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catena-Poly[[bis[1-(2-hydroxyethyl)-1*H*-tetrazole-κN^4]copper(II)]-di-μ-chlorido]: a powder study

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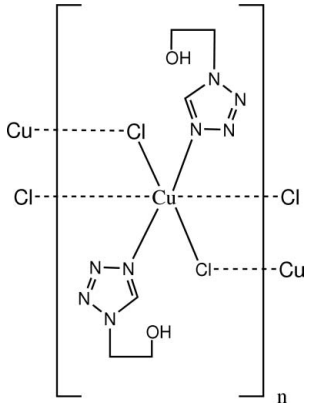
Key indicators: powder X-ray study; T = 295 K; mean σ(Cu–N) = 0.010 Å; disorder in main residue; R factor = 0.042; wR factor = 0.067.

The crystal structure of the title polymeric complex, $[CuCl_2(C_3H_6N_4O)_2]_n$, was obtained by the Rietveld refinement from laboratory X-ray powder diffraction data collected at room temperature. The unique Cu^{II} ion lies on an inversion center and is in a slightly distorted octahedral coordination environment. In the hydroxyethyl group, all H atoms, the O atom and its attached C atom are disordered over two positions; the site occupancy factors are *ca* 0.6 and 0.4. The OH group is involved in an intramolecular O—H···N hydrogen bond.

Related literature

For related literature, see: Ivashkevich *et al.* (2001); Ivashkevich, Lyakhov *et al.* (2005); Ivashkevich, Voitekhovich & Lyakhov (2005); Stassen *et al.* (2002); Werner *et al.* (1985); Allen (2002); Virovets *et al.* (1995, 1996).



Experimental

Crystal data

$[CuCl_2(C_3H_6N_4O)_2]$
M_r = 362.69
Monoclinic, $P2_1/c$
a = 13.3349 (11) Å
b = 6.7406 (6) Å
c = 7.3419 (5) Å
β = 105.450 (8)°
V = 636.08 (9) Å^3
Z = 2
Cu $K\alpha$ radiation
T = 295 (2) K
Specimen shape: flat sheet
30 × 30 × 1 mm
Specimen prepared at 100 kPa
Specimen prepared at 295(2) K
Particle morphology: plate, green

Data collection

HZG-4A (Carl Zeiss, Jena) diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
Scan method: step
$2\theta_{min}$ = 5.0, $2\theta_{max}$ = 100.0°
Increment in 2θ = 0.02°

Refinement

R_p = 0.042
R_{wp} = 0.067
R_{exp} = 0.086
R_B = 0.029
S = 0.78
Wavelength of incident radiation: 1.5418 Å
Excluded region(s): none
Profile function: pseudo-Voigt
785 reflections
48 parameters
21 restraints
H-atom parameters constrained
Preferred orientation correction: Marsh–Dollase function (Marsh, 1932; Dollase, 1986)

Table 1
Selected geometric parameters (Å, °).

Cu—Cl	2.234 (7)	Cu—Cl^{i}	3.008 (7)
Cu—N4	1.979 (10)	Cu—Cu^{ii}	4.9835 (4)
Cl—Cu—N4	89.8 (7)	Cl^{i}—Cu—N4	92.6 (5)
Cl—Cu—Cl^{i}	90.8 (2)	N4—Cu—N4^{iii}	180
Cl—Cu—Cl^{iii}	180	Cl^{iv}—Cu—N4	87.4 (5)
Cl—Cu—N4^{iii}	90.2 (7)	Cu—Cl—Cu^{ii}	143.5 (2)
Cl—Cu—Cl^{iv}	89.2 (2)		

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, -y, -z+1$; (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
O1—H1···N2	0.82	2.35	3.08 (3)	149
O2—H2···N2	0.82	2.46	3.02 (3)	126
C5—H5···Cl^{ii}	0.93	2.72	3.34 (2)	126

Symmetry code: (ii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: local program; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: local program; program(s) used to refine structure: *FULLPROF* and *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *FULLPROF* and *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2648).

