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Bis(guanidinium) tetraiodidomercurate(II)

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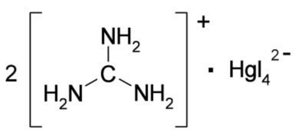
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(N–C) = 0.02 Å; R factor = 0.059; wR factor = 0.135; data-to-parameter ratio = 23.2.

The Hg atom in the crystal structure of the title compound, $(CH_6N_3)_2[HgI_4]$, is tetrahedrally coordinated by four I atoms. The $[HgI_4]^{2-}$ ions are interconnected to the $[C(NH_2)_3]^+$ ions by N—H⋯I hydrogen bonds, forming a three-dimensional network. The four different observed Hg—I distances [2.760 (2), 2.7762 (15), 2.8098 (14) and 2.833 (2) Å] are consistent with four different ^{127}I NQR frequencies observed, showing the existence of four unique I atoms in the tetraiodidomercurate unit.

Related literature

For synthetic methods, see: Furukawa *et al.* (2005); For the ability of the guanidinium ion to make hydrogen bonds and its unique planar shape, see: Terao *et al.* (2000). Hg–halogen bonds are sensitive to intermolecular interactions such as hydrogen bonding (Ishihara *et al.*, 2002), as evidenced by the halogen NQR of Hg compounds in which the resonance frequencies are widely spread (Furukawa *et al.*, 2005). For background to this study, see: Terao *et al.* (2009).



Experimental

Crystal data

$(CH_6N_3)_2[HgI_4]$
M_r = 828.37
Triclinic, $P\bar{1}$
a = 8.981 (2) Å
b = 8.996 (2) Å
c = 12.302 (3) Å
α = 105.80 (3)°
β = 95.79 (4)°
γ = 118.46 (2)°
V = 808.9 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 17.13 mm^{-1}
T = 298 K
0.42 × 0.38 × 0.32 mm

Data collection

Stoe IPDS-I diffractometer
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1999)
T_{min} = 0.017, T_{max} = 0.057
14500 measured reflections
3613 independent reflections
1846 reflections with $I > 2\sigma(I)$
R_{int} = 0.118

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.135
S = 0.81
3613 reflections
156 parameters
32 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 3.08 e Å^{-3}
$\Delta\rho_{min}$ = −2.71 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N11—H11A⋯I1^{i}	0.87 (4)	3.00 (4)	3.78 (2)	151 (2)
N12—H12A⋯I2	0.87 (4)	3.46 (2)	3.83 (2)	123 (2)
N13—H13A⋯I3^{ii}	0.87 (4)	2.96 (4)	3.80 (2)	161 (2)
N13—H13B⋯I1^{i}	0.87 (4)	2.88 (4)	3.69 (2)	156 (2)
N21—H21A⋯I3^{iii}	0.87 (4)	3.03 (4)	3.82 (2)	151 (2)
N21—H21B⋯I2	0.87 (4)	2.91 (4)	3.74 (2)	162 (6)
N22—H22A⋯I4^{iv}	0.87 (9)	2.98 (4)	3.82 (2)	162 (2)
N22—H22B⋯I3^{iii}	0.87 (10)	3.05 (4)	3.81 (2)	147 (2)
N23—H23A⋯I4^{iv}	0.87 (9)	2.91 (4)	3.71 (2)	153 (2)
N23—H23B⋯I2	0.87 (4)	2.99 (4)	3.82 (2)	161 (6)

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

Data collection: *EXPOSE* (Stoe & Cie, 1999); cell refinement: *CELL* (Stoe & Cie, 1999); data reduction: *XPREP* (Bruker, 2003); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL93* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL93*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2201).

