



**HAL**  
open science

## **A new copper(II) coordination polymer containing chains of interconnected paddle-wheel antiferromagnetic clusters**

Sofiane Bouheroum, Aouatef Cherouana, Adel Beghidja, Slimane Dahaoui, Pierre Rabu

### ► **To cite this version:**

Sofiane Bouheroum, Aouatef Cherouana, Adel Beghidja, Slimane Dahaoui, Pierre Rabu. A new copper(II) coordination polymer containing chains of interconnected paddle-wheel antiferromagnetic clusters. *Acta Crystallographica Section C: Structural Chemistry* [2014-..], 2017, 73 (12), pp.1050-1055. <10.1107/S2053229617013766>. <hal-02342549>

**HAL Id: hal-02342549**

**<https://hal.science/hal-02342549v1>**

Submitted on 31 Oct 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# A new copper(II) coordination polymer containing chains of interconnected paddle-wheel anti-ferromagnetic clusters

Sofiane Bouheroum,<sup>a,b</sup> Aouatef Cherouana,<sup>a\*</sup> Adel Beghidja,<sup>a</sup> Slimane Dahaoui<sup>c</sup> and Pierre Rabu<sup>d</sup>

Received 24 July 2017

Accepted 25 September 2017

Edited by D. S. Yufit, University of Durham, England

**Keywords:** one-dimensional coordination polymer; binuclear copper(II) complex; crystal structure; hydrogen bonds; magnetic properties.

**CCDC reference:** 1515175

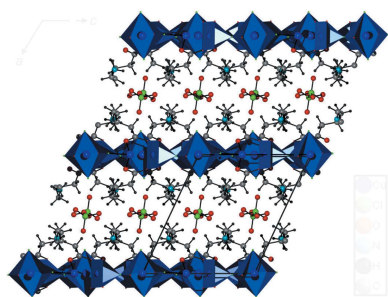
**Supporting information:** this article has supporting information at journals.iucr.org/c

<sup>a</sup>Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale (URCHEMS), Département de Chimie Université, Frères Mentouri de Constantine, 25000 Constantine, Algeria, <sup>b</sup>Centre de Développement des Technologies Avancées (CDTA), UROP, Sétif 19000, Algeria, <sup>c</sup>CRM2 (UMR UL–CNRS 7036) Faculté des Sciences et Technologies, Université de Lorraine, BP 70239 Boulevard des Aiguillettes, 54506 Vandoeuvre-lès-Nancy Cedex, France, and <sup>d</sup>Institut de Physique et Chimie des Matériaux de Strasbourg, UMR7504 CNRS–UNISTRA and NIE, 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France. \*Correspondence e-mail: c\_aouatef@yahoo.fr

The construction of supramolecular architectures based on inorganic–organic coordination frameworks with weak noncovalent interactions has implications for the rational design of functional materials. A new crystalline binuclear copper(II) one-dimensional polymeric chain, namely *catena*-poly[[[tetrakis( $\mu$ -4-azaniumylbutanoato- $\kappa^2 O:O'$ )dicopper(II)( $Cu-Cu$ )]- $\mu$ -chlorido-[diaquadichloridocopper(II)]- $\mu$ -chlorido] bis(perchlorate)],  $\{[Cu_3Cl_4(C_4H_9NO_2)_4(H_2O)_2](ClO_4)_2\}_n$ , was obtained by the reaction of 4-aminobutyric acid (GABA) with  $CuCl_2 \cdot 2H_2O$  in aqueous solution. The structure was established by single-crystal X-ray diffraction and was also characterized by IR spectroscopy and magnetic measurements. The crystal structure consists of  $\{[Cu_2(GABA)_4]\{CuCl_4(H_2O)_2\}^+\}$  cations and isolated perchlorate anions. Two symmetry-related  $Cu^{II}$  centres are bridged *via* carboxylate O atoms into a classical paddle-wheel configuration, with a  $Cu \cdots Cu$  distance of 2.643 (1) Å, while bridging Cl atoms complete the square-pyramidal geometry of the metal atoms. The Cl atoms connect the paddlewheel moieties to a second  $Cu^{II}$  atom lying on an octahedral site, resulting in infinite helical chains along the *c* axis. The packing motif exhibits channels containing free perchlorate anions. The crystal structure is stabilized by hydrogen bonds between the perchlorate anions, the coordinated water molecules and the ammonium groups of the polymeric chains. The magnetic analysis of the title compound indicates a nontrivial antiferromagnetic behaviour arising from alternating weak–strong antiferromagnetic coupling between neighbouring  $Cu^{II}$  centres.

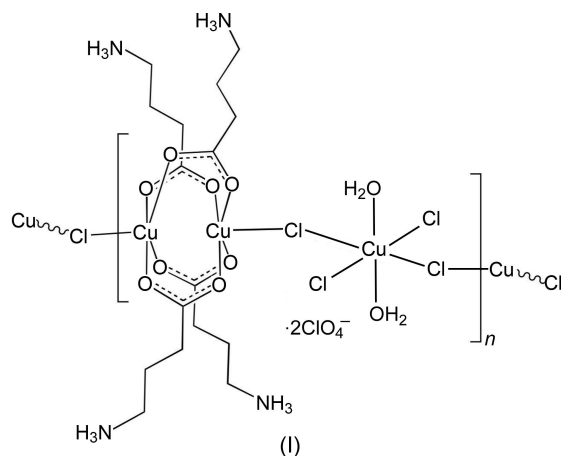
## 1. Introduction

The investigation of novel metal–organic coordination polymers has attracted a great deal of research interest as a result of their ability to form interesting structures with potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics and electrical conductivity (Mitzi, 1999). In particular, the construction of supramolecular architectures (Moulton & Zaworotko, 2001) based on inorganic–organic coordination frameworks with weak noncovalent interactions (Steiner, 2002; Desiraju, 2002) is an exciting area of research that has implications for the rational design of functional materials (Evans & Lin, 2002). The selection of ligands is very important in the construction of these coordination polymers. In this respect, organic carboxylate ligands are widely used to design extended one-, two- or three-dimensional systems with interesting magnetic properties. These ligands show a variety of coordination modes with different metal atoms (Evans &



© 2017 International Union of Crystallography

Lin, 2002). Among carboxylate ligands, 4-aminobutyric acid (GABA) is of biological interest because it is a major inhibitory neurotransmitter physiologically active in the central nervous system (Licata *et al.*, 2009; Karakossian *et al.*, 2005). Interestingly, Yogeewari and co-workers have synthesized new GABA derivatives useful in the treatment of neurological disorders with anticonvulsant and antinociceptive activities (Yogeewari *et al.*, 2007). There are two crystal forms of GABA, *viz.* the stable monoclinic phase (Tomita *et al.*, 1973) and the metastable tetragonal phase (Dobson & Gerkin, 1996). Many derivatives of GABA have been synthesized and reported, such as the potassium salt of GABA (Tokuoka *et al.*, 1981), GABA hydrochloride (Steward *et al.*, 1973) and [CdBr<sub>2</sub>(GABA)<sub>2</sub>] (Dan & Rao, 2005). Recently, Fabbiani and co-workers reported the structure of hydrated GABA obtained under high pressure (Fabbiani *et al.*, 2014). We describe, in this article, the synthesis, X-ray crystal structure and magnetic properties of a new coordination polymer based on GABA and copper, namely *catena*-poly[[tetrakis( $\mu$ -4-azaniumylbutanoato)dicopper(II)(Cu–Cu)]- $\mu$ -chlorido-[diaqua-dichloridocopper(II)]- $\mu$ -chlorido bis(perchlorate)], (I).



## 2. Experimental

### 2.1. Instruments and materials

**2.1.1. Instruments.** FT-IR spectra were recorded on an ATI Mattson Genesis in the region 400–4000 cm<sup>-1</sup> by transmission through 0.1 mm thick KBr pellets containing the powder sample. Magnetic measurements were performed using a Quantum Design SQUID-MPMS magnetometer. Susceptibility was measured on heating in an applied field of 5 kOe and isothermal magnetization was performed at 1.8 K in a field in the range  $\pm 50$  kOe. Diamagnetic corrections were estimated from Pascal's constants and the sample holder contribution.

**2.1.2. Materials.** All reagents and solvents for the synthesis and analysis were commercially available, were purchased from Sigma–Aldrich and were used without further purification. All manipulations were performed in air.