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supporting information

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catena-Poly[[bis[1-(2-hydroxyethyl)-1*H*-tetrazole-κN^4]copper(II)]-di-μ-chlorido]: a powder study

Ludmila S. Ivashkevich, Alexander S. Lyakhov, Tatiyana V. Serebryanskaya and Pavel N. Gaponik

S1. Comment

Complexes of copper(II) chloride with substituted tetrazoles attract attention because of their magnetic bahaviour at low temperatures. Among them, there are layered coordination polymers with square grids of only Cu and Cl atoms, of the composition $CuCl_2L_2$, where L = 1-ethyltetrazole (Virovets *et al.*, 1995), 1-allyltetrazole (Virovets *et al.*, 1996), 1-(2-azidoethyl)terazole (Ivashkevich *et al.*, 2001), 1-(2-chloroethyl)tetrazole (Stassen *et al.*, 2002), 1-benzyltetrazole (Ivashkevich, Voitekhovich & Lyakhov, 2005), and 1-methyltetrazole (Ivashkevich, Lyakhov, Ivashkevich, Degtyarik & Gaponik, 2005). These compounds crystallize in the space group $P2_1/c$ and are isotypic. Here, we present another example, poly[[bis(1-(2-hydroxyethyl)tetrazole-N^4)copper(II)]-di-μ-chloro], (I), (Fig. 1). As it is difficult to obtain single crystals for structural analysis, the compound (I) was investigated by X-ray powder diffraction.

The Cu atom lies on inversion center and shows a slightly distorted octahedral coordination environment. Equatorial sites are occupied by two *trans* positioned N atoms and two Cl atoms; Cl atoms lying in axial positions are essentially more distant from the Cu atom (Table 1). Each Cl atom is a bridge between the neighbouring Cu atoms, forming two different in length Cu—Cl bonds, with Cu—Cl—Cu angle of 143.4 (2)°. These bonds are responsible for the formation of polymeric layers parallel to the yz plane (Fig. 2). Within a layer, the shortest Cu···Cu distance is 4.9835 (4) Å, whereas between two neighbouring layers, the closest Cu centers are separated by cell dimension a. Only van der Waals interactions are between the layers.

The 2-hydroxyethyl substituent at the tetrazole ring atom N1 was found to be disordered over two positions, with almost equal occupancies of 0.562 (12) for C71—O1 and 0.438 (12) for C72—O2 (Fig. 1). For both positions, OH groups are involved in intramolecular hydrogen bonds O—H···N. There are also hydrogen bonds C—H···Cl (Table 2).

S2. Experimental

A solution, containing 2.13 g (0.0125 mol) of $CuCl_2.2H_2O$ in 75 ml of ethanol, was added to a slightly heated solution of 1-(2-hydroxyethyl)tetrazole (2.85 g, 0.025 mol) in a solvent mixture (45 ml of ethanol and 30 ml of n-buthanol), with stirring at room temperature. After stirring the reaction mixture for 10 min, the obtained green crystals of (I) were filtered off, air dried and recrystallized from (ethanol—n-buthanol) mixture (v/v = 4:1) [3.55 g, yield 78.3%]. Calc.(%): Cu 17.52, Cl 19.59. Found (%): Cu 18.2, Cl 20.1.

S3. Refinement

The monoclinic unit-cell dimensions of (I) were determined with the indexing program TREOR90 (Werner *et al.*, 1985). The obtained values indicated isotypism of (I) with layered coordination polymers $CuCl_2L_2$ (L = 1-alkyltetrazole) that crystallize in the monoclinic space group $P2_1/c$. This space group and the atomic coordinates of $CuCl_2L_2$ with L = 1-ethyl-tetrazole (Virovets *et al.*, 1995) were used as starting parameters for the Rietveld refinement with the FULLPROF

program (Rodríguez-Carvajal, 2001). Background intensity was found by Fourier filtering technique as implemented in the FULLPROF program, under visual inspection of the resulting background curve. Correction for profile asymmetry was made for reflections up to 2θ=30°. A Marsh-Dollase correction of intensities for [100] preferred orientation of plate-like grains in the sample (Marsh, 1932; Dollase, 1986) was applied.