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supporting information

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Bis(guanidinium) tetraiodidomercurate(II)

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S1. Comment

The ability of guanidium ion, $[C(NH_2)_3]^+$ in making hydrogen bonds and its unique planar shape has been recognized (Terao *et al.*, 2000). Further, the guanidium ions tend to undergo reorientation motions about their (pseudo) C_3 axes in the crystals. Due to the soft nature, Hg atoms are amenable to polarization and thus the Hg-halogen bonds are sensitive to the intermolecular interactions such as hydrogen bonding (Ishihara *et al.*, 2002). This was evident in the halogen NQR of the Hg compounds in which the resonance frequencies are widely spread (Furukawa *et al.*, 2005). Thus the study of the structure and bonding of this class of compounds is interesting. As a part of our investigations in this direction (Terao *et al.*, 2009), we report herein the crystal structure of Guanidinium tetraiodomercurate(II) (I). In the structure, the mercury atom is tetrahedrally coordinated by four iodine atoms and the resulting HgI_4 tetrahedra are interconnected to the $[C(NH_2)_3]^+$ ions by iodine-hydrogen bonds forming a three-dimensional network (Fig. 1). Four different Hg—I distances were observed which are consistent with four different I-127 NQR frequencies observed (Furukawa *et al.*, 2005), establishing the existence of four inequivalent I atoms in the tetraiodomercurate unit. The packing diagram of the crystal structure, as viewed in the direction of *c* axis is shown in Fig. 3.

S2. Experimental

Guanidinium tetraiodomercurate(II) was prepared by slow concentration of methanolic solution containing mercuric iodide (0.01 mol, 4.54 g) and guanidium iodide (0.024 mol, 4.48 g) in slightly more than 1:2 molar ratio. The purity of the compound was checked by elemental analysis and characterized by its NMR and NQR spectra (Furukawa *et al.*, 2005). The single crystals used in X-ray diffraction studies were grown in methanolic solution by a slow evaporation at room temperature.

S3. Refinement

The N—H distances were restrained to 0.87–0.88 Å and the coordinates of the H atoms were refined with isotropic displacement parameters set to 1.2 times of the U_{eq} of the parent atom.

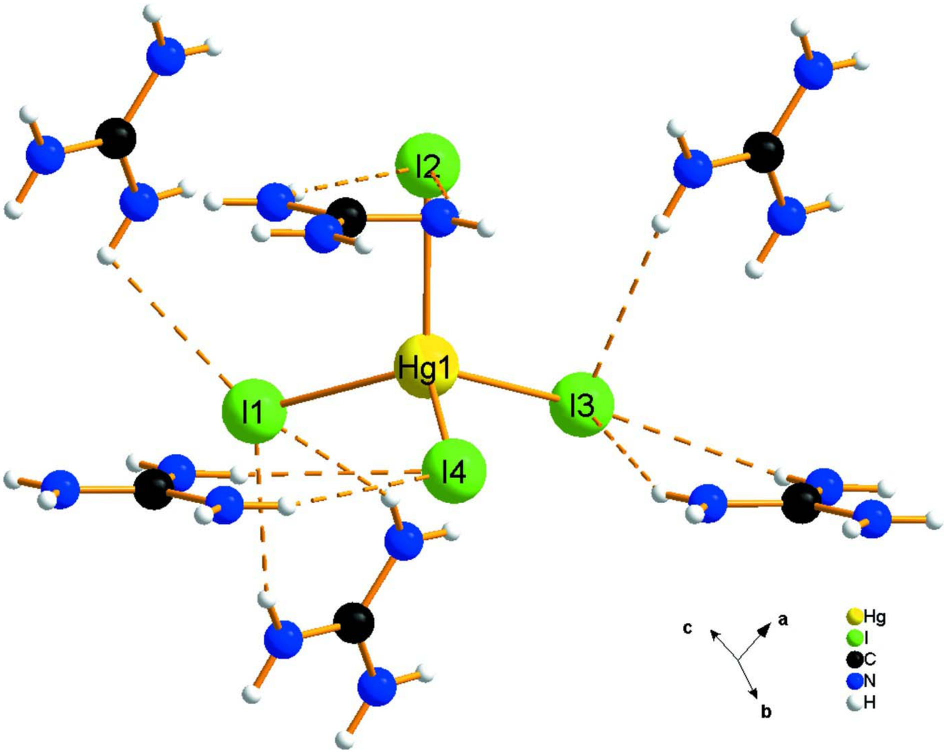

Figure 1

Molecular structure of (I), showing the atom labeling scheme. The displacement ellipsoids are drawn at the 50% probability level. The H atoms are represented as small spheres of arbitrary radii.

