C11—N11	120.42 (15)	C21—N23—H23B	115.0 (15)
N12—C11—N11	119.33 (15)	H23A—N23—H23B	124 (2)

Symmetry code: (i) −*x*+3/2, −*y*+1/2, −*z*+1.

Hydrogen-bond geometry (Å, º)

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*···O3ⁱⁱ	0.87 (2)	2.20 (2)	2.9854 (18)	148.8 (19)
N12—H12*A*···O1ⁱⁱⁱ	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*···O3ⁱᵛ	0.86 (2)	1.95 (2)	2.8013 (18)	170 (2)
N13—H13*B*···O2ⁱⁱⁱ	0.88 (2)	2.00 (2)	2.8788 (18)	175 (2)
N21—H21*A*···O2ᵛ	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*···O1ᵛⁱ	0.89 (2)	2.14 (2)	2.9844 (19)	156.4 (18)
N23—H23*A*···O1ᵛⁱ	0.89 (2)	2.39 (2)	3.170 (2)	147.0 (18)
N23—H23*A*···O2ᵛⁱⁱ	0.89 (2)	2.52 (2)	3.0010 (18)	114.7 (16)
N23—H23*B*···O1ᵛⁱⁱ	0.85 (2)	2.38 (2)	3.0632 (19)	138.1 (19)

Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*+1; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) *x*, *y*+1, *z*; (v) *x*+1/2, *y*−1/2, *z*; (vi) *x*+1/2, *y*+1/2, *z*; (vii) −*x*+2, *y*, −*z*+1/2.