The Rietveld refinement, performed primarily by using individual isotropic displacement parameters for non-H atoms, revealed rather high values of B_{iso} for atoms of C—O fragment. From this fact an assumption was made that C—O fragment was disordered over two positions. It was confirmed in subsequent refinement by introducing disorder positions for the above C and O atoms. In final refinement, all non-H atoms were refined with overall B_{iso} parameter.

All H atoms were placed in geometrically calculated positions, using the program *SHELXL97* (Sheldrick, 2008), with displacement parameter $B_{iso}(H)=1.2B_{iso}(C)$ for H atom at C5 tetrazole ring atom and $B_{iso}(H)=1.5B_{iso}(C,O)$ for the methylene and hydroxyl groups.

Soft restraints on some interatomic distances and bond angles of ligand molecule, based on a geometric analysis of a large number of 1-substituted tetrazoles (Cambridge Structural Database, version 5.29 of November 2007; Allen, 2002), were used in the Rietved refinement. Observed, calculated and difference difraction patterns are shown in Fig. 3.

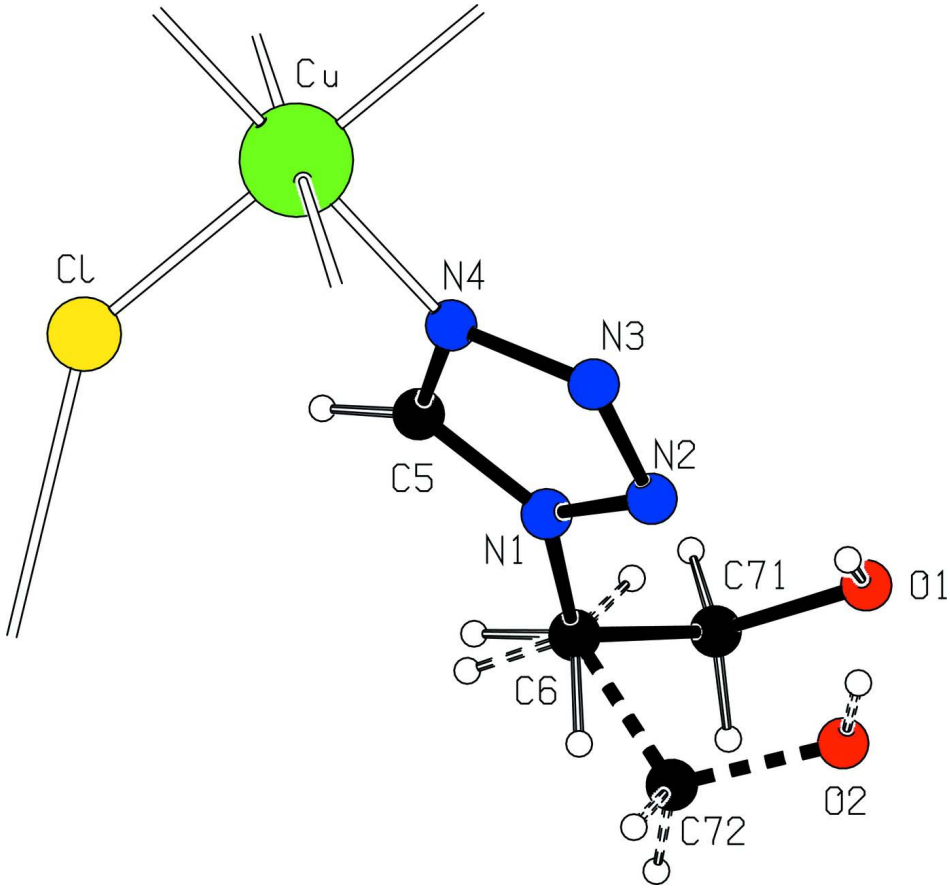

Figure 1

The asymmetric unit of (I) with the atomic numbering scheme. 2-hydroxyethyl substituent is shown as disordered over two positions.