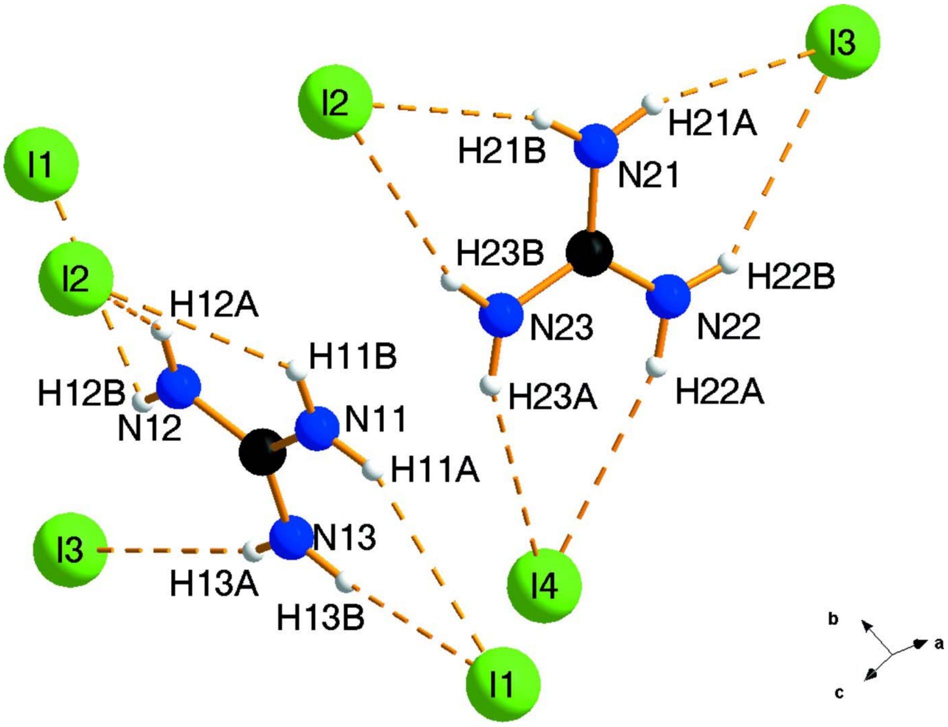

Figure 2

Two distinct guanidinium ions in the crystal structure of (I) along with the numbering of the atoms.