### 2.2. Synthesis and crystallization

An aqueous solution (10 ml) of 4-aminobutyric acid (0.137 g, 1 mmol) was mixed with an aqueous solution (15 ml)

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[Cu <sub>3</sub> Cl <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]- (ClO <sub>4</sub> ) <sub>2</sub>
<i>M<sub>r</sub></i>	979.82
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.946 (3), 12.568 (3), 11.044 (2)
$\beta$ (°)	115.18 (3)
<i>V</i> (Å <sup>3</sup> )	1626.2 (7)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.52
Crystal size (mm)	0.10 $\times$ 0.10 $\times$ 0.08
Data collection	
Diffractometer	Oxford Diffraction Supernova four-circle diffractometer equipped with an Atlas CCD detector
Absorption correction	Integration (DeTitta, 1985)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.720, 0.853
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	19050, 3805*, 15048
<i>R<sub>int</sub></i>	0.038
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.654
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.044, 0.109, 0.99
No. of reflections	19050
No. of parameters	217
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.26, -1.92

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2008), *SIR97* (Altomare *et al.*, 1999), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2012) and *OLEX2* (Dolomanov *et al.*, 2009). Note: (\*) Because twin refinement was used, the input data were not merged for the least-squares calculations.

of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.170 g, 1 mmol) at room temperature with constant stirring and gentle heating for 1 h. An aqueous solution of lithium perchlorate (0.106 g, 1 mmol) was added dropwise and the final mixture was kept at room temperature. After several weeks, green crystals appeared, from which crystals suitable for X-ray analysis were chosen. **CAUTION!** Perchlorate salts are potentially dangerous and should be handled with appropriate care.

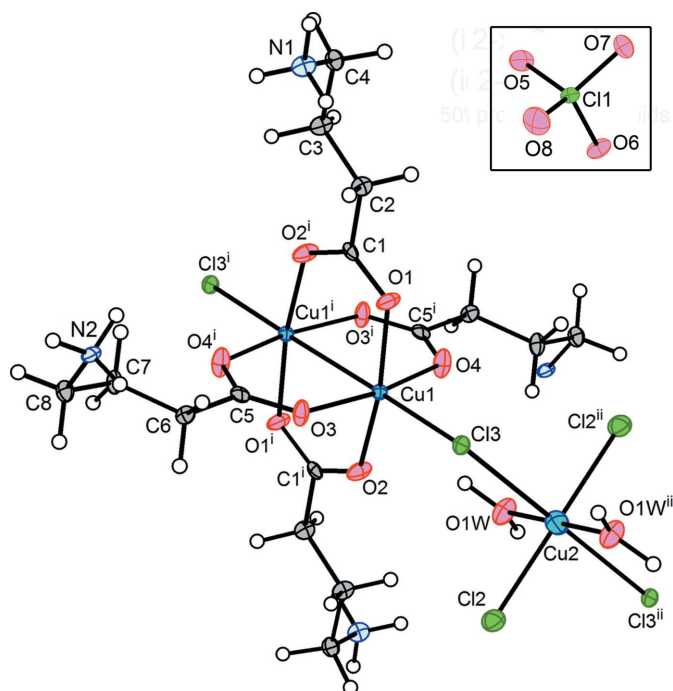
### 2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms (ligand and water) were located in difference electron-density maps and treated as riding on their parent atoms, with C–H = 0.99 Å, N–H = 0.91 Å and O–H = 1.00 Å, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N,O). The sample crystal was twinned, with major and minor twin components of 0.5507 (19) and 0.4493 (19), respectively. As a consequence, a twin refinement by means of the *SHELXL* HKLF 5 instruction (Sheldrick, 2015) was employed.

## 3. Results and discussion

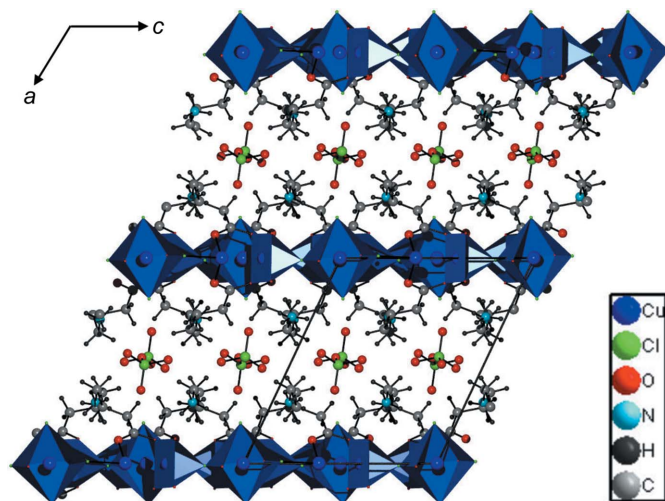
### 3.1. Crystal structure

The crystal structure of the title compound consists of cationic polymeric chains, built on an alternating sequence of


**Figure 1**

Displacement ellipsoid plot (50% probability level) of (I). The inset shows the perchlorate anion, but the orientation is not the same as that of the main fragment. [Symmetry codes: (i)  $-x + 2, -y + 2, -z + 1$ ; (ii)  $-x + 2, -y + 2, -z$ .]

dimeric  $[\text{Cu}_2\text{Cl}_2\text{O}_8]$  copper(II) entities and octahedral  $[\text{CuCl}_4(\text{H}_2\text{O})_2]$  groups, the two entities sharing Cl atoms. Perchlorate anions balance the charge of the copper framework, functionalized with ammonium-carboxylate groups (Fig. 1). Selected bond lengths and angles are listed in Table 2. The dimeric unit exists as a divalent cation with the two  $\text{Cu}^{\text{II}}$  atoms bridged by the carboxylate groups of four GABA ligands. The GABA ligand is in its zwitterionic form (4-azaniumylbutanoate) and is thus neutral. Atom Cu1 adopts a square-pyramidal geometry, with four carboxylate O atoms in


**Figure 2**

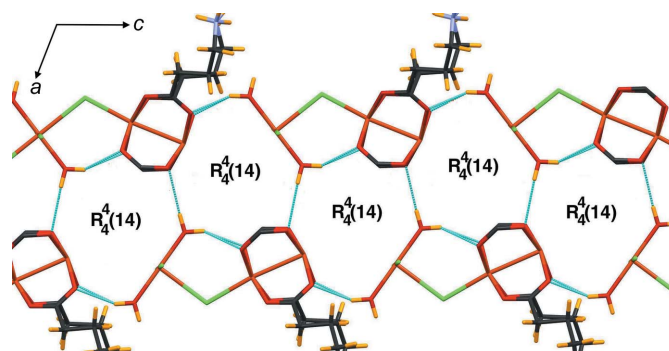
View along  $b$  of the structure of (I), showing the polyhedra around the  $\text{Cu}^{\text{II}}$  atoms and the perchlorate anions in the inter-chain channels.

**Table 2**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu1—Cl3	2.4312 (18)	Cu2—O1W	2.030 (5)
Cu1—O1	1.966 (5)	O1—C1	1.260 (9)
Cu1—O2	1.977 (6)	O2—Cl <sup>i</sup>	1.256 (10)
Cu1—O3	1.975 (6)	O3—C5	1.256 (9)
Cu1—O4	1.974 (6)	O4—C5 <sup>i</sup>	1.265 (9)
Cu2—Cl2	2.331 (2)	N1—C4	1.502 (9)
Cu2—Cl3	2.7554 (17)	N2—C8	1.487 (9)
Cl3—Cu1—O1	93.59 (16)	Cl3—Cu2—O1W <sup>ii</sup>	88.83 (15)
Cl3—Cu1—O2	98.67 (16)	Cu1—Cl3—Cu2	113.22 (6)
Cl3—Cu1—O3	92.31 (16)	Cu1—O1—C1	124.4 (5)
Cl3—Cu1—O4	99.40 (17)	Cu1—O2—Cl <sup>i</sup>	122.7 (5)
O1—Cu1—O2	167.7 (2)	Cu1—O3—C5	125.7 (5)
O1—Cu1—O3	90.3 (2)	Cu1—O4—C5 <sup>i</sup>	120.6 (6)
O1—Cu1—O4	88.6 (2)	O2 <sup>i</sup> —C1—C2	119.9 (6)
O2—Cu1—O3	90.5 (2)	O1—C1—C2	115.3 (7)
O2—Cu1—O4	88.2 (2)	O1—C1—O2 <sup>i</sup>	124.8 (7)
O3—Cu1—O4	168.3 (2)	N1—C4—C3	110.5 (7)
Cl2—Cu2—Cl3	89.13 (7)	O3—C5—O4 <sup>i</sup>	125.3 (7)
Cl2—Cu2—O1W	89.49 (19)	O3—C5—C6	116.8 (6)
Cl2—Cu2—Cl3 <sup>ii</sup>	90.87 (7)	O4 <sup>i</sup> —C5—C6	117.9 (7)
Cl2—Cu2—O1W <sup>ii</sup>	90.51 (19)	N2—C8—C7	111.8 (7)
Cl3—Cu2—O1W	91.17 (15)		