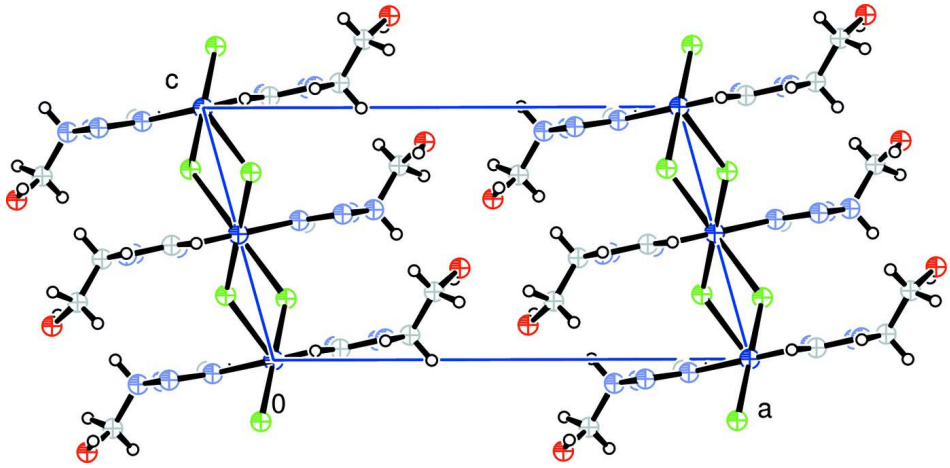

Figure 2

Layered structure of (I), viewed along the *b* axis. Disordered 2-hydroxyethyl substituent is shown only in position with occupancy factor of 0.562 (12).

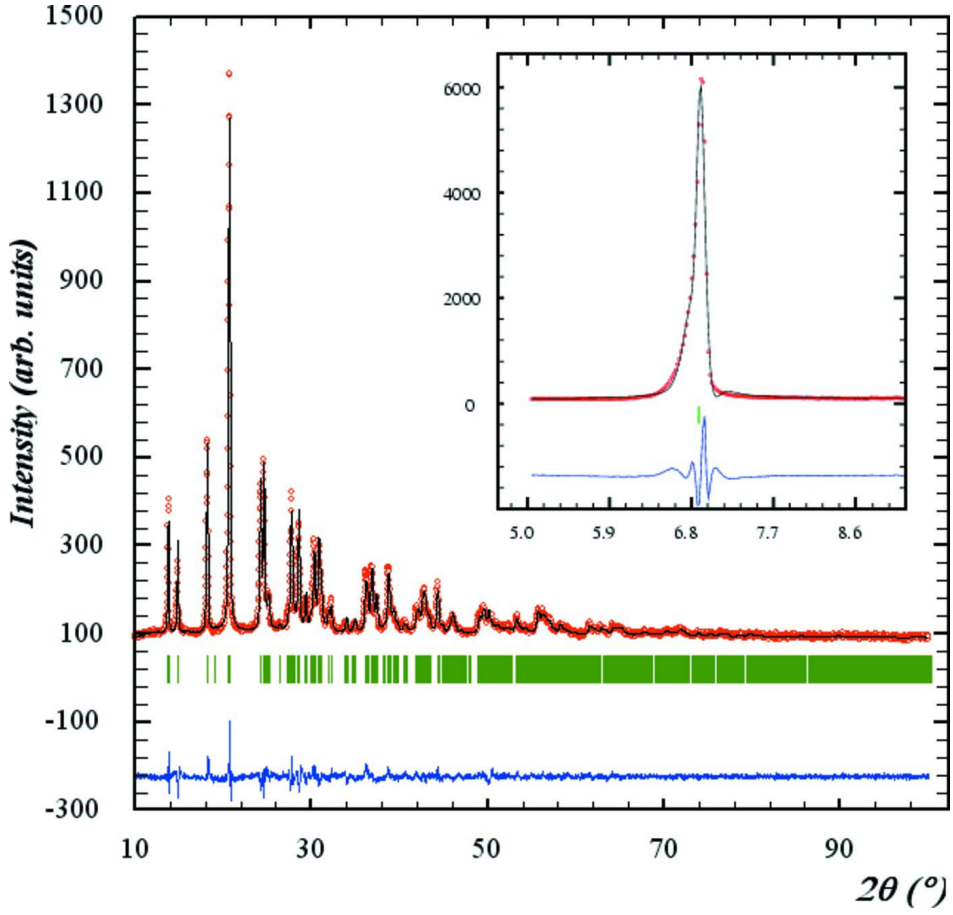

Figure 3

The Rietveld plot, showing the observed (circles), calculated (line) and difference patterns for (I). The reflection positions are shown above the difference pattern.

