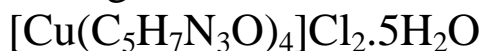




# Synthesis, characterization and supramolecular structure of a Cu(II) complex with the potentially bidentate ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one:



K. Kaabi<sup>1</sup>, M. Zeller<sup>2</sup> and C. Ben Nasr<sup>1,\*</sup>

<sup>1</sup>Laboratoire de chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisie.

<sup>2</sup>Youngstown State University, Department of Chemistry, One University Plaza, Youngstown, Ohio 44555-3663, USA.

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## ABSTRACT

The crystal structure of the new complex  $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})_4]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  has been determined by single crystal X-ray diffraction, and the compound was characterized by infrared spectroscopy and thermal analysis. The compound crystallizes in the monoclinic space group  $P2_1/c$  with lattice parameters  $a = 15.304(4)$ ,  $b = 13.528(3)$ ,  $c = 15.071(4)$  Å,  $\beta = 90.120(5)^\circ$ ,  $V = 3120.0(13)$  Å<sup>3</sup>, and  $Z = 4$ . The solid state structure exhibits pronounced pseudosymmetry emulating an orthorhombic  $Pccn$  setting which is broken only by ordering of solvate water and chlorine anions in channels stretching along the  $c$ -axis of the unit cell. Structural and IR data indicate that the title compound is present as the keto tautomer 2-amino-6-methylpyrimidin-4-(1*H*)-one rather than in the enol form 2-amino-6-methyl-4-pyrimidinol. The Cu(II) atoms are four-coordinated in a square planar fashion by nitrogen atoms of four 2-amino-6-methylpyrimidin-4-(1*H*)-one ligands. The crystal structure is stabilized by O–H···O, N–H···O, N–H···Cl and O–H···Cl hydrogen bonds with pillars of the cationic complexes alternating with channels occupied by the chlorine anions and water molecules.

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## Introduction

Pyrimidines and their derivatives have been widely used in fields ranging from medicinal to industrial applications. Several pyrimidine derivatives such as for example the barbiturates are therapeutically active compounds that have been used as e.g. anesthetics, but due to their addiction and overdose potential they have been largely supplanted by other less harmful drugs. As pyridine related compounds pyrimidines are also ideally suited as ligands to build coordination complexes with virtually any kind of metal cation. The pyrimidine ring system provides a potential binding site for metals and so any information on their coordinating properties is important for understanding the role of metal ions in biological systems [1–4]. The chemistry of copper complexes with ligands of biological relevance in which the metal centers are at close proximity to another is one of the central themes of current research [5–7] due to their interesting structural, electrochemical and magnetic properties [8] and also because of their relevance as synthetic models [9, 10] for active sites of several metalloenzymes [11].

As part of our continued involvement in the metal complexes of ligands of interesting molecular structures for suitable applications [12], we report here the synthesis and characterization of the Cu(II) complex of the pyrimidine ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one,  $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})_4]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ .

## Materials and Methods

### Chemical preparation

An aqueous solution of  $\text{CuCl}_2$  (0.014 g,  $5 \cdot 10^{-5}$  mol) in water (10 mL) was added dropwise to a solution of 2-amino-4-hydroxy-6-methylpyrimidine (0.250 g,  $2 \cdot 10^{-4}$  mol) in ethanol

(10 mL). After stirring for 30 min, the mixture was filtered. Blue crystals suitable for X-ray analysis were obtained by evaporating the filtrate at room temperature (yield 47 %). Elemental analysis, calculated: C 33.10, H 5.24, N 23.17 %; found: C 33.37, H 5.65, N 23.05 %.

### Investigative techniques

The title compound has been studied by single crystal X-ray diffraction, infrared spectroscopy and thermal analysis (differential thermal analysis, DTA, and thermal gravimetric analysis, TGA).

### X-ray diffraction

A single crystal was carefully selected under a microscope and was mounted on a Mitegen micromesh mount with the help of a trace of mineral oil. X-ray diffraction data were collected at 100 K on a Bruker Smart APEX CCD area-detector diffractometer using the  $\omega$  scan technique with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107$  Å). Data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [13]. SHELXS-97 and SHELXM [14] were used to solve the structure and SHELXL 6.14 [15] and full-matrix least-squares techniques were used for refinement. The correct unit cell and space group assignment proved difficult. Using the default settings of the programs Apex2 [13] and XPREP [14] yielded an orthorhombic setting with  $Pccn$  as the space group, and with unit cell axes of  $a = 13.528$ ,  $b = 15.304$  and  $c = 15.071$  Å. The structure could however initially not be solved in this setting. To avoid problems from a potential wrong space group assignment the structure was then solved without any symmetry constraints (in space group  $P1$ ), yielding a structure that accurately described