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

the basal plane and a Cl3 atom in the apical site, and is slightly displaced from the basal plane by 0.206 (1)  $\text{\AA}$ . The Cl—Cu $\cdots$ Cu<sup>i</sup> angle of 173.56 (1) $^\circ$  [symmetry code: (i)  $-x + 2, -y + 2, -z + 1$ ] indicates that the Cl—Cu $\cdots$ Cu<sup>i</sup> moiety is not strictly linear, similar to other compounds with a similar dimeric copper core (Jeziarska *et al.*, 1998; Chen *et al.*, 1998). Atom Cu2 is located on an inversion centre and exhibits a distorted octahedral geometry whose base is formed by two Cl atoms and two coordinated water molecules. The apical positions are occupied by a bridging Cl2 atom shared with the square pyramid of Cu1, giving an alternating succession of square-pyramidal and octahedral  $\text{Cu}^{\text{II}}$  ions along the  $c$  axis (Fig. 2). The distortion of the Cu2 geometry is due to an elongation of the two axial bonds resulting from the Jahn–Teller effect. The crystal structure of (I) involves an extensive hydrogen-bond network. These hydrogen bonds occur within and between the chains, as well as between the polymeric chains and perchlorate anions (Table 3). The coordinated water molecules act as hydrogen-bond donors for symmetry-


**Figure 3**

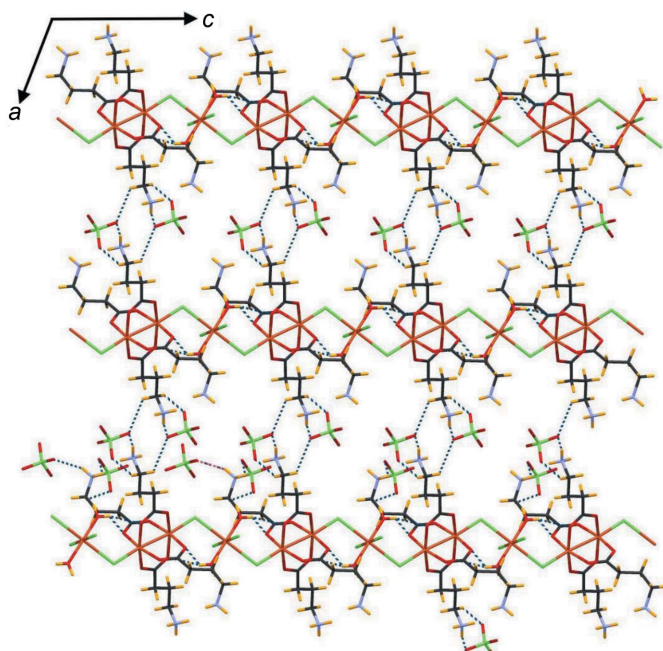
The hydrogen-bond scheme involving the water molecules. Ligand atoms have been omitted for clarity.

**Table 3**  
Hydrogen-bond geometry (Å, °).

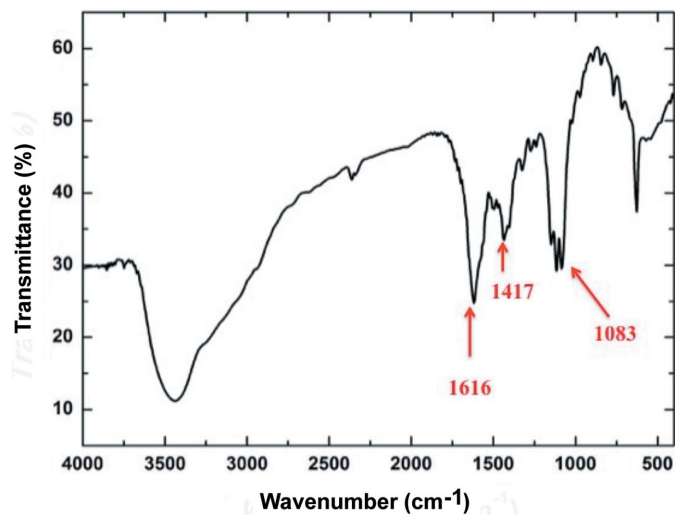
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1W—H1WA···O2	1.0000	2.2500	3.046 (9)	135.00
O1W—H1WA···O4	1.0000	2.5000	3.234 (7)	130.00
N1—H1A···Cl2 <sup>iii</sup>	0.9100	2.3200	3.214 (6)	166.00
N1—H1B···O1 <sup>iv</sup>	0.9100	2.1800	3.075 (9)	169.00
N1—H1B···O4 <sup>iv</sup>	0.9100	2.4500	2.989 (9)	118.00
N1—H1C···O5 <sup>v</sup>	0.9100	2.5900	3.015 (9)	109.00
N1—H1C···O5 <sup>vi</sup>	0.9100	2.2600	3.074 (8)	148.00
O1W—H1WB···O1 <sup>vii</sup>	0.9900	2.3500	3.252 (7)	151.00
N2—H2A···O6 <sup>viii</sup>	0.9100	2.5000	3.146 (8)	128.00
N2—H2A···Cl2 <sup>iv</sup>	0.9100	2.4900	3.245 (6)	140.00
N2—H2B···O7	0.9100	2.1100	2.956 (8)	154.00
N2—H2C···Cl3 <sup>iv</sup>	0.9100	2.4600	3.316 (7)	157.00
N2—H2C···O3 <sup>iv</sup>	0.9100	2.5000	3.075 (7)	122.00
C2—H2D···Cl2 <sup>iii</sup>	0.9900	2.8200	3.708 (7)	149.00
C2—H2D···Cl3 <sup>iv</sup>	0.9900	2.8000	3.511 (8)	129.00
C4—H4A···O5 <sup>v</sup>	0.9900	2.5800	3.215 (9)	122.00
C6—H6A···N2	0.9900	2.6100	3.031 (9)	106.00
C8—H8B···O8 <sup>viii</sup>	0.9900	2.5100	3.294 (9)	136.00

Symmetry codes: (iii)  $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$ ; (iv)  $x, -y+\frac{3}{2}, z+\frac{1}{2}$ ; (v)  $x+1, y, z$ ; (vi)  $-x+2, -y+1, -z+2$ ; (vii)  $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$ ; (viii)  $-x+1, -y+1, -z+1$ .

related chelated carboxylate O atoms (O1, O2 and O4). Atom H1WA forms two intra-polymer hydrogen bonds with atoms O2 and O4, thus reinforcing these polymeric chains, while atom H1WB provides the connection between two different chains *via* an H1WB···O1<sup>vii</sup> interaction. The combination of these three hydrogen bonds results in rings with the motif  $R_4^4(14)$  (Etter, 1990; Bernstein *et al.*, 1995), which repeats along the *c* axis, giving rise to a ribbon structure with the graph-set descriptor  $C[R_4^4(14)]$  (Fig. 3). Perchlorate anions are



**Figure 4**  
A view of the three-dimensional network of the title compound formed *via* N—H···O and C—H···O hydrogen bonds between GABA ligands and perchlorate anions, showing the alternation of the cationic and anionic layers.

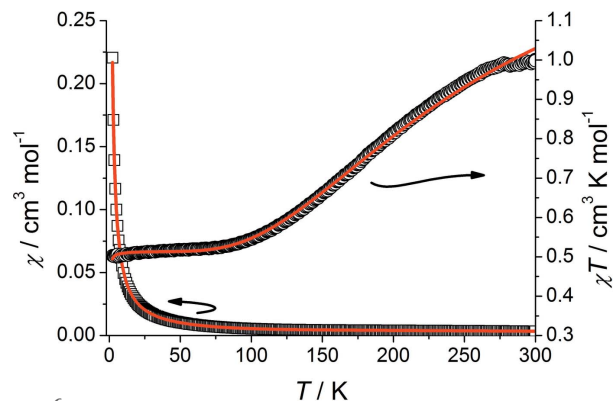


**Figure 5**  
The FT-IR spectrum of (I).

sandwiched between these polymeric ribbons, generating an alternating succession of cationic layers and perchlorate layers (Fig. 4). These units are linked by N—H···O and C—H···O hydrogen bonds involving the GABA ligand, thus forming a three-dimensional hydrogen-bond network. All hydrogen bonds have significant strength and should thus participate in the global stabilization of the structure.