catena-Poly[[bis[1-(2-hydroxyethyl)-1H-tetrazole-κN^4]copper(II)]- di-μ-chlorido]

Crystal data

$[CuCl_2(C_3H_6N_4O)_2]$
M_r = 362.69
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 13.3349 (11) Å
b = 6.7406 (6) Å
c = 7.3419 (5) Å
β = 105.450 (8)°
V = 636.08 (9) Å^3
Z = 2
$F(000)$ = 366.0
D_x = 1.894 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.5418 Å
T = 295 K
Particle morphology: plate
green
flat sheet, 30 × 30 mm
Specimen preparation: Prepared at 295 K and 100 kPa

Data collection

HZG-4A (Carl Zeiss, Jena) diffractometer
Radiation source: fine-focus sealed X-ray tube, BSV-29
Ni filtered monochromator
Specimen mounting: packed powder pellet
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 5.000°, $2\theta_{max}$ = 100.000°, $2\theta_{step}$ = 0.020°

Refinement

Refinement on I_{net}
Least-squares matrix: full with fixed elements per cycle
R_p = 0.042
R_{wp} = 0.067
R_{exp} = 0.086
R_{Bragg} = 0.029
χ^2 = 0.608
4751 data points
Excluded region(s): none
Profile function: psevdo-Voigt
48 parameters
21 restraints
0 constraints
H-atom parameters constrained
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.02
Background function: Fourier filtering
Preferred orientation correction: Marsh–Dollase function (Marsh, 1932; Dollase, 1986)

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu	0.00000	0.00000	0.50000	0.0309 (10)*	
Cl	−0.0624 (4)	0.2048 (11)	0.2569 (10)	0.0309 (10)*	
N1	0.24708 (16)	0.3706 (2)	0.583 (4)	0.0309 (10)*	
N2	0.2982 (2)	0.19676 (13)	0.595 (3)	0.0309 (10)*	
N3	0.2308 (2)	0.05581 (18)	0.577 (3)	0.0309 (10)*	
N4	0.1358 (4)	0.1377 (3)	0.553 (4)	0.0309 (10)*	
C5	0.14654 (16)	0.3314 (4)	0.545 (5)	0.0309 (10)*	
H5	0.09292	0.42403	0.51621	0.0309 (10)*	
C6	0.3006 (6)	0.5643 (10)	0.5973 (16)	0.0309 (10)*	
H61A	0.24602	0.66346	0.56434	0.0309 (10)*	0.562 (12)
H61B	0.33551	0.56618	0.49731	0.0309 (10)*	0.562 (12)
C71	0.3778 (18)	0.641 (2)	0.768 (3)	0.0309 (10)*	0.562 (12)
H71A	0.41791	0.74586	0.73283	0.0309 (10)*	0.562 (12)
H71B	0.34071	0.69633	0.85467	0.0309 (10)*	0.562 (12)
O1	0.4451 (15)	0.489 (3)	0.862 (5)	0.0309 (10)*	0.562 (12)
H1	0.42627	0.38207	0.81168	0.0309 (10)*	0.562 (12)

H62A	0.31564	0.60902	0.72756	0.0309 (10)*	0.438 (12)
H62B	0.25331	0.65967	0.52039	0.0309 (10)*	0.438 (12)
C72	0.3987 (12)	0.565 (7)	0.539 (4)	0.0309 (10)*	0.438 (12)
H72A	0.38957	0.48960	0.42321	0.0309 (10)*	0.438 (12)
H72B	0.41727	0.69967	0.51599	0.0309 (10)*	0.438 (12)
O2	0.479 (2)	0.480 (6)	0.684 (5)	0.0309 (10)*	0.438 (12)
H2	0.46854	0.35907	0.68929	0.0309 (10)*	0.438 (12)

