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Poly[methylamine-μ-oxalato-copper(II)]

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Key indicators

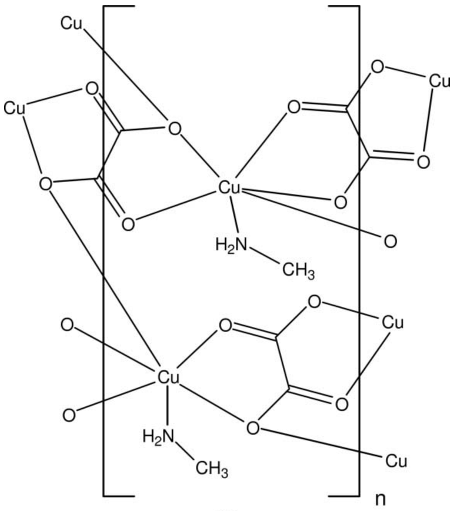
Single-crystal X-ray study
T = 566 K
Mean σ(C–C) = 0.008 Å
R factor = 0.057
wR factor = 0.130
Data-to-parameter ratio = 15.5

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

The six-coordinate copper(II) ions in the title compound, $[Cu(C_2O_4)(CH_5N)]$, experience a Jahn–Teller distortion. The structure is a two-dimensional coordination network, with three crystallographically independent oxalate ions, two of them centrosymmetric, bridging Cu^{II} ions in three different coordination modes. Each Cu ion is also coordinated by methylamine which is involved in both intra- and interlayer hydrogen bonding.

Comment

The oxalate ligand is known for its chelating and bridging coordination modes. It is used by magnetochemists to mediate significant exchange interactions and can result in magnetically ordered materials (Coronado *et al.*, 2000; Decurtins *et al.*, 1993; Demunno *et al.*, 1995; Hursthouse *et al.*, 2004; Julve *et al.*, 1984; Keene *et al.*, 2004; Mathoniere *et al.*, 1996; Price *et al.*, 2001). We present here the structure of $[Cu(ox)(CH_3NH_2)]$ (ox = oxalate), (I).



(I)

The asymmetric unit of (I) contains two Cu atoms, two methylamine molecules, and one complete and two halves of oxalate anions (Fig. 1). The Cu^{II} cations each have a $CuNO_5$ coordination and show a large Jahn–Teller-induced tetragonal elongation. While the coordination environment of each Cu^{II} ion is very similar (Table 1), the coordination of the three oxalate ions differs significantly (Fig. 2). The structure of (I) is a complex two-dimensional coordination network that can best be viewed by initially considering only the short Cu—O/N contacts (<2.05 Å). The structure is built from two distinct copper oxalate chains. Chain *A* (Fig. 3) is formed from Cu1 and the oxalate containing C1 and C2; it consists of a simple

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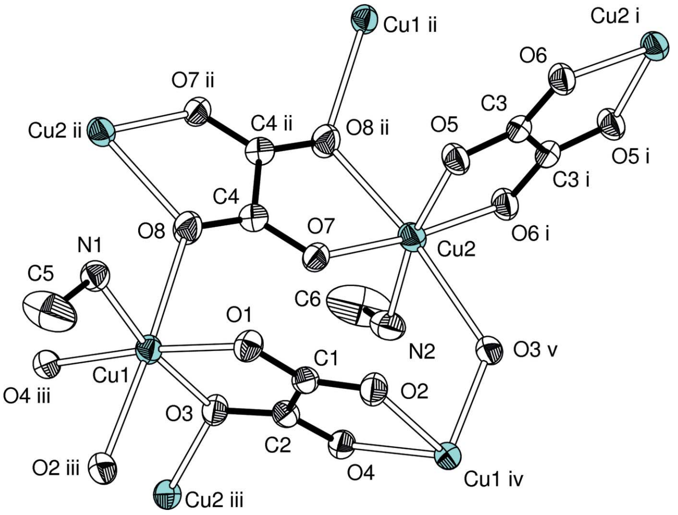

Figure 1

Fig. 1. The asymmetric unit of (I) and selected symmetry-equivalent atoms, showing the coordination of both metal ions and ligands. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, -y, 1 - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $x, \frac{1}{2} - y, -\frac{1}{2} + z$].