### 3.2. FT-IR spectroscopic study

The IR spectrum of the title compound (Fig. 5) shows broad stretching bands in the 3100–3500  $\text{cm}^{-1}$  range, assignable to the antisymmetrical and symmetrical H—O—H stretching vibrations (Chen *et al.*, 1998) of water molecules. These bands overlap other stretching bands resulting from N—H···O and OW—H···O moieties. The band at 1083  $\text{cm}^{-1}$  corresponds to uncoordinated perchlorate ions (Chaplin, 2016; Deacon & Phillips, 1980). The FT-IR spectrum also exhibits two strong bands at 1616 and 1417  $\text{cm}^{-1}$  which are assigned to the antisymmetrical and symmetrical stretching vibrations of the carboxylate groups of the ligand, respectively. The difference



**Figure 6**  
 $\chi$  (black squares) and  $\chi T$  (black circles) as a function of temperature measured in a field of 5000 Oe for (I). The red solid lines correspond to the best fit of the data (see text).

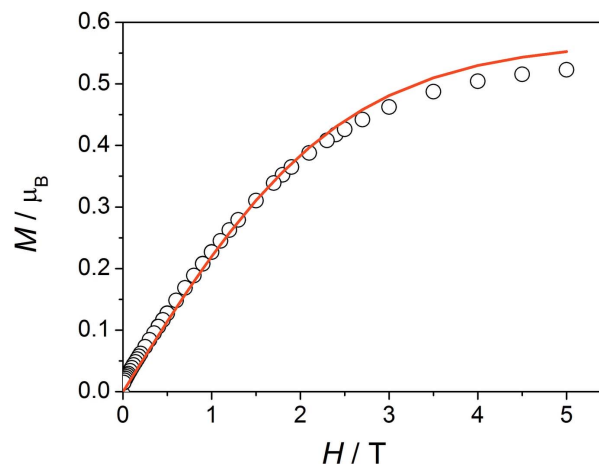
of  $199\text{ cm}^{-1}$  between the antisymmetrical and symmetrical stretching vibrations is in agreement with the *syn-syn* bidentate bridging  $\mu_2, \kappa^2 O:O'$ -mode of the carboxylate groups (Schechter *et al.*, 1995; Zeleňák *et al.*, 2004). Bands between  $1000$  and  $1250\text{ cm}^{-1}$  are attributed to C–C and C–N stretching vibration bands of the GABA ligand (Zeleňák *et al.*, 2007).

### 3.3. Magnetic properties

The magnetic properties of (I) were studied on randomly oriented polycrystalline samples. The magnetic susceptibility is plotted as  $\chi T$  and  $\chi$  versus  $T$  curves in (Fig. 6). The magnetic susceptibility increases continuously from room temperature to 2 K. The  $\chi T$  ( $T$ ) product decreases steeply from  $1.04\text{ cm}^3\text{ K mol}^{-1}$  at 300 K, reaching a plateau at *ca*  $0.50\text{ cm}^3\text{ K mol}^{-1}$  below 100 K. The high temperature value is below that expected for three  $\text{Cu}^{2+}$  ions ( $0.4\text{--}0.5\text{ cm}^3\text{ K per Cu mol}$ ). The plateau below 100 K agrees quite well with the contribution of one  $\text{Cu}^{\text{II}}$  atom. Accordingly, the magnetization versus field curve shown in Fig. 7 suggests a paramagnetic-like behaviour at 1.8 K. However, the saturation value of  $0.55\ \mu_{\text{B}}/\text{Cu}^{2+}$  ion at  $H = 5\text{ T}$  is almost half of that expected for one  $S = \frac{1}{2}$  spin. Hence, the magnetic behaviour of (I) does not simply consist of the superposition of antiferromagnetic dimers and isolated paramagnetic centres. Rather, it suggests the presence of strong antiferromagnetic coupling all along the chains. Actually, based on the structure, one can consider two interactions, namely  $J_1$  between adjacent Cu1 and Cu2 atoms, and  $J_2$  within the  $\text{Cu1}\cdots\text{Cu1}$  dimeric units. To evaluate these exchange interaction values, the experimental data were fitted using a numerical approach to solve the Hamiltonian corresponding to the present chain structure:

$$\hat{H} = - \sum_{i=1}^N \left[ J_1 (\hat{S}_{3i} \cdot \hat{S}_{3i+1} + \hat{S}_{3i} \cdot \hat{S}_{3i-1}) + J_2 \hat{S}_{3i+1} \cdot \hat{S}_{3i+2} \right] - g\mu_{\text{B}} \sum_{i=1}^N \hat{S}_i \cdot \vec{H}.$$

In this expression, the first term holds for the exchange coupling along  $\{\text{Cu1}\cdots\text{Cu2}\cdots\text{Cu1}\cdots\text{Cu1}\}_n$  chains. The Landé factor  $g$  was kept identical for all spin centres. The actual model for a chain should involve an infinity of spin centres. Due to computation limitations, the number of spins were limited. To avoid a symmetry breaking artefact for finite linear chains, the data were fitted by iterative diagonalization of the exchange interaction matrix written on the basis of the above Hamiltonian for rings of 12  $S = \frac{1}{2}$  spins (*SPIN*; Legoll *et al.*, 2017). [*SPIN* is code for the calculation and fitting of the magnetic properties of low-dimensional systems. The code encompasses one diagonalization subroutine from the library of IDRIS (Orsay, France). The minimization program *MINUIT* from the CERN library (CERN, Geneva, Switzerland) is included for fitting the experimental curves.] The result of the numerical approach is shown in Fig. 7. A good agreement was obtained for  $J_1/k = -12.5$  (2) K,  $J_2/k = -473$  (2) K and  $g = 2.28$  (1). The  $g$  value, which is a mean



**Figure 7**  
Isothermal magnetization of (I) recorded at 1.8 K. The full line corresponds to the direct calculation of  $M(H)$  with the values of  $J_1$ ,  $J_2$  and  $g$  obtained by fitting the susceptibility data.

value for the two  $\text{Cu}^{\text{II}}$  sites, is within the range reported in the literature (Carlin, 1986). The very strong value of  $J_2$  is in agreement with that observed in similar paddlewheel dimers (Kahn, 1993; Carlin, 1986). Thus, the behaviour of the chains appears dominated by that of the strongly antiferromagnetic  $\text{Cu1}\cdots\text{Cu1}$  dimers. However, the paramagnetic Cu2 centres are not innocent, as they act as a relay between the paddlewheel units, transmitting significant antiferromagnetic interactions along the chains. Using the same numerical procedure as above, we have calculated the magnetization versus field variation with the fitted values of  $J_1$ ,  $J_2$  and  $g$ . A pretty good agreement was obtained when compared with the experimental data, as shown in Fig. 7, which confirms the significance of the values obtained.

### Acknowledgements

The authors acknowledge CRM2, Institut Jean Barriol (UMR 7036 CNRS, University de Lorraine, France), for providing access to crystallographic experimental facilities.

### References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brandenburg, K. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Carlin, R. L. (1986). In *Magnetochemistry*. Berlin: Springer-Verlag.
- Chaplin, M. (2016). *Water Absorption Spectrum*. Available online: [http://www1.lsbu.ac.uk/water/water\\_vibrational\\_spectrum.html](http://www1.lsbu.ac.uk/water/water_vibrational_spectrum.html). (Accessed 12 May 2016.)
- Chen, X.-M., Feng, X.-L., Xu, Z.-T., Zhang, X.-H. & Mak, T. C. W. (1998). *Polyhedron*, **17**, 2639–2646.
- Dan, M. & Rao, C. N. R. (2005). *Chem. Eur. J.* **11**, 7102–7109.
- Deacon, G. B. & Phillips, R. J. (1980). *Coord. Chem. Rev.* **33**, 227–250.
- Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.
- DeTitta, G. T. (1985). *J. Appl. Cryst.* **18**, 75–79.

- Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* **C52**, 3075–3078.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Evans, O. R. & Lin, W. (2002). *Acc. Chem. Res.* **35**, 511–522.
- Fabbiani, F. B. A., Buth, G., Levendisc, D. C. & Cruz-Cabeza, A. J. (2014). *Chem. Commun.* **50**, 1817–1819.
- Jeziarska, J., Glowiak, T., Ozarowski, A., Yablokov, Yu. V. & Rzaczyńska, Z. (1998). *Inorg. Chim. Acta*, **28–36**, 275–276.
- Kahn, O. (1993). In *Molecular Magnetism*. Weinheim: VCH.
- Karakossian, S. R., Spencer, A. Q., Gomez, O. R., Padilla, A., Sacher, D. D. F., Loo, N., Nelson, S. & Eskandari, S. (2005). *J. Membr. Biol.* **203**, 65–82.
- Legoll, P., Drillon, M., Rabu, P. & Maingot, F. (2017). *SPIN*. Version 2.35. CNRS, Orsay, France, and CERN, Geneva, Switzerland.
- Licata, S. C., Platt, D. M., Cook, J. M., Van Linn, M. L. & Rowlett, J. K. (2009). *Psychopharmacology (Berlin)*, **203**, 539–546.
- Mitzi, D. B. (1999). *Prog. Inorg. Chem.* **48**, 1–121.
- Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.
- Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction, Wrocław, Poland.
- Schechter, B., Arnon, R. & Wilchek, M. (1995). *React. Polym.* **25**, 167–175.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
- Steward, E. G., Player, R. B. & Warner, D. (1973). *Acta Cryst.* **B29**, 2825–2826.
- Tokuoka, R., Abe, M., Matsumoto, K., Shirakawa, K., Fujiwara, T. & Tomita, K.-I. (1981). *Acta Cryst.* **B37**, 445–447.
- Tomita, K., Higashi, H. & Fujiwara, T. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2199–2204.
- Yogeeswari, P., Ragavendran, J. V., Sriram, D., Nageswari, Y., Kavaya, R., Sreevatsan, N., Vanitha, K. & Stables, J. (2007). *J. Med. Chem.* **50**, 2459–2467.
- Zeleňák, V., Sabo, M., Massa, W. & Černák, J. (2004). *Acta Cryst.* **C60**, m85–m87.
- Zeleňák, V., Vargova, Z. & Gyoryova, K. (2007). *Spectrochim. Acta Part A*, **66**, 262–272.