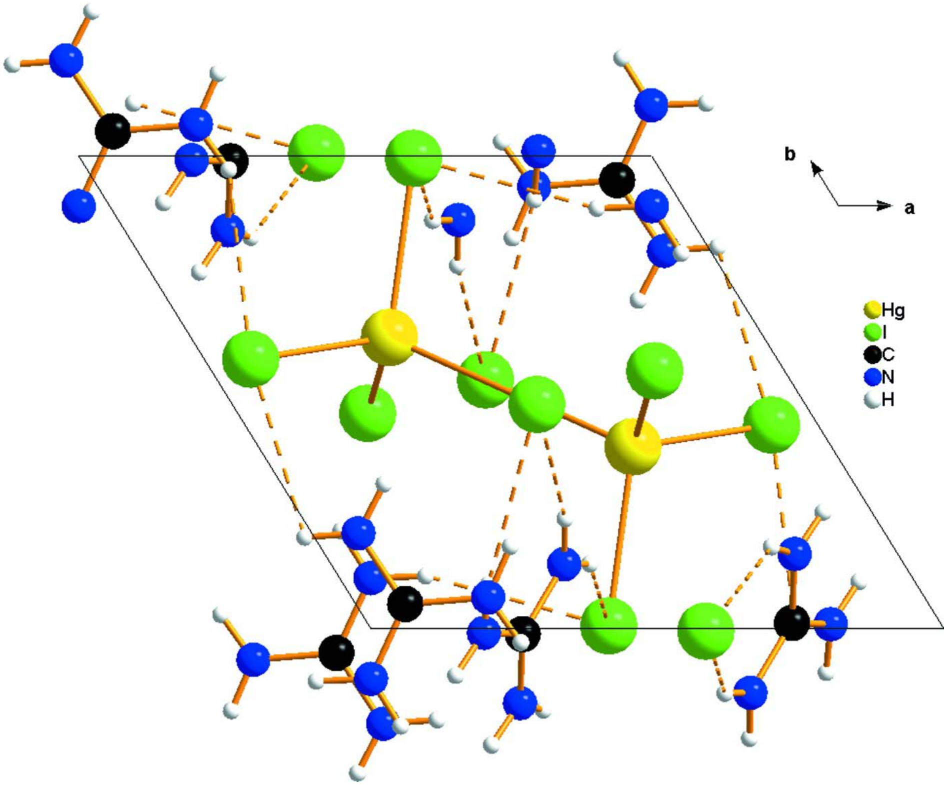

Figure 3

Packing diagram of (I) as viewed in the direction of *c* axis.

Bis(guanidinium) tetraiodidomercurate(II)

Crystal data

$(CH_6N_3)_2[HgI_4]$
$M_r = 828.37$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.981$ (2) Å
$b = 8.996$ (2) Å
$c = 12.302$ (3) Å
$\alpha = 105.80$ (3)°
$\beta = 95.79$ (4)°
$\gamma = 118.46$ (2)°
$V = 808.9$ (5) Å^3
$Z = 2$
$F(000) = 716$
$D_x = 3.401$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2000 reflections
$\theta = 2.7$–28.0°
$\mu = 17.13$ mm^{-1}
$T = 298$ K
Cylindric, yellow
0.42 × 0.38 × 0.32 mm

Data collection

Stoe IPDS-I diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
imaging plate dynamic profile intergration scans
Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1999)
$T_{min} = 0.017$, $T_{max} = 0.057$
14500 measured reflections
3613 independent reflections
1846 reflections with $I > 2\sigma(I)$

$R_{int} = 0.118$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.7°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.135$
$S = 0.81$
3613 reflections
156 parameters
32 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.08$ e Å^{-3}
$\Delta\rho_{min} = -2.71$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00075 (10)

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}
Hg1	0.34641 (9)	0.61562 (10)	0.73508 (6)	0.0667 (3)
I1	0.0809 (2)	0.5696 (2)	0.84518 (10)	0.0650 (3)
I2	0.53156 (14)	0.4740 (2)	0.82071 (9)	0.0607 (3)
I3	0.58185 (14)	0.9944 (2)	0.80058 (10)	0.0627 (3)
I4	0.22651 (14)	0.4550 (2)	0.49342 (9)	0.0673 (3)
C1	0.0864 (17)	0.0540 (15)	0.8824 (8)	0.051 (3)
N11	0.2387 (17)	0.0661 (18)	0.9149 (13)	0.072 (4)
H11A	0.246 (12)	−0.030 (7)	0.902 (4)	0.12 (3)*
H11B	0.333 (7)	0.174 (5)	0.9499 (19)	0.12 (3)*
N12	0.0824 (14)	0.2000 (14)	0.9034 (11)	0.066 (4)
H12A	0.179 (2)	0.3056 (13)	0.9387 (16)	0.12 (3)*
H12B	−0.0169 (19)	0.193 (2)	0.8825 (17)	0.12 (3)*
N13	−0.0542 (16)	−0.1065 (19)	0.8300 (14)	0.080 (4)
H13A	−0.152 (4)	−0.111 (8)	0.810 (3)	0.12 (3)*
H13B	−0.054 (9)	−0.207 (5)	0.815 (3)	0.12 (3)*
C2	0.2590 (18)	−0.012 (2)	0.5152 (16)	0.067 (4)
N21	0.4067 (18)	0.136 (2)	0.5198 (14)	0.086 (5)
H21A	0.453 (8)	0.138 (11)	0.461 (4)	0.12 (3)*
H21B	0.457 (8)	0.232 (6)	0.584 (3)	0.12 (3)*
N22	0.1800 (17)	−0.158 (2)	0.4211 (13)	0.092 (5)

