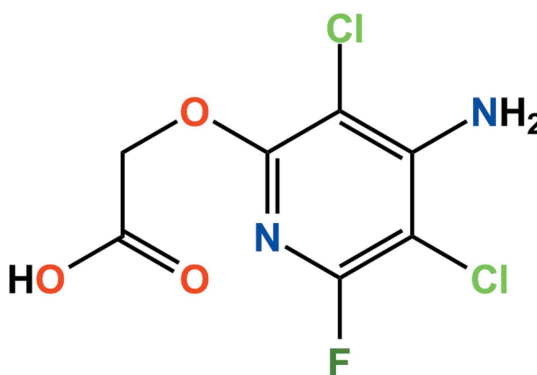# Crystal structure of fluroxypyr

Hyunjin Park, Myong Yong Choi,* Eunjin Kwon and Tae Ho Kim*

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In the title pyridine herbicide {systematic name: 2-[(4-amino-3,5-dichloro-6-fluoropyridin-2-yl)oxy]acetic acid}, $C_7H_5Cl_2FN_2O_3$, the mean plane of the carboxylic acid substituent and the pyridyl ring plane subtend a dihedral angle of 77.5 (1)°. In the crystal, pairs of O—H···O hydrogen bonds form inversion dimers with $R_2^2(8)$ ring motifs. These are extended into chains along [011] by N—H···F hydrogen bonds. In addition, intermolecular N—H···O hydrogen bonds and weak π–π interactions [ring centroid separation = 3.4602 (9) Å] connect these chains into a three-dimensional network.

1. Chemical context

Fluroxypyr belongs to the pyridine family of herbicides. It is widely used on cereal crops, olive trees and fallow croplands to control broad-leaf weeds (Moreno-Castilla *et al.*, 2012; Wang *et al.*, 2011). Pyridine herbicides such as fluroxypyr are effective and popular chemicals for post-emergence broad-leaf weed control, particularly in turf during cool seasons. The efficacy of this herbicide may be affected by environmental conditions including the relative humidity, temperature and soil moisture. Because of this, its application often provides inconsistent broad-leaf weed control in winter or early spring (Reed & McCullough, 2012). Until now, its crystal structure had not been reported and we describe it herein.

2. Structural commentary

The structure of fluroxypyr is shown in Fig. 1. The dihedral angle between the mean plane of the carboxylic acid group (C6/C7/O2/O3) and the pyridyl ring (N1/C1–C5) is 77.5 (1)°. All bond lengths and bond angles are normal and comparable to those observed in the crystal structure of a related pyridine-containing herbicide (Cho *et al.*, 2015).
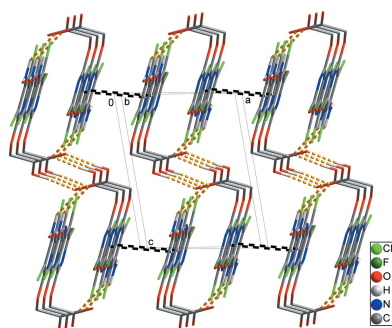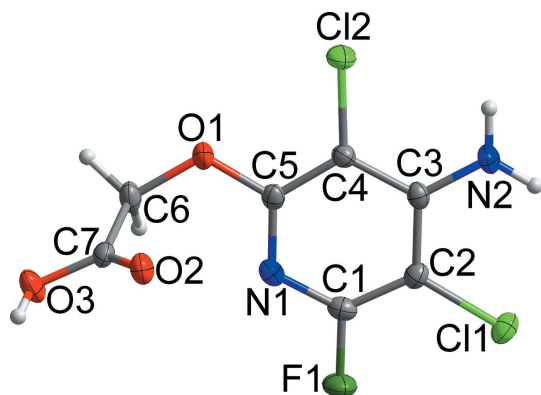
Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