## supporting information

*Acta Cryst.* (2017). C73 [https://doi.org/10.1107/S2053229617013766]

## A new copper(II) coordination polymer containing chains of interconnected paddle-wheel antiferromagnetic clusters

**Sofiane Bouheroum, Aouatef Cherouana, Adel Beghidja, Slimane Dahaoui and Pierre Rabu**

### Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2008); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2008); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2008); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

**catena-Poly[[[tetrakis( $\mu$ -4-azaniumylbutanoato- $\kappa^2$ O':O')dicopper(II)(Cu—Cu)]- $\mu$ -chlorido-[diaquadichloridocopper(II)]- $\mu$ -chlorido] bis(perchlorate)]**

### Crystal data

[Cu<sub>3</sub>Cl<sub>4</sub>(C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>  
 $M_r = 979.82$   
 Monoclinic,  $P2_1/c$   
 Hall symbol: -P 2ybc  
 $a = 12.946$  (3) Å  
 $b = 12.568$  (3) Å  
 $c = 11.044$  (2) Å  
 $\beta = 115.18$  (3)°  
 $V = 1626.2$  (7) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 994$   
 $D_x = 2.001$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 19042 reflections  
 $\theta = 2.6$ – $27.7^\circ$   
 $\mu = 2.52$  mm<sup>-1</sup>  
 $T = 100$  K  
 Prism, green  
 $0.1 \times 0.1 \times 0.08$  mm

### Data collection

Oxford Diffraction KappaCCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$  scans  
 Absorption correction: integration  
 (DeTitta, 1985)  
 $T_{\min} = 0.720$ ,  $T_{\max} = 0.853$

19050 measured reflections  
 19050 independent reflections  
 15048 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\max} = 27.7^\circ$ ,  $\theta_{\min} = 2.6^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -16 \rightarrow 16$   
 $l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.109$   
 $S = 0.99$   
 19050 reflections  
 217 parameters  
 3 restraints

Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: difference Fourier map  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0667P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 1.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.92 \text{ e } \text{\AA}^{-3}$$

### Special details

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refined as a 2-component twin.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.99887 (8)	0.95931 (5)	0.38914 (7)	0.0087 (2)
Cu2	1.00000	1.00000	0.00000	0.0236 (4)
Cl2	0.80176 (13)	0.99175 (15)	-0.11378 (19)	0.0213 (5)
Cl3	0.98967 (15)	0.86597 (11)	0.19198 (15)	0.0141 (4)
O1	1.1161 (4)	0.8638 (4)	0.5140 (5)	0.0208 (17)
O1W	0.9850 (5)	1.1296 (3)	0.1010 (5)	0.0243 (16)
O2	0.8865 (5)	1.0727 (4)	0.2988 (5)	0.0187 (17)
O3	0.8778 (4)	0.8696 (4)	0.3998 (5)	0.0188 (17)
O4	1.1208 (5)	1.0625 (4)	0.4120 (5)	0.0205 (17)
N1	1.2977 (5)	0.5897 (5)	0.9106 (6)	0.0156 (19)
N2	0.7144 (5)	0.5913 (5)	0.6050 (5)	0.0139 (19)
C1	1.1480 (6)	0.8635 (6)	0.6389 (7)	0.010 (2)
C2	1.2308 (6)	0.7758 (5)	0.7141 (7)	0.0139 (19)
C3	1.2774 (7)	0.7837 (6)	0.8644 (8)	0.014 (2)
C4	1.3600 (6)	0.6939 (5)	0.9343 (8)	0.013 (2)
C5	0.8440 (6)	0.8730 (6)	0.4908 (7)	0.013 (2)
C6	0.7515 (6)	0.7943 (5)	0.4807 (7)	0.012 (2)
C7	0.7261 (7)	0.7881 (6)	0.6029 (7)	0.016 (2)
C8	0.6543 (6)	0.6931 (5)	0.6004 (8)	0.014 (2)
Cl1	0.51942 (12)	0.47535 (11)	0.74998 (16)	0.0153 (5)
O5	0.4947 (4)	0.5097 (3)	0.8587 (5)	0.0218 (17)
O6	0.4636 (4)	0.5401 (5)	0.6359 (5)	0.0306 (17)
O7	0.6421 (3)	0.4820 (3)	0.7932 (5)	0.0189 (16)
O8	0.4841 (4)	0.3669 (4)	0.7191 (5)	0.0277 (17)
H1WA	0.98700	1.13870	0.19200	0.0300*
H1A	1.26710	0.57390	0.82180	0.0190*
H1B	1.24090	0.59460	0.93820	0.0190*
H1C	1.34730	0.53750	0.95750	0.0190*
H1WB	0.98210	1.20340	0.06870	0.0300*
H2A	0.69960	0.57060	0.52030	0.0170*
H2B	0.68940	0.54040	0.64480	0.0170*
H2C	0.79090	0.60060	0.65280	0.0170*
H2D	1.19180	0.70640	0.68550	0.0160*
H2E	1.29550	0.77710	0.68880	0.0160*
H3A	1.21320	0.78180	0.89070	0.0170*
H3B	1.31700	0.85280	0.89400	0.0170*

H4A	1.41910	0.69000	0.89990	0.0160*
H4B	1.39850	0.70850	1.03150	0.0160*
H6A	0.77430	0.72260	0.46370	0.0140*
H6B	0.68020	0.81360	0.40220	0.0140*
H7A	0.79900	0.78480	0.68440	0.0190*
H7B	0.68580	0.85370	0.60800	0.0190*
H8A	0.63500	0.69660	0.67800	0.0160*
H8B	0.58210	0.69510	0.51790	0.0160*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0090 (3)	0.0082 (3)	0.0092 (5)	0.0004 (4)	0.0041 (5)	0.0003 (3)
Cu2	0.0205 (5)	0.0270 (6)	0.0234 (8)	0.0014 (7)	0.0095 (8)	-0.0013 (5)
Cl2	0.0209 (7)	0.0233 (8)	0.0184 (10)	-0.0014 (8)	0.0072 (8)	0.0037 (7)
Cl3	0.0136 (7)	0.0187 (7)	0.0110 (8)	0.0012 (7)	0.0062 (8)	-0.0022 (5)
O1	0.025 (3)	0.027 (3)	0.009 (3)	0.015 (3)	0.006 (2)	0.004 (2)
O1W	0.036 (3)	0.021 (2)	0.020 (3)	0.002 (2)	0.016 (3)	0.0000 (19)
O2	0.027 (3)	0.016 (3)	0.010 (3)	0.009 (2)	0.005 (2)	-0.001 (2)
O3	0.019 (3)	0.026 (3)	0.016 (3)	-0.013 (2)	0.012 (2)	-0.010 (2)
O4	0.027 (3)	0.019 (3)	0.023 (3)	-0.011 (2)	0.018 (2)	-0.010 (2)
N1	0.020 (3)	0.009 (4)	0.016 (3)	0.001 (2)	0.006 (3)	0.000 (2)
N2	0.013 (3)	0.018 (4)	0.009 (3)	0.000 (2)	0.003 (2)	0.005 (2)
C1	0.007 (3)	0.008 (4)	0.017 (4)	-0.001 (3)	0.006 (3)	0.003 (3)
C2	0.017 (3)	0.010 (3)	0.014 (4)	0.002 (3)	0.006 (3)	0.000 (3)
C3	0.019 (4)	0.010 (4)	0.012 (4)	0.002 (3)	0.005 (3)	-0.002 (3)
C4	0.013 (3)	0.012 (4)	0.016 (4)	-0.002 (3)	0.007 (3)	-0.001 (3)
C5	0.010 (3)	0.013 (4)	0.016 (4)	0.007 (3)	0.005 (3)	0.006 (3)
C6	0.014 (3)	0.009 (4)	0.012 (4)	-0.002 (2)	0.005 (3)	0.001 (3)
C7	0.017 (4)	0.016 (4)	0.020 (4)	-0.002 (3)	0.013 (3)	0.001 (3)
C8	0.014 (3)	0.011 (4)	0.018 (4)	-0.002 (3)	0.009 (3)	0.001 (3)
Cl1	0.0135 (7)	0.0211 (9)	0.0096 (8)	-0.0012 (6)	0.0033 (7)	-0.0001 (7)
O5	0.016 (3)	0.031 (3)	0.019 (3)	0.0065 (19)	0.008 (2)	-0.004 (2)
O6	0.025 (3)	0.045 (3)	0.015 (3)	0.001 (2)	0.002 (2)	0.020 (3)
O7	0.013 (2)	0.021 (3)	0.024 (3)	0.0007 (19)	0.009 (2)	0.000 (2)
O8	0.031 (3)	0.021 (3)	0.031 (3)	-0.010 (2)	0.013 (3)	-0.008 (2)