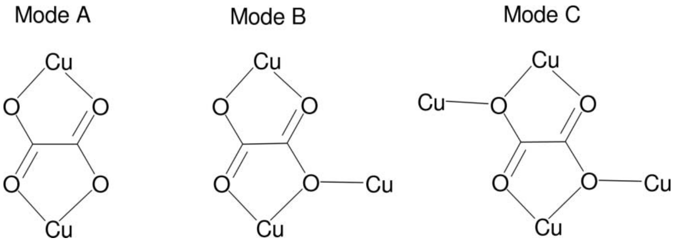

Figure 2

Schematic illustration of the three oxalate coordination modes seen in (I).

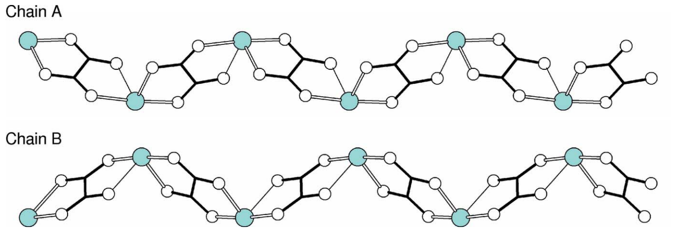

Figure 3

Two types of copper oxalate chain (*A* top and *B* bottom) from which the extended structure is built.

alternation of these components, with a |–Cu1–ox*B*|$_n$ repeat unit and a Cu···Cu separation of 5.530 (3) Å. Chain *B* (Fig. 3) is built from Cu2 and the crystallographically centrosymmetric oxalate anions containing C3 and C4. It has a more complex topology with a |–Cu2–ox*A*–Cu2–ox*C*–|$_n$ repeat unit and alternating Cu···Cu separations of 5.537 (9) and 5.192 (9) Å. The longer Cu—O interactions link neighbouring chains into a corrugated two-dimensional structure in the *bc* plane (Fig. 4). The coordinated methylamine displays both intra- and inter-layer hydrogen bonding (Table 2).

Surprisingly, there are very few structures that contain copper and either methyl- or ethylamine. Chemically, the most similar compound with a known structure is [Cu(NH$_3$)(ox)] (Cavalca *et al.*, 1972). Indeed, the structure of this compound shows remarkable similarity to that of (I). [Cu(NH$_3$)(ox)] also has a two-dimensional character, being built from Cu(ox) chains with the type *B* structure described above. Here, neighbouring chains are linked through the long Cu—O interactions into a two-dimensional sheet structure, with a topology that is different from that seen in (I).

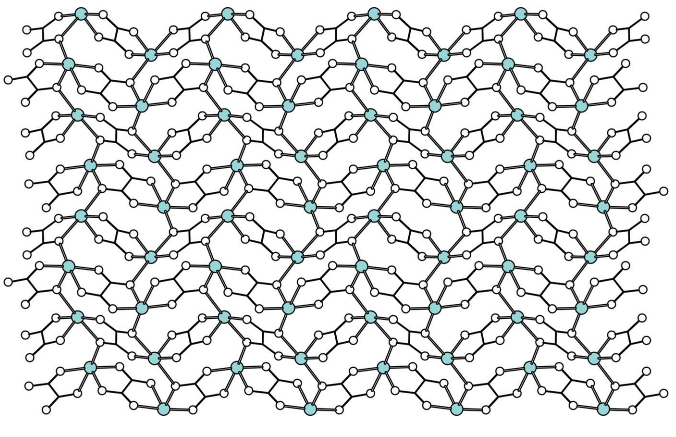

Figure 4

The complex two-dimensional Cu(ox) network, viewed along the *a* axis.

Experimental

Single crystals of (I) were synthesized by dissolving synthetic mooloolite, *viz*. [Cu(ox)]·0.33H$_2$O (1.000 g, 6.35 mmol), in an aqueous methylamine solution (20 ml, 40% *w*/*w*). The resultant dark-blue solution was further diluted with distilled water to a volume of 100 ml and left to evaporate. Blue crystals of (I) formed as a minor product amongst a large proportion of finely divided [Cu(ox)]·0.33H$_2$O.