3. Supramolecular features

In the crystal, the solid-state structure is stabilized by pairs of N2—H2B⋯O2 hydrogen bonds, forming inversion dimers with $R_2^2(18)$ ring motifs (Table 1 and Fig. 2). These dimers are linked by pairs of O3—H3⋯O2^i/O2 hydrogen bonds that form classical carboxylic-acid-based inversion dimers with $R_2^2(8)$ ring motifs. These contacts form chains propagating along [011] (yellow dashed lines in Fig. 2). In addition, intermolecular N2—H2A⋯F1 hydrogen bonds connect these chains, yielding sheets extending parallel to the bc plane (red dashed line in Fig. 3). These sheets are further linked by weak intermolecular π–π interactions between the pyridyl rings (N1/C1–C5) [$Cg1$⋯$Cg1^{iv}$ = 3.4602 (9) Å; symmetry code: (iv) $-x, -y + 2, -z$], resulting in a three-dimensional network structure (black dashed lines in Fig. 4).
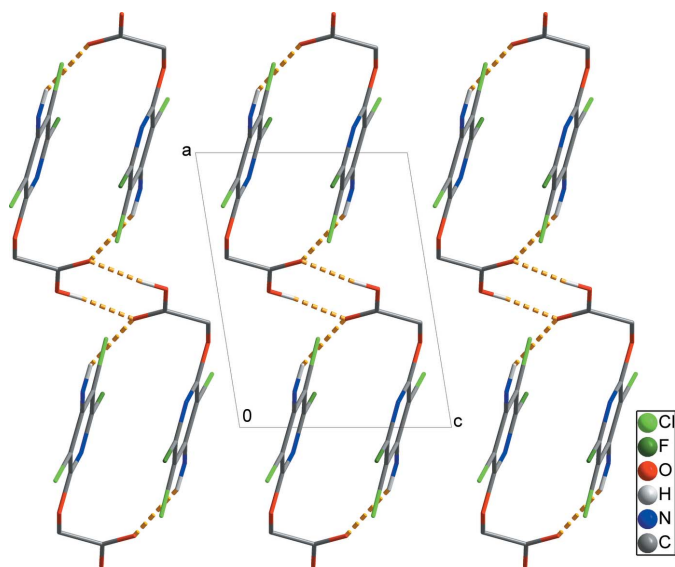
Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O2^i	0.84	1.84	2.6801 (15)	174
N2—H2A⋯F1^{ii}	0.88	2.39	2.9950 (15)	126
N2—H2B⋯O2^{iii}	0.88	2.25	3.0201 (16)	146

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y + 2, -z$.

4. Database survey

We have reported the crystal structure of several pesticides including compounds with pyridine rings (Cho *et al.*, 2015; Kang *et al.*, 2015; Kwon *et al.*, 2016; Park *et al.*, 2016). In addition, a database search (CSD; Groom *et al.*, 2006) yielded
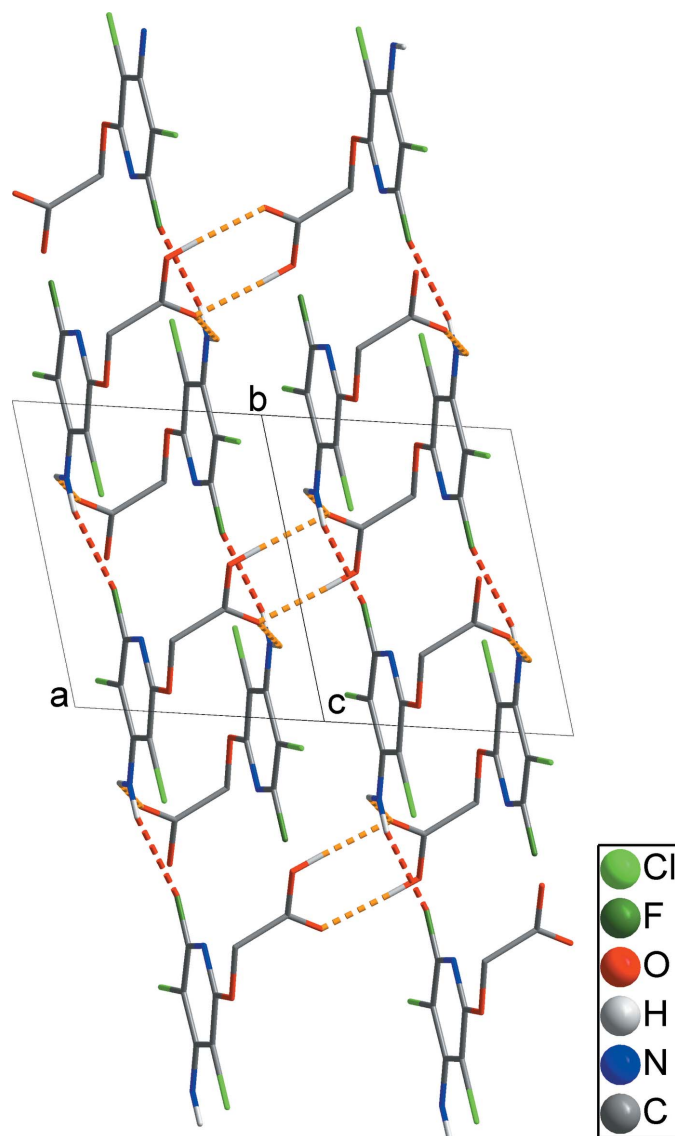
Figure 3
The two-dimensional network formed through intermolecular N—H⋯F hydrogen bonds (red dashed lines). Intermolecular O/N–H⋯O hydrogen bonds within a chain are shown as yellow dashed lines. H atoms not involved in these interactions have been omitted for clarity.