*Geometric parameters (Å, °)*

Cu1—Cl3	2.4312 (18)	N1—H1C	0.9100
Cu1—O1	1.966 (5)	N1—H1A	0.9100
Cu1—O2	1.977 (6)	N2—H2C	0.9100
Cu1—O3	1.975 (6)	N2—H2A	0.9100
Cu1—O4	1.974 (6)	N2—H2B	0.9100
Cu2—Cl2	2.331 (2)	C1—C2	1.515 (10)
Cu2—Cl3	2.7554 (17)	C2—C3	1.509 (11)
Cu2—O1W	2.030 (5)	C3—C4	1.520 (11)
Cu2—Cl2 <sup>i</sup>	2.331 (2)	C5—C6	1.520 (11)

Cu2—C13 <sup>i</sup>	2.7554 (17)	C6—C7	1.521 (11)
Cu2—O1W <sup>i</sup>	2.030 (5)	C7—C8	1.506 (11)
C11—O7	1.453 (5)	C2—H2E	0.9900
C11—O5	1.434 (5)	C2—H2D	0.9900
C11—O6	1.413 (6)	C3—H3B	0.9900
C11—O8	1.432 (5)	C3—H3A	0.9900
O1—C1	1.260 (9)	C4—H4A	0.9900
O2—C1 <sup>ii</sup>	1.256 (10)	C4—H4B	0.9900
O3—C5	1.256 (9)	C6—H6A	0.9900
O4—C5 <sup>ii</sup>	1.265 (9)	C6—H6B	0.9900
O1W—H1WB	0.9900	C7—H7B	0.9900
O1W—H1WA	1.0000	C7—H7A	0.9900
N1—C4	1.502 (9)	C8—H8A	0.9900
N2—C8	1.487 (9)	C8—H8B	0.9900
N1—H1B	0.9100		
Cu1…O1W	3.775 (5)	O8…H2A <sup>x</sup>	2.8100
Cu1…N2 <sup>iii</sup>	3.739 (6)	O8…H2E <sup>xiii</sup>	2.8200
Cu1…O3 <sup>ii</sup>	3.072 (5)	O8…H4B <sup>vii</sup>	2.6900
Cu1…O1 <sup>ii</sup>	3.108 (5)	O8…H8B <sup>x</sup>	2.5100
Cu1…O2 <sup>ii</sup>	3.145 (5)	N1…C12 <sup>iv</sup>	3.214 (6)
Cu1…O4 <sup>ii</sup>	3.193 (6)	N1…O5 <sup>vii</sup>	3.074 (8)
Cu1…N1 <sup>iii</sup>	3.824 (7)	N1…O7 <sup>vii</sup>	3.155 (8)
Cu1…H1WB <sup>iv</sup>	3.2400	N1…Cu1 <sup>xii</sup>	3.824 (7)
Cu1…H1WA	3.0900	N1…O1 <sup>xii</sup>	3.075 (9)
Cu1…H1B <sup>iii</sup>	3.0200	N1…O5 <sup>xv</sup>	3.015 (9)
Cu1…H2C <sup>iii</sup>	2.9400	N1…O4 <sup>xii</sup>	2.989 (9)
Cu2…H2D <sup>v</sup>	3.5700	N2…O7	2.956 (8)
Cu2…H2D <sup>iii</sup>	3.5700	N2…O6 <sup>x</sup>	3.146 (8)
Cl2…Cl3	3.582 (3)	N2…Cu1 <sup>xii</sup>	3.739 (6)
Cl2…O1W	3.077 (5)	N2…Cl2 <sup>xii</sup>	3.245 (6)
Cl2…O6 <sup>vi</sup>	3.394 (6)	N2…Cl3 <sup>xii</sup>	3.316 (7)
Cl2…N1 <sup>v</sup>	3.214 (6)	N2…O2 <sup>xii</sup>	3.120 (8)
Cl2…O1W <sup>i</sup>	3.104 (7)	N2…O3 <sup>xii</sup>	3.075 (7)
Cl2…N2 <sup>iii</sup>	3.245 (6)	N1…H2D	2.7000
Cl2…Cl3 <sup>i</sup>	3.636 (3)	N2…H6A	2.6100
Cl3…O1W <sup>i</sup>	3.389 (6)	C1…O7 <sup>xvi</sup>	2.904 (9)
Cl3…N2 <sup>iii</sup>	3.316 (7)	C1…C5	3.564 (12)
Cl3…O4	3.373 (5)	C2…Cl3 <sup>xii</sup>	3.511 (8)
Cl3…O1W	3.455 (4)	C2…O7 <sup>xvi</sup>	3.089 (8)
Cl3…Cl2	3.582 (3)	C4…O5 <sup>xv</sup>	3.215 (9)
Cl3…O1	3.221 (5)	C4…O5 <sup>vii</sup>	3.414 (8)
Cl3…C6 <sup>iii</sup>	3.590 (8)	C5…C1	3.564 (12)
Cl3…O2	3.357 (6)	C5…O7 <sup>iii</sup>	3.172 (9)
Cl3…O3	3.193 (6)	C6…Cl3 <sup>xii</sup>	3.590 (8)
Cl3…Cl2 <sup>i</sup>	3.636 (3)	C8…O8 <sup>x</sup>	3.294 (9)
Cl3…C2 <sup>iii</sup>	3.511 (8)	C8…O6	3.282 (10)
Cl1…H1C <sup>vii</sup>	2.9500	C1…H1WA <sup>ii</sup>	3.0500