H22A	0.085 (3)	−0.246 (11)	0.427 (11)	0.12 (3)*
H22B	0.212 (14)	−0.173 (18)	0.357 (5)	0.12 (3)*
N23	0.193 (2)	−0.009 (3)	0.6078 (14)	0.110 (7)
H23A	0.098 (3)	−0.100 (11)	0.610 (12)	0.12 (3)*
H23B	0.252 (13)	0.093 (8)	0.668 (7)	0.12 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0686 (4)	0.0651 (5)	0.0641 (4)	0.0319 (4)	0.0196 (3)	0.0262 (4)
I1	0.0802 (7)	0.0566 (7)	0.0743 (7)	0.0413 (6)	0.0367 (6)	0.0307 (6)
I2	0.0632 (6)	0.0535 (7)	0.0608 (6)	0.0271 (6)	0.0115 (5)	0.0233 (5)
I3	0.0605 (6)	0.0547 (7)	0.0725 (7)	0.0284 (6)	0.0193 (5)	0.0259 (6)
I4	0.0606 (6)	0.0668 (8)	0.0540 (6)	0.0182 (6)	0.0137 (5)	0.0237 (6)
C1	0.060 (9)	0.039 (10)	0.050 (8)	0.023 (8)	0.014 (7)	0.017 (8)
N11	0.063 (9)	0.069 (11)	0.111 (12)	0.045 (8)	0.032 (9)	0.047 (10)
N12	0.063 (8)	0.039 (9)	0.077 (9)	0.022 (7)	−0.004 (7)	0.009 (8)
N13	0.068 (9)	0.053 (11)	0.113 (13)	0.033 (9)	0.004 (9)	0.027 (10)
C2	0.053 (9)	0.047 (12)	0.076 (12)	0.014 (9)	0.003 (9)	0.016 (10)
N21	0.079 (10)	0.048 (11)	0.088 (11)	0.005 (9)	0.033 (9)	0.013 (9)
N22	0.076 (10)	0.054 (12)	0.060 (9)	−0.012 (9)	0.006 (8)	−0.006 (8)
N23	0.074 (11)	0.096 (15)	0.077 (11)	−0.007 (10)	0.032 (10)	0.010 (11)

Geometric parameters (Å, º)

Hg1—I4	2.760 (2)	N11—H11A	0.88 (8)
Hg1—I1	2.7762 (15)	N11—H11B	0.87 (5)
Hg1—I2	2.8098 (14)	N12—H12A	0.87 (2)
Hg1—I3	2.833 (2)	N12—H12B	0.87 (2)
I1—H13B^{i}	2.87 (7)	N13—H13A	0.87 (5)
I1—H11A^{i}	3.00 (4)	N13—H13B	0.88 (6)
I2—H21B	2.91 (3)	C2—N22	1.30 (2)
I2—H23B	2.99 (5)	C2—N21	1.34 (2)
I3—H13A^{ii}	2.97 (5)	C2—N23	1.34 (2)
I3—H22B^{iii}	3.05 (7)	N21—H21B	0.87 (4)
I3—H21A^{iii}	3.03 (4)	N21—H21A	0.87 (7)
I3—H12B^{ii}	3.057 (19)	N22—H22B	0.87 (9)
C1—N13	1.29 (2)	N22—H22A	0.87 (9)
C1—N12	1.29 (2)	N23—H23A	0.87 (9)
C1—N11	1.32 (2)	N23—H23B	0.87 (8)
I4—Hg1—I1	113.75 (5)	H13A—N13—H13B	120 (6)
I4—Hg1—I2	109.54 (5)	H13A—N13—C1	117 (4)
I1—Hg1—I2	108.81 (4)	H13B—N13—C1	123 (4)
I4—Hg1—I3	109.38 (6)	N22—C2—N21	120.3 (17)
I1—Hg1—I3	107.26 (5)	N22—C2—N23	119.8 (15)
I2—Hg1—I3	107.93 (5)	N21—C2—N23	119.9 (17)
N13—C1—N12	121.1 (14)	H21B—N21—H21A	120 (7)