Figure 2
A view along the b axis of the crystal packing of the title compound. The chains are formed through intermolecular O—H⋯O and N—H⋯O hydrogen bonds (yellow dashed lines). H atoms not involved in these interactions have been omitted for clarity.
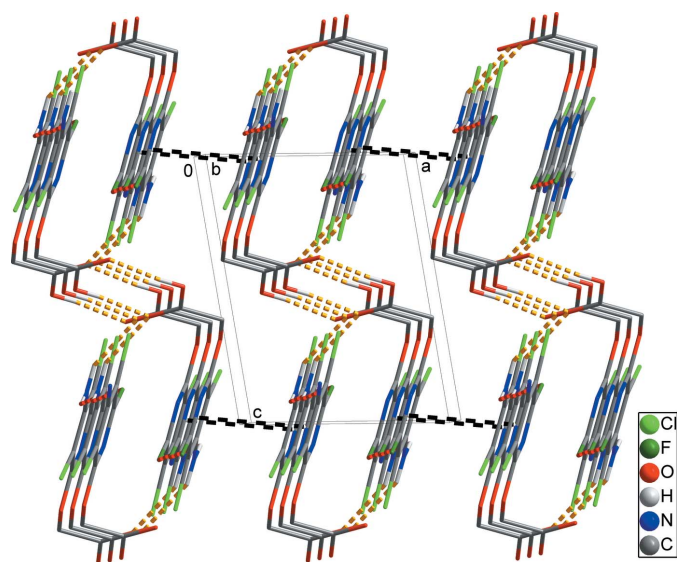
Figure 4
A packing diagram showing the three-dimensional architecture formed by weak π–π interactions (black dashed lines). Intermolecular O—H···O, N—H···O and N—H···F hydrogen bonds within a sheet are shown as yellow and red dashed lines. H atoms not involved in intermolecular interactions have been omitted for clarity.

two other comparable structures, 2-[(3,5,6-trichloropyridin-2-yl)oxy]acetic acid (Cho *et al.*, 2014) and 2,4,5-trichlorophenoxyacetic acid (Smith *et al.*, 1976).

5. Synthesis and crystallization

The title compound was purchased from Dr. Ehrenstorfer GmbH. Colorless single crystals suitable for X-ray diffraction were obtained from a CH_3CN solution by slow evaporation at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and refined using a riding model with d(O—H) = 0.84 Å, $U_{iso} = 1.5U_{eq}$(C) for the O—H group, d(N—H) = 0.88 Å, $U_{iso} = 1.2U_{eq}$(C) for the amine group, and d(C—H) = 0.99 Å, $U_{iso} = 1.2U_{eq}$(C) for the CH_2 group.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_5Cl_2FN_2O_3$
M_r	255.03
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	7.1116 (9), 7.6131 (9), 8.9414 (11)
α, β, γ (°)	86.927 (6), 80.354 (6), 72.587 (5)
V (Å^3)	455.38 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.72
Crystal size (mm)	$0.23 \times 0.22 \times 0.04$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.690, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8052, 2092, 1972
R_{int}	0.023
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.076, 1.12
No. of reflections	2092
No. of parameters	137
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.38

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2010).