C11...H2B	3.0100	C1...H1WB <sup>iv</sup>	2.9800
C12...H6A <sup>iii</sup>	2.8900	C1...H1B <sup>iii</sup>	2.9800
C12...H2A <sup>iii</sup>	2.4900	C2...H1A	2.7600
C12...H1A <sup>v</sup>	2.3200	C4...H8B <sup>xvii</sup>	2.9700
C12...H2D <sup>v</sup>	2.8200	C6...H2C	3.0000
C13...H1WA <sup>iv</sup>	3.0900	C6...H2A	2.9700
C13...H6A <sup>iii</sup>	3.0600	C6...H8A <sup>iii</sup>	3.0300
C13...H7A <sup>iii</sup>	3.0800	H1WA...C1 <sup>ii</sup>	3.0500
C13...H2C <sup>iii</sup>	2.4600	H1WA...O4	2.5000
C13...H2D <sup>iii</sup>	2.8000	H1WA...C13 <sup>v</sup>	3.0900
O1...C13	3.221 (5)	H1WA...Cu1	3.0900
O1...N1 <sup>iii</sup>	3.075 (9)	H1WA...O2	2.2500
O1...O3	2.793 (8)	H1WA...H3A <sup>ii</sup>	2.5600
O1...O4	2.751 (7)	H1A...C12 <sup>iv</sup>	2.3200
O1...C5 <sup>ii</sup>	3.352 (9)	H1A...O5 <sup>xv</sup>	2.9100
O1...Cu1 <sup>ii</sup>	3.108 (5)	H1A...C2	2.7600
O1W...C12 <sup>i</sup>	3.104 (7)	H1A...H2D	2.1800
O1W...C12	3.077 (5)	H1B...O7 <sup>vii</sup>	2.8600
O1W...O4	3.234 (7)	H1B...Cu1 <sup>xii</sup>	3.0200
O1W...C13 <sup>i</sup>	3.389 (6)	H1B...H3A	2.4000
O1W...Cu1	3.775 (5)	H1B...O1 <sup>xii</sup>	2.1800
O1W...O2	3.046 (9)	H1B...O4 <sup>xii</sup>	2.4500
O1W...C13	3.455 (4)	H1B...C1 <sup>xii</sup>	2.9800
O2...O1W	3.046 (9)	H1C...H7B <sup>xiii</sup>	2.4000
O2...C5 <sup>ii</sup>	3.338 (10)	H1C...C11 <sup>vii</sup>	2.9500
O2...O3	2.807 (7)	H1C...O5 <sup>vii</sup>	2.2600
O2...Cu1 <sup>ii</sup>	3.145 (5)	H1C...O5 <sup>xv</sup>	2.5900
O2...N2 <sup>iii</sup>	3.120 (8)	H1C...O7 <sup>vii</sup>	2.7100
O2...C13	3.357 (6)	H1WB...C1 <sup>v</sup>	2.9800
O2...O4	2.748 (9)	H1WB...O1 <sup>v</sup>	2.3500
O2...O7 <sup>iii</sup>	3.213 (8)	H1WB...O3 <sup>v</sup>	2.6900
O3...O1	2.793 (8)	H1WB...Cu1 <sup>v</sup>	3.2400
O3...C1	3.370 (9)	H2A...C6	2.9700
O3...N2 <sup>iii</sup>	3.075 (7)	H2A...H6A	2.3400
O3...C13	3.193 (6)	H2A...O6 <sup>x</sup>	2.5000
O3...Cu1 <sup>ii</sup>	3.072 (5)	H2A...O8 <sup>x</sup>	2.8100
O3...O2	2.807 (7)	H2A...C12 <sup>xii</sup>	2.4900
O3...C1 <sup>ii</sup>	3.380 (9)	H2B...O7	2.1100
O4...C1 <sup>ii</sup>	3.410 (11)	H2B...O2 <sup>xii</sup>	2.7800
O4...Cu1 <sup>ii</sup>	3.193 (6)	H2B...O6	2.8800
O4...O2	2.748 (9)	H2B...H3B <sup>xiii</sup>	2.3900
O4...O1W	3.234 (7)	H2B...C11	3.0100
O4...N1 <sup>iii</sup>	2.989 (9)	H2C...C6	3.0000
O4...C13	3.373 (5)	H2C...C13 <sup>xii</sup>	2.4600
O4...O1	2.751 (7)	H2C...O2 <sup>xii</sup>	2.6800
O5...O5 <sup>viii</sup>	3.075 (7)	H2C...O3 <sup>xii</sup>	2.5000
O5...N1 <sup>vii</sup>	3.074 (8)	H2C...H7A	2.3400
O5...N1 <sup>ix</sup>	3.015 (9)	H2C...Cu1 <sup>xii</sup>	2.9400

O5...C4 <sup>ix</sup>	3.215 (9)	H2C...H6A	2.5300
O5...C4 <sup>vii</sup>	3.414 (8)	H2D...N1	2.7000
O6...N2 <sup>x</sup>	3.146 (8)	H2D...H1A	2.1800
O6...C8	3.282 (10)	H2D...C13 <sup>xii</sup>	2.8000
O6...C12 <sup>xi</sup>	3.394 (6)	H2D...Cu2 <sup>iv</sup>	3.5700
O7...O2 <sup>xii</sup>	3.213 (8)	H2D...C12 <sup>iv</sup>	2.8200
O7...C5 <sup>xii</sup>	3.172 (9)	H2D...Cu2 <sup>xii</sup>	3.5700
O7...N2	2.956 (8)	H2E...H4A	2.4500
O7...C2 <sup>xiii</sup>	3.089 (8)	H2E...O7 <sup>xvi</sup>	2.6800
O7...N1 <sup>vii</sup>	3.155 (8)	H2E...O8 <sup>xvi</sup>	2.8200
O7...C1 <sup>xiii</sup>	2.904 (9)	H3A...O1 <sup>xii</sup>	2.8700
O8...C8 <sup>x</sup>	3.294 (9)	H3A...H1WA <sup>ii</sup>	2.5600
O1...H1B <sup>iii</sup>	2.1800	H3A...O2 <sup>ii</sup>	2.6600
O1...H3A <sup>iii</sup>	2.8700	H3A...H1B	2.4000
O1...H1WB <sup>iv</sup>	2.3500	H3A...O1W <sup>ii</sup>	2.8300
O1W...H3A <sup>ii</sup>	2.8300	H3B...H2B <sup>xvi</sup>	2.3900
O2...H3B <sup>ii</sup>	2.7500	H3B...O2 <sup>ii</sup>	2.7500
O2...H1WA	2.2500	H3B...O6 <sup>xvii</sup>	2.8700
O2...H2B <sup>iii</sup>	2.7800	H3B...O7 <sup>xvi</sup>	2.8500
O2...H3A <sup>ii</sup>	2.6600	H4A...O5 <sup>xv</sup>	2.5800
O2...H2C <sup>iii</sup>	2.6800	H4A...H2E	2.4500
O3...H1WB <sup>iv</sup>	2.6900	H4A...H8B <sup>xvii</sup>	2.4300
O3...H7A <sup>iii</sup>	2.9000	H4B...O8 <sup>vii</sup>	2.6900
O3...H2C <sup>iii</sup>	2.5000	H6A...H2A	2.3400
O4...H7B <sup>ii</sup>	2.8100	H6A...H2C	2.5300
O4...H7A <sup>ii</sup>	2.6100	H6A...C12 <sup>xii</sup>	2.8900
O4...H1B <sup>iii</sup>	2.4500	H6A...N2	2.6100
O4...H1WA	2.5000	H6A...C13 <sup>xii</sup>	3.0600
O5...H1C <sup>vii</sup>	2.2600	H6B...H8A <sup>iii</sup>	2.2900
O5...H1C <sup>ix</sup>	2.5900	H6B...O7 <sup>iii</sup>	2.7900
O5...H1A <sup>ix</sup>	2.9100	H7A...O4 <sup>ii</sup>	2.6100
O5...H4A <sup>ix</sup>	2.5800	H7A...C13 <sup>xii</sup>	3.0800
O6...H3B <sup>xiv</sup>	2.8700	H7A...O3 <sup>xii</sup>	2.9000
O6...H2B	2.8800	H7A...H2C	2.3400
O6...H2A <sup>x</sup>	2.5000	H7B...H1C <sup>xvi</sup>	2.4000
O6...H8A	2.8500	H7B...O4 <sup>ii</sup>	2.8100
O7...H2E <sup>xiii</sup>	2.6800	H8A...O6	2.8500
O7...H2B	2.1100	H8A...C6 <sup>xii</sup>	3.0300
O7...H6B <sup>xii</sup>	2.7900	H8A...H6B <sup>xii</sup>	2.2900
O7...H1B <sup>vii</sup>	2.8600	H8B...C4 <sup>xiv</sup>	2.9700
O7...H3B <sup>xiii</sup>	2.8500	H8B...H4A <sup>xiv</sup>	2.4300
O7...H1C <sup>vii</sup>	2.7100	H8B...O8 <sup>x</sup>	2.5100
Cl3—Cu1—O1	93.59 (16)	C8—N2—H2A	109.00
Cl3—Cu1—O2	98.67 (16)	C8—N2—H2B	109.00
Cl3—Cu1—O3	92.31 (16)	C8—N2—H2C	109.00
Cl3—Cu1—O4	99.40 (17)	H2B—N2—H2C	109.00
O1—Cu1—O2	167.7 (2)	O2 <sup>ii</sup> —C1—C2	119.9 (6)