Geometric parameters (Å, º)

Cu—Cl	2.234 (7)	N3—N4	1.350 (11)
Cu—N4	1.979 (10)	N4—C5	1.316 (4)
Cu—Cl^{i}	3.008 (7)	C6—C71	1.49 (2)
Cu—Cl^{ii}	2.234 (7)	C6—C72	1.48 (2)
Cu—N4^{ii}	1.979 (10)	C5—H5	0.9300
Cu—Cl^{iii}	3.008 (7)	C6—H61B	0.9700
O1—C71	1.41 (3)	C6—H62A	0.9700
O2—C72	1.42 (5)	C6—H61A	0.9700
O1—H1	0.8200	C6—H62B	0.9700
O2—H2	0.8200	C71—H71A	0.9700
N1—N2	1.346 (6)	C71—H71B	0.9700
N1—C5	1.321 (15)	C72—H72A	0.9700
N1—C6	1.478 (8)	C72—H72B	0.9700
N2—N3	1.291 (7)	Cu—Cu^{iv}	4.9835 (4)
Cl—Cu—N4	89.8 (7)	N1—C6—C72	115 (2)
Cl—Cu—Cl^{i}	90.8 (2)	N1—C6—C71	125.5 (14)
Cl—Cu—Cl^{ii}	180	O1—C71—C6	111.5 (15)
Cl—Cu—N4^{ii}	90.2 (7)	O2—C72—C6	110 (2)
Cl—Cu—Cl^{iii}	89.2 (2)	N1—C5—H5	126.00
Cl^{i}—Cu—N4	92.6 (5)	N4—C5—H5	126.00
Cl^{ii}—Cu—N4	90.2 (7)	N1—C6—H61B	106.00
N4—Cu—N4^{ii}	180	N1—C6—H62A	108.00
Cl^{iii}—Cu—N4	87.4 (5)	N1—C6—H62B	108.00
Cl^{i}—Cu—Cl^{ii}	89.2 (2)	C71—C6—H61A	106.00
Cl^{i}—Cu—N4^{ii}	87.4 (5)	C71—C6—H61B	106.00
Cl^{i}—Cu—Cl^{iii}	180.00	H61A—C6—H61B	106.00
Cl^{ii}—Cu—N4^{ii}	89.8 (7)	C72—C6—H62A	109.00
Cl^{ii}—Cu—Cl^{iii}	90.8 (2)	C72—C6—H62B	109.00
Cl^{iii}—Cu—N4^{ii}	92.6 (5)	H62A—C6—H62B	107.00
Cu—Cl—Cu^{iv}	143.5 (2)	N1—C6—H61A	106.00
C71—O1—H1	109.00	O1—C71—H71A	109.00
C72—O2—H2	109.00	O1—C71—H71B	109.00
N2—N1—C6	122.6 (7)	C6—C71—H71B	109.00
C5—N1—C6	129.4 (6)	H71A—C71—H71B	108.00
N2—N1—C5	107.9 (5)	C6—C71—H71A	109.00
N1—N2—N3	107.9 (6)	C6—C72—H72A	110.00
N2—N3—N4	108.4 (3)	C6—C72—H72B	110.00

Cu—N4—N3	127.6 (3)	O2—C72—H72A	110.00
N3—N4—C5	107.5 (8)	O2—C72—H72B	109.00
Cu—N4—C5	124.1 (9)	H72A—C72—H72B	108.00
N1—C5—N4	107.8 (9)		

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) −*x*, −*y*, −*z*+1; (iii) *x*, −*y*+1/2, *z*+1/2; (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*
O1—H1···N2	0.8200	2.3500	3.08 (3)	149.00
O2—H2···N2	0.8200	2.4600	3.02 (3)	126.00
C5—H5···Cl^{iv}	0.9300	2.7200	3.34 (2)	126.00

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