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Crystal structure of fluroxypyr

Hyunjin Park, Myong Yong Choi, Eunjin Kwon and Tae Ho Kim

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

2-[(4-Amino-3,5-dichloro-6-fluoropyridin-2-yl)oxy]acetic acid

Crystal data

$C_7H_5Cl_2FN_2O_3$	$Z = 2$
$M_r = 255.03$	$F(000) = 256$
Triclinic, $P\overline{1}$	$D_x = 1.860$ Mg m^{-3}
$a = 7.1116$ (9) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.6131$ (9) Å	Cell parameters from 6070 reflections
$c = 8.9414$ (11) Å	$\theta = 2.8$–27.5°
$\alpha = 86.927$ (6)°	$\mu = 0.72$ mm^{-1}
$\beta = 80.354$ (6)°	$T = 173$ K
$\gamma = 72.587$ (5)°	Plate, colourless
$V = 455.38$ (10) Å^3	$0.23 \times 0.22 \times 0.04$ mm

Data collection

Bruker APEXII CCD diffractometer	2092 independent reflections
φ and ω scans	1972 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$R_{int} = 0.023$
	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$T_{min} = 0.690$, $T_{max} = 0.746$	$h = -9\rightarrow8$
8052 measured reflections	$k = -9\rightarrow9$
	$l = -10\rightarrow11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.2062P]$
$wR(F^2) = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} < 0.001$
2092 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
137 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
0 restraints	

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.43701 (6)	0.90760 (5)	−0.32138 (4)	0.02990 (12)
Cl2	0.09018 (6)	1.29195 (5)	0.19394 (4)	0.02692 (11)
F1	0.37852 (14)	0.60390 (12)	−0.12163 (11)	0.0298 (2)
O1	0.08333 (16)	0.93076 (14)	0.31061 (11)	0.0234 (2)
O2	0.41952 (15)	0.68493 (14)	0.39455 (11)	0.0225 (2)
O3	0.24193 (16)	0.50096 (15)	0.50373 (13)	0.0278 (2)
H3	0.3515	0.4408	0.5295	0.042*
N1	0.23296 (18)	0.76320 (16)	0.09169 (14)	0.0202 (2)
N2	0.2865 (2)	1.24580 (17)	−0.12976 (14)	0.0244 (3)
H2A	0.2414	1.3515	−0.0813	0.029*
H2B	0.3429	1.2417	−0.2255	0.029*
C1	0.3133 (2)	0.76709 (19)	−0.05118 (17)	0.0202 (3)
C2	0.3356 (2)	0.91926 (19)	−0.13244 (15)	0.0192 (3)
C3	0.26931 (19)	1.08983 (18)	−0.05718 (15)	0.0177 (3)
C4	0.1811 (2)	1.08826 (18)	0.09480 (15)	0.0176 (3)
C5	0.16793 (19)	0.92352 (19)	0.16331 (15)	0.0178 (3)
C6	0.0683 (2)	0.7624 (2)	0.38160 (17)	0.0242 (3)
H6A	0.0248	0.6917	0.3114	0.029*
H6B	−0.0345	0.7900	0.4736	0.029*
C7	0.2634 (2)	0.64680 (19)	0.42518 (15)	0.0197 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0345 (2)	0.0351 (2)	0.01671 (18)	−0.00767 (16)	0.00124 (14)	−0.00224 (14)
Cl2	0.0359 (2)	0.01784 (17)	0.02395 (19)	−0.00397 (14)	−0.00232 (14)	−0.00355 (13)
F1	0.0372 (5)	0.0182 (4)	0.0318 (5)	−0.0048 (4)	−0.0035 (4)	−0.0076 (4)
O1	0.0270 (5)	0.0214 (5)	0.0177 (5)	−0.0044 (4)	0.0008 (4)	0.0058 (4)
O2	0.0245 (5)	0.0241 (5)	0.0208 (5)	−0.0101 (4)	−0.0048 (4)	0.0060 (4)
O3	0.0243 (5)	0.0232 (5)	0.0355 (6)	−0.0081 (4)	−0.0051 (5)	0.0130 (4)
N1	0.0209 (6)	0.0169 (5)	0.0232 (6)	−0.0058 (4)	−0.0055 (5)	0.0035 (4)
N2	0.0318 (7)	0.0200 (6)	0.0216 (6)	−0.0103 (5)	−0.0013 (5)	0.0055 (5)
C1	0.0195 (6)	0.0167 (6)	0.0242 (7)	−0.0035 (5)	−0.0058 (5)	−0.0025 (5)
C2	0.0190 (6)	0.0226 (7)	0.0158 (6)	−0.0060 (5)	−0.0025 (5)	−0.0002 (5)
C3	0.0170 (6)	0.0189 (6)	0.0183 (6)	−0.0065 (5)	−0.0053 (5)	0.0037 (5)
C4	0.0186 (6)	0.0155 (6)	0.0181 (6)	−0.0038 (5)	−0.0035 (5)	0.0002 (5)
C5	0.0150 (6)	0.0200 (6)	0.0173 (6)	−0.0036 (5)	−0.0037 (5)	0.0033 (5)
C6	0.0236 (7)	0.0258 (7)	0.0218 (7)	−0.0081 (6)	−0.0014 (5)	0.0090 (6)
C7	0.0252 (7)	0.0202 (6)	0.0132 (6)	−0.0073 (5)	−0.0005 (5)	0.0007 (5)