O1—Cu1—O3	90.3 (2)	O1—C1—C2	115.3 (7)
O1—Cu1—O4	88.6 (2)	O1—C1—O2 <sup>ii</sup>	124.8 (7)
O2—Cu1—O3	90.5 (2)	C1—C2—C3	114.4 (6)
O2—Cu1—O4	88.2 (2)	C2—C3—C4	112.1 (7)
O3—Cu1—O4	168.3 (2)	N1—C4—C3	110.5 (7)
Cl2—Cu2—Cl3	89.13 (7)	O3—C5—O4 <sup>ii</sup>	125.3 (7)
Cl2—Cu2—O1W	89.49 (19)	O3—C5—C6	116.8 (6)
Cl2—Cu2—Cl2 <sup>i</sup>	180.00	O4 <sup>ii</sup> —C5—C6	117.9 (7)
Cl2—Cu2—Cl3 <sup>i</sup>	90.87 (7)	C5—C6—C7	115.4 (6)
Cl2—Cu2—O1W <sup>i</sup>	90.51 (19)	C6—C7—C8	112.9 (6)
Cl3—Cu2—O1W	91.17 (15)	N2—C8—C7	111.8 (7)
Cl2 <sup>i</sup> —Cu2—Cl3	90.87 (7)	C1—C2—H2D	109.00
Cl3—Cu2—Cl3 <sup>i</sup>	180.00	C1—C2—H2E	109.00
Cl3—Cu2—O1W <sup>i</sup>	88.83 (15)	H2D—C2—H2E	108.00
Cl2 <sup>i</sup> —Cu2—O1W	90.51 (19)	C3—C2—H2E	109.00
Cl3 <sup>i</sup> —Cu2—O1W	88.83 (15)	C3—C2—H2D	109.00
O1W—Cu2—O1W <sup>i</sup>	180.00	C4—C3—H3A	109.00
Cl2 <sup>i</sup> —Cu2—Cl3 <sup>i</sup>	89.13 (7)	C2—C3—H3B	109.00
Cl2 <sup>i</sup> —Cu2—O1W <sup>i</sup>	89.49 (19)	C2—C3—H3A	109.00
Cl3 <sup>i</sup> —Cu2—O1W <sup>i</sup>	91.17 (15)	C4—C3—H3B	109.00
Cu1—Cl3—Cu2	113.22 (6)	H3A—C3—H3B	108.00
O5—C11—O8	108.9 (3)	H4A—C4—H4B	108.00
O6—C11—O7	109.4 (3)	N1—C4—H4A	110.00
O6—C11—O8	110.2 (3)	N1—C4—H4B	110.00
O7—C11—O8	109.1 (3)	C3—C4—H4A	109.00
O5—C11—O6	111.2 (3)	C3—C4—H4B	110.00
O5—C11—O7	108.0 (3)	C5—C6—H6B	108.00
Cu1—O1—C1	124.4 (5)	C7—C6—H6A	108.00
Cu1—O2—C1 <sup>ii</sup>	122.7 (5)	C5—C6—H6A	108.00
Cu1—O3—C5	125.7 (5)	H6A—C6—H6B	107.00
Cu1—O4—C5 <sup>ii</sup>	120.6 (6)	C7—C6—H6B	108.00
H1WA—O1W—H1WB	104.00	C8—C7—H7A	109.00
Cu2—O1W—H1WB	124.00	C6—C7—H7B	109.00
Cu2—O1W—H1WA	133.00	C6—C7—H7A	109.00
H1A—N1—H1B	109.00	C8—C7—H7B	109.00
C4—N1—H1A	109.00	H7A—C7—H7B	108.00
C4—N1—H1C	109.00	H8A—C8—H8B	108.00
H1B—N1—H1C	109.00	N2—C8—H8A	109.00
H1A—N1—H1C	110.00	N2—C8—H8B	109.00
C4—N1—H1B	109.00	C7—C8—H8A	109.00
H2A—N2—H2C	110.00	C7—C8—H8B	109.00
H2A—N2—H2B	109.00		
O1—Cu1—Cl3—Cu2	-131.91 (18)	Cl2 <sup>i</sup> —Cu2—Cl3—Cu1	81.65 (9)
O2—Cu1—Cl3—Cu2	46.8 (2)	O1W <sup>i</sup> —Cu2—Cl3—Cu1	171.1 (2)
O3—Cu1—Cl3—Cu2	137.66 (17)	Cu1—O1—C1—C2	174.1 (5)
O4—Cu1—Cl3—Cu2	-42.78 (18)	Cu1—O1—C1—O2 <sup>ii</sup>	-3.6 (11)
Cl3—Cu1—O1—C1	-170.4 (6)	Cu1—O2—C1 <sup>ii</sup> —O1 <sup>ii</sup>	0.0 (12)

O3—Cu1—O1—C1	-78.0 (6)	Cu1—O2—C1 <sup>ii</sup> —C2 <sup>ii</sup>	177.6 (5)
O4—Cu1—O1—C1	90.3 (6)	Cu1—O3—C5—C6	-178.5 (5)
Cl3—Cu1—O2—C1 <sup>ii</sup>	172.2 (6)	Cu1—O3—C5—O4 <sup>ii</sup>	2.9 (11)
O3—Cu1—O2—C1 <sup>ii</sup>	79.8 (6)	Cu1—O4—C5 <sup>ii</sup> —O3 <sup>ii</sup>	2.5 (11)
O4—Cu1—O2—C1 <sup>ii</sup>	-88.6 (6)	Cu1—O4—C5 <sup>ii</sup> —C6 <sup>ii</sup>	-178.9 (5)
Cl3—Cu1—O3—C5	175.4 (6)	O1—C1—C2—C3	173.9 (7)
O1—Cu1—O3—C5	81.8 (6)	O2 <sup>ii</sup> —C1—C2—C3	-8.3 (11)
O2—Cu1—O3—C5	-85.9 (6)	C1—C2—C3—C4	-179.9 (7)
Cl3—Cu1—O4—C5 <sup>ii</sup>	-177.9 (5)	C2—C3—C4—N1	-68.8 (9)
O1—Cu1—O4—C5 <sup>ii</sup>	-84.5 (6)	O3—C5—C6—C7	170.5 (7)
O2—Cu1—O4—C5 <sup>ii</sup>	83.7 (6)	O4 <sup>ii</sup> —C5—C6—C7	-10.7 (10)
Cl2—Cu2—Cl3—Cu1	-98.35 (9)	C5—C6—C7—C8	-167.0 (7)
O1W—Cu2—Cl3—Cu1	-8.9 (2)	C6—C7—C8—N2	63.8 (8)

Symmetry codes: (i)  $-x+2, -y+2, -z$ ; (ii)  $-x+2, -y+2, -z+1$ ; (iii)  $x, -y+3/2, z-1/2$ ; (iv)  $-x+2, y-1/2, -z+1/2$ ; (v)  $-x+2, y+1/2, -z+1/2$ ; (vi)  $-x+1, y+1/2, -z+1/2$ ; (vii)  $-x+2, -y+1, -z+2$ ; (viii)  $-x+1, -y+1, -z+2$ ; (ix)  $x-1, y, z$ ; (x)  $-x+1, -y+1, -z+1$ ; (xi)  $-x+1, y-1/2, -z+1/2$ ; (xii)  $x, -y+3/2, z+1/2$ ; (xiii)  $-x+2, y-1/2, -z+3/2$ ; (xiv)  $x-1, -y+3/2, z-1/2$ ; (xv)  $x+1, y, z$ ; (xvi)  $-x+2, y+1/2, -z+3/2$ ; (xvii)  $x+1, -y+3/2, z+1/2$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA $\cdots$ O2	1.0000	2.2500	3.046 (9)	135.00
O1W—H1WA $\cdots$ O4	1.0000	2.5000	3.234 (7)	130.00
N1—H1A $\cdots$ Cl2 <sup>iv</sup>	0.9100	2.3200	3.214 (6)	166.00
N1—H1B $\cdots$ O1 <sup>xii</sup>	0.9100	2.1800	3.075 (9)	169.00
N1—H1B $\cdots$ O4 <sup>xii</sup>	0.9100	2.4500	2.989 (9)	118.00
N1—H1C $\cdots$ O5 <sup>xv</sup>	0.9100	2.5900	3.015 (9)	109.00
N1—H1C $\cdots$ O5 <sup>vii</sup>	0.9100	2.2600	3.074 (8)	148.00
O1W—H1WB $\cdots$ O1 <sup>v</sup>	0.9900	2.3500	3.252 (7)	151.00
N2—H2A $\cdots$ O6 <sup>x</sup>	0.9100	2.5000	3.146 (8)	128.00
N2—H2A $\cdots$ Cl2 <sup>xii</sup>	0.9100	2.4900	3.245 (6)	140.00
N2—H2B $\cdots$ O7	0.9100	2.1100	2.956 (8)	154.00
N2—H2C $\cdots$ Cl3 <sup>xii</sup>	0.9100	2.4600	3.316 (7)	157.00
N2—H2C $\cdots$ O3 <sup>xii</sup>	0.9100	2.5000	3.075 (7)	122.00
C2—H2D $\cdots$ Cl2 <sup>iv</sup>	0.9900	2.8200	3.708 (7)	149.00
C2—H2D $\cdots$ Cl3 <sup>xii</sup>	0.9900	2.8000	3.511 (8)	129.00
C4—H4A $\cdots$ O5 <sup>xv</sup>	0.9900	2.5800	3.215 (9)	122.00
C6—H6A $\cdots$ N2	0.9900	2.6100	3.031 (9)	106.00
C8—H8B $\cdots$ O8 <sup>x</sup>	0.9900	2.5100	3.294 (9)	136.00

Symmetry codes: (iv)  $-x+2, y-1/2, -z+1/2$ ; (v)  $-x+2, y+1/2, -z+1/2$ ; (vii)  $-x+2, -y+1, -z+2$ ; (x)  $-x+1, -y+1, -z+1$ ; (xii)  $x, -y+3/2, z+1/2$ ; (xv)  $x+1, y, z$ .