Crystal data

[Cu(C$_2$O$_4$)(CH$_5$N)]
$M_r = 365.24$
Monoclinic, $P2_1/c$
$a = 9.421$ (8) Å
$b = 12.668$ (12) Å
$c = 9.392$ (7) Å
$\beta = 102.53$ (7)°
$V = 1094.1$ (16) Å^3
$Z = 4$
$D_x = 2.217$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.92$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.04 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.859$, $T_{\max} = 0.891$
11196 measured reflections
2525 independent reflections
1816 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.076$
$\theta_{\max} = 27.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.130$
$S = 1.08$
2525 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 2.4064P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.955 (4)	Cu2—O7	1.967 (4)
Cu1—N1	1.992 (5)	Cu2—N2	1.974 (5)
Cu1—O4^{i}	2.004 (4)	Cu2—O5	1.994 (4)
Cu1—O3	2.025 (4)	Cu2—O6^{ii}	2.002 (4)
Cu1—O2^{i}	2.307 (4)	Cu2—O8^{iii}	2.311 (4)
O1—Cu1—N1	91.98 (18)	O7—Cu2—N2	92.53 (19)
N1—Cu1—O4^{i}	91.02 (17)	O7—Cu2—O5	93.08 (16)
O1—Cu1—O3	83.91 (15)	N2—Cu2—O6^{ii}	90.85 (18)
O4^{i}—Cu1—O3	93.74 (15)	O5—Cu2—O6^{ii}	84.50 (16)
O1—Cu1—O2^{i}	97.03 (15)	O7—Cu2—O8^{iii}	78.20 (15)
N1—Cu1—O2^{i}	98.67 (18)	N2—Cu2—O8^{iii}	100.3 (2)
O4^{i}—Cu1—O2^{i}	78.06 (15)	O5—Cu2—O8^{iii}	89.80 (18)
O3—Cu1—O2^{i}	89.74 (16)	O6^{ii}—Cu2—O8^{iii}	95.65 (16)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{v}	0.9	2.22	3.042 (7)	153
N1—H1*B*···O6^{vi}	0.9	2.39	3.256 (7)	161
N2—H2*B*···O4	0.9	2.42	3.137 (7)	137

Symmetry codes: (v) $-x, -y, -z+1$; (vi) $x, y, z+1$.

H atoms were positioned geometrically, with N—H = 0.90 Å for amine H and C—H = 0.96 Å for methyl H atoms, and were constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = $xU_{\rm eq}$(C,N), where x = 1.2 for amine H and x = 1.5 for methyl H atoms.

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: *SIR92* (Altomare *et al.*, 1993) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999).

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supporting information

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Crystal data

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Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.421 (8) Å
b = 12.668 (12) Å
c = 9.392 (7) Å
β = 102.53 (7)°
V = 1094.1 (16) Å^3
Z = 4
$F(000)$ = 728
D_x = 2.217 Mg m^{-3}
Melting point: N/A K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3698 reflections
θ = 2.9–27.5°
μ = 3.92 mm^{-1}
T = 566 K
Block, blue
0.04 × 0.03 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
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11196 measured reflections
2525 independent reflections
1816 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 27.7°, θ_{min} = 3.2°
$h = -10 \rightarrow 12$
$k = -16 \rightarrow 14$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.130
S = 1.08
2525 reflections
163 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 2.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 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.

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

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.19173 (7)	0.14720 (5)	0.67560 (7)	0.0302 (2)