N13—C1—N11	119.7 (14)	H21B—N21—C2	119 (6)
N12—C1—N11	119.2 (14)	H21A—N21—C2	121 (6)
H11A—N11—H11B	120 (7)	H22B—N22—H22A	120 (11)
H11A—N11—C1	120 (11)	H22B—N22—C2	127 (9)
H11B—N11—C1	118 (6)	H22A—N22—C2	114 (9)
H12A—N12—H12B	120 (2)	H23A—N23—H23B	120 (11)
H12A—N12—C1	119.9 (19)	H23A—N23—C2	125 (10)
H12B—N12—C1	120.0 (18)	H23B—N23—C2	115 (10)

N13—C1—N11—H11A	0.0 (6)	N22—C2—N21—H21B	180.0 (5)
N12—C1—N11—H11A	−180.0 (5)	N23—C2—N21—H21B	−0.1 (6)
N13—C1—N11—H11B	180.0 (6)	N22—C2—N21—H21A	0.0 (5)
N12—C1—N11—H11B	0.0 (5)	N23—C2—N21—H21A	179.9 (6)
N13—C1—N12—H12A	−180.0 (6)	N21—C2—N22—H22B	0.1 (6)
N11—C1—N12—H12A	0.0 (4)	N23—C2—N22—H22B	−179.9 (6)
N13—C1—N12—H12B	0.1 (9)	N21—C2—N22—H22A	180.0 (5)
N11—C1—N12—H12B	−180.0 (8)	N23—C2—N22—H22A	0.1 (6)
N12—C1—N13—H13A	−0.1 (10)	N22—C2—N23—H23A	−0.2 (11)
N11—C1—N13—H13A	179.9 (7)	N21—C2—N23—H23A	179.9 (8)
N12—C1—N13—H13B	−179.9 (7)	N22—C2—N23—H23B	−179.9 (7)
N11—C1—N13—H13B	0.1 (10)	N21—C2—N23—H23B	0.1 (9)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*+1, *z*; (iii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···I1^{iv}	0.87 (4)	3.00 (4)	3.78 (2)	151 (2)
N12—H12*A*···I2	0.87 (4)	3.46 (2)	3.83 (2)	123 (2)
N13—H13*A*···I3^{v}	0.87 (4)	2.96 (4)	3.80 (2)	161 (2)
N13—H13*B*···I1^{iv}	0.87 (4)	2.88 (4)	3.69 (2)	156 (2)
N21—H21*A*···I3^{iii}	0.87 (4)	3.03 (4)	3.82 (2)	151 (2)
N21—H21*B*···I2	0.87 (4)	2.91 (4)	3.74 (2)	162 (6)
N22—H22*A*···I4^{vi}	0.87 (9)	2.98 (4)	3.82 (2)	162 (2)
N22—H22*B*···I3^{iii}	0.87 (10)	3.05 (4)	3.81 (2)	147 (2)
N23—H23*A*···I4^{vi}	0.87 (9)	2.91 (4)	3.71 (2)	153 (2)
N23—H23*B*···I2	0.87 (4)	2.99 (4)	3.82 (2)	161 (6)

Symmetry codes: (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*−1, *z*; (v) *x*−1, *y*−1, *z*; (vi) −*x*, −*y*, −*z*+1.