Geometric parameters (Å, º)

Cl1—C2	1.7181 (14)	N2—C3	1.3506 (17)
Cl2—C4	1.7216 (14)	N2—H2A	0.8800
F1—C1	1.3403 (16)	N2—H2B	0.8800
O1—C5	1.3499 (17)	C1—C2	1.370 (2)
O1—C6	1.4243 (17)	C2—C3	1.4080 (19)
O2—C7	1.2143 (17)	C3—C4	1.3990 (19)
O3—C7	1.3158 (17)	C4—C5	1.3877 (19)
O3—H3	0.8400	C6—C7	1.505 (2)
N1—C1	1.3117 (19)	C6—H6A	0.9900
N1—C5	1.3268 (18)	C6—H6B	0.9900
C5—O1—C6	117.32 (11)	C5—C4—C3	119.78 (12)
C7—O3—H3	109.5	C5—C4—Cl2	121.01 (11)
C1—N1—C5	116.03 (12)	C3—C4—Cl2	119.20 (10)
C3—N2—H2A	120.0	N1—C5—O1	119.54 (12)
C3—N2—H2B	120.0	N1—C5—C4	123.51 (13)
H2A—N2—H2B	120.0	O1—C5—C4	116.96 (12)
N1—C1—F1	115.22 (12)	O1—C6—C7	112.12 (12)
N1—C1—C2	126.49 (13)	O1—C6—H6A	109.2
F1—C1—C2	118.29 (13)	C7—C6—H6A	109.2
C1—C2—C3	118.00 (13)	O1—C6—H6B	109.2
C1—C2—Cl1	122.11 (11)	C7—C6—H6B	109.2
C3—C2—Cl1	119.88 (10)	H6A—C6—H6B	107.9
N2—C3—C4	122.43 (12)	O2—C7—O3	124.35 (13)
N2—C3—C2	121.39 (12)	O2—C7—C6	124.46 (13)
C4—C3—C2	116.17 (12)	O3—C7—C6	111.18 (12)
C5—N1—C1—F1	179.85 (11)	C2—C3—C4—Cl2	−178.35 (10)
C5—N1—C1—C2	−0.2 (2)	C1—N1—C5—O1	179.97 (12)
N1—C1—C2—C3	0.9 (2)	C1—N1—C5—C4	0.1 (2)
F1—C1—C2—C3	−179.10 (12)	C6—O1—C5—N1	−0.13 (18)
N1—C1—C2—Cl1	−178.05 (11)	C6—O1—C5—C4	179.71 (12)
F1—C1—C2—Cl1	1.94 (19)	C3—C4—C5—N1	−0.9 (2)
C1—C2—C3—N2	179.92 (13)	Cl2—C4—C5—N1	179.01 (10)
Cl1—C2—C3—N2	−1.09 (18)	C3—C4—C5—O1	179.27 (11)
C1—C2—C3—C4	−1.55 (19)	Cl2—C4—C5—O1	−0.82 (17)
Cl1—C2—C3—C4	177.43 (10)	C5—O1—C6—C7	78.48 (15)
N2—C3—C4—C5	−179.93 (12)	O1—C6—C7—O2	−4.9 (2)
C2—C3—C4—C5	1.56 (19)	O1—C6—C7—O3	173.75 (12)
N2—C3—C4—Cl2	0.16 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2[i]	0.84	1.84	2.6801 (15)	174

N2—H2*A*⋯F1[ii]	0.88	2.39	2.9950 (15)	126
N2—H2*B*⋯O2[iii]	0.88	2.25	3.0201 (16)	146

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