Cu2	0.49291 (8)	0.10215 (6)	0.23795 (7)	0.0328 (2)
O1	0.0744 (4)	0.1432 (3)	0.4765 (4)	0.0332 (9)
O2	0.0588 (4)	0.2250 (3)	0.2635 (4)	0.0368 (9)
O3	0.3028 (4)	0.2615 (3)	0.5955 (4)	0.0318 (9)
O4	0.3051 (4)	0.3347 (3)	0.3809 (4)	0.0308 (9)
O5	0.3811 (4)	−0.0131 (3)	0.1192 (4)	0.0347 (9)
O6	0.3845 (4)	−0.0980 (3)	−0.0886 (4)	0.0347 (9)
O7	0.3817 (4)	0.0902 (3)	0.3919 (4)	0.0346 (9)
O8	0.3739 (4)	0.0225 (3)	0.6094 (4)	0.0414 (10)
N1	0.0929 (5)	0.0199 (4)	0.7323 (5)	0.0349 (11)
H1A	0.0647	−0.0205	0.6523	0.042*
H1B	0.159	−0.0174	0.7963	0.042*
N2	0.5906 (5)	0.2327 (4)	0.3227 (5)	0.0410 (12)
H2A	0.5823	0.2806	0.2506	0.049*
H2B	0.5412	0.2579	0.3873	0.049*
C1	0.1168 (6)	0.2084 (4)	0.3928 (6)	0.0278 (11)
C2	0.2527 (6)	0.2730 (4)	0.4620 (6)	0.0289 (12)
C3	0.4327 (6)	−0.0315 (4)	0.0094 (6)	0.0288 (12)
C4	0.4293 (6)	0.0320 (4)	0.5010 (6)	0.0312 (12)
C5	−0.0350 (9)	0.0366 (7)	0.7974 (10)	0.082 (3)
H5A	−0.0722	−0.0305	0.8199	0.123*
H5B	−0.109	0.0737	0.7293	0.123*
H5C	−0.0069	0.0774	0.8851	0.123*
C6	0.7426 (9)	0.2267 (7)	0.3953 (11)	0.091 (3)
H6A	0.7761	0.2954	0.4308	0.137*
H6B	0.7985	0.2025	0.3275	0.137*
H6C	0.754	0.1783	0.4756	0.137*

Atomic displacement parameters (Å^{2})

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0351 (4)	0.0295 (4)	0.0264 (4)	−0.0041 (3)	0.0077 (3)	0.0003 (3)
Cu2	0.0383 (4)	0.0320 (4)	0.0306 (4)	−0.0011 (3)	0.0132 (3)	−0.0022 (3)
O1	0.032 (2)	0.033 (2)	0.033 (2)	−0.0071 (18)	0.0063 (16)	0.0037 (16)
O2	0.042 (2)	0.039 (2)	0.028 (2)	−0.0024 (19)	0.0053 (17)	0.0027 (17)
O3	0.037 (2)	0.033 (2)	0.025 (2)	−0.0045 (17)	0.0043 (16)	0.0024 (16)
O4	0.034 (2)	0.030 (2)	0.027 (2)	−0.0002 (16)	0.0045 (16)	0.0014 (15)
O5	0.041 (2)	0.037 (2)	0.030 (2)	−0.0049 (19)	0.0163 (17)	−0.0047 (17)
O6	0.042 (2)	0.036 (2)	0.028 (2)	−0.0060 (18)	0.0129 (17)	−0.0022 (17)
O7	0.041 (2)	0.035 (2)	0.030 (2)	0.0112 (18)	0.0115 (17)	0.0070 (16)
O8	0.046 (3)	0.046 (2)	0.037 (2)	0.013 (2)	0.0203 (19)	0.0100 (19)
N1	0.040 (3)	0.033 (3)	0.032 (2)	−0.005 (2)	0.009 (2)	0.000 (2)
N2	0.045 (3)	0.033 (3)	0.047 (3)	−0.002 (2)	0.015 (2)	−0.007 (2)
C1	0.029 (3)	0.027 (3)	0.029 (3)	0.001 (2)	0.010 (2)	0.001 (2)
C2	0.031 (3)	0.029 (3)	0.029 (3)	0.003 (2)	0.011 (2)	0.000 (2)
C3	0.034 (3)	0.027 (3)	0.025 (3)	0.003 (2)	0.007 (2)	0.005 (2)
C4	0.033 (3)	0.029 (3)	0.032 (3)	0.001 (2)	0.007 (2)	0.000 (2)
C5	0.091 (6)	0.059 (5)	0.119 (7)	−0.023 (5)	0.071 (6)	−0.024 (5)

C6	0.041 (5)	0.076 (6)	0.150 (9)	−0.003 (4)	0.004 (5)	−0.044 (6)

Geometric parameters (Å, º)

Cu1—O1	1.955 (4)	C1—O1	1.264 (6)
Cu1—N1	1.992 (5)	C2—O3	1.249 (6)
Cu1—O4^{i}	2.004 (4)	C2—O4	1.265 (6)
Cu1—O3	2.025 (4)	C2—C1	1.539 (8)
Cu1—O2^{i}	2.307 (4)	C3—O5	1.254 (6)
Cu2—O7	1.967 (4)	C3—O6	1.258 (6)
Cu2—N2	1.974 (5)	C3—C3^{ii}	1.541 (11)
Cu2—O5	1.994 (4)	C4—O8	1.247 (6)
Cu2—O6^{ii}	2.002 (4)	C4—O7	1.262 (6)
Cu2—O8^{iii}	2.311 (4)	C4—C4^{iii}	1.564 (11)
O2—Cu1^{iv}	2.307 (4)	C5—N1	1.480 (9)
O4—Cu1^{iv}	2.004 (4)	C5—H5A	0.96
O6—Cu2^{ii}	2.002 (4)	C5—H5B	0.96
O8—Cu2^{iii}	2.311 (4)	C5—H5C	0.96
N1—H1A	0.9	C6—N2	1.448 (9)
N1—H1B	0.9	C6—H6A	0.96
N2—H2A	0.9	C6—H6B	0.96
N2—H2B	0.9	C6—H6C	0.96
C1—O2	1.237 (6)		
O1—Cu1—N1	91.98 (18)	Cu1—N1—H1B	107.9
O1—Cu1—O4^{i}	174.59 (16)	H1A—N1—H1B	107.2
N1—Cu1—O4^{i}	91.02 (17)	C6—N2—Cu2	118.2 (5)
O1—Cu1—O3	83.91 (15)	C6—N2—H2A	107.8
N1—Cu1—O3	171.04 (17)	Cu2—N2—H2A	107.8
O4^{i}—Cu1—O3	93.74 (15)	C6—N2—H2B	107.8
O1—Cu1—O2^{i}	97.03 (15)	Cu2—N2—H2B	107.8
N1—Cu1—O2^{i}	98.67 (18)	H2A—N2—H2B	107.1
O4^{i}—Cu1—O2^{i}	78.06 (15)	O2—C1—O1	126.1 (5)
O3—Cu1—O2^{i}	89.74 (16)	O2—C1—C2	118.3 (5)
O7—Cu2—N2	92.53 (19)	O1—C1—C2	115.5 (5)
O7—Cu2—O5	93.08 (16)	O3—C2—O4	124.4 (5)
N2—Cu2—O5	169.25 (19)	O3—C2—C1	117.5 (5)
O7—Cu2—O6^{ii}	173.43 (16)	O4—C2—C1	118.2 (5)
N2—Cu2—O6^{ii}	90.85 (18)	O5—C3—O6	125.7 (5)
O5—Cu2—O6^{ii}	84.50 (16)	O5—C3—C3^{ii}	118.3 (6)
O7—Cu2—O8^{iii}	78.20 (15)	O6—C3—C3^{ii}	116.0 (6)
N2—Cu2—O8^{iii}	100.3 (2)	O8—C4—O7	125.5 (5)
O5—Cu2—O8^{iii}	89.80 (18)	O8—C4—C4^{iii}	117.9 (6)
O6^{ii}—Cu2—O8^{iii}	95.65 (16)	O7—C4—C4^{iii}	116.5 (6)
C1—O1—Cu1	112.9 (3)	N1—C5—H5A	109.5
C1—O2—Cu1^{iv}	108.2 (3)	N1—C5—H5B	109.5
C2—O3—Cu1	110.0 (3)	H5A—C5—H5B	109.5
C2—O4—Cu1^{iv}	117.0 (3)	N1—C5—H5C	109.5

C3—O5—Cu2	110.1 (3)	H5A—C5—H5C	109.5
C3—O6—Cu2^{ii}	111.0 (3)	H5B—C5—H5C	109.5
C4—O7—Cu2	119.3 (4)	N2—C6—H6A	109.5
C4—O8—Cu2^{iii}	107.8 (3)	N2—C6—H6B	109.5
C5—N1—Cu1	117.7 (4)	H6A—C6—H6B	109.5
C5—N1—H1A	107.9	N2—C6—H6C	109.5
Cu1—N1—H1A	107.9	H6A—C6—H6C	109.5
C5—N1—H1B	107.9	H6B—C6—H6C	109.5

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1^{v}	0.9	2.22	3.042 (7)	153
N1—H1*B*···O6^{vi}	0.9	2.39	3.256 (7)	161
N2—H2*B*···O4	0.9	2.42	3.137 (7)	137

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