the cationic metal complex but with no meaningful model for the chloride anions or solvate molecules. A search for missing symmetry (using the program Platon [16, 17]) indicated the originally suggested space group *Pccn*, and the structure was then refined in this setting. The best R1 value that could be obtained was however ca 11%, and the anion and solvate section of the structure had to be refined with a 1:1 disorder of water and chlorine atoms. The high R value (much larger than would be expected based on the quality of the data) prompted a more detailed analysis. A close inspection of the diffraction patterns showed slight splitting of reflections at high diffraction angles, indicating that the structure might not be orthorhombic but monoclinic or triclinic and twinned by pseudo-merohedry. Inspection of systematic absences suggested each two of the glide planes and two fold axes of the apparent orthorhombic *Pccn* setting to be not quite realized. The remaining systematic absences suggested a monoclinic setting with space group *P2<sub>1</sub>/c* with unit cell axes in the order  $a = 15.304(4)$ ,  $b = 13.528(3)$  and  $c = 15.071(4)$  Å. The data were thus reintegrated under the assumption of perfect overlap of reflections of two twin domains, the intensity data were again corrected for absorption using the new monoclinic Laue setting and attempts were made to solve the structure in *P2<sub>1</sub>/c*, but again no meaningful solution could be obtained. The structure was again solved in *P1* using Patterson methods to locate the copper atoms, and pseudo-merohedral twinning was introduced prior to refinement by addition of the twin law 1 0 0, 0 -1 0, 0 0 -1. Successive addition of atoms yielded again the cationic metal complexes and a disordered model for the chloride anions and interstitial water molecules. A Platon search for missing symmetry indicated the originally suggested space group *Pccn*, but with only the monoclinic 2<sub>1</sub> screw axis and the *c*-glide plane 100% abided, and the pseudo-symmetry elements of the orthorhombic setting only 91 and 93% observed (with defaults Platon settings of 0.45 Å displacement for inversion and translation operations and 0.25 Å for rotational symmetry operations). Transformation of the space group to *P2<sub>1</sub>/c* reduced the unit cell content to one cation and seven interstitial atoms (chloride or water oxygen atoms). Application of occupancy factors to these seven atoms and successive refinement cycles finally allowed an unambiguous assignment of Cl and O atoms without use of a disorder model with an R1 value smaller than 5% in line with the quality of the experimental data. Water hydrogen atoms were then located in difference density maps and were refined with weak O–H and H···H distance restraints (0.84(2) and 1.35(2) Å). The final ratio for the twinning by pseudo-merohedry refined to 0.560(1) to 0.440(1). In the final model the orthorhombic symmetry is largely observed by the cationic complexes, but broken by the chloride and water molecules. In the hypothetical orthorhombic setting the water molecule of oxygen O8 would be equivalent to chlorine Cl1, and the water molecule of O6 to chlorine Cl2 (Figure 2). Comparison of calculated and observed structure factors after completion of the model indicated that reflection 1 0 0 was obstructed by the beam stop and it was omitted from the refinement. Despite of the large correlation of parameters of atoms related by pseudosymmetry no restraints or constraints for non-hydrogen atoms needed to be applied. Drawings were made with Mercury [18]. Final crystal data, experimental and data collection parameters are summarized in Table 1.

#### Thermal analysis

Thermal analysis was performed using a “multimodule 92 Setaram” analyzer operated between room temperature and 420 °C with an average heating rate of 5 °C.min<sup>-1</sup>.

#### IR Spectroscopy

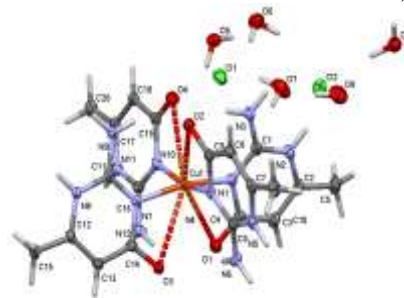
The spectrum was recorded in the range 4000 - 400 cm<sup>-1</sup> with a “Perkin-Elmer FTIR 1000” spectrophotometer using a sample dispersed in spectroscopically pure KBr pressed into a pellet.

#### Results and Discussion

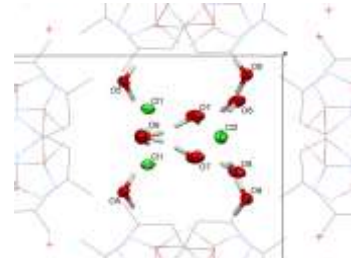
##### X-ray diffraction study

The main geometrical features of the different chemical entities of the coordination compound [Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub>]Cl<sub>2</sub>·5H<sub>2</sub>O are reported in Tables 2 and 3.

The asymmetric unit of the title compound consists of a Cu<sup>2+</sup> cation coordinated by four 2-amino-6-methylpyrimidin-4-(1*H*)-one molecules, two Cl<sup>-</sup> anions, and five not coordinated interstitial water molecules (Fig. 1). The compound crystallized in a monoclinic setting in *P2<sub>1</sub>/c*. The overall structure is however metrically orthorhombic (with a refined monoclinic  $\beta$  angle of 90.120(5)°), and most of the features of the structure emulate a higher symmetry setting in the orthorhombic space group *Pccn*. The orthorhombic symmetry is observed by the cationic complexes, but broken by the chloride and water molecules. In the monoclinic setting all water molecules and chloride anions are in distinct positions and not disordered, see Figure 2. In the hypothetical orthorhombic setting each of the chloride anions would share an approximate position with one of the interstitial water molecules (Cl1 with O8, Cl2 with O6). The ordering of chloride and water molecules also induces slight positional shifts for the other interstitial water molecules (that of O5 and O9) which otherwise would also have been equivalent. The crystal under investigation had been twinned by pseudo-merohedry based on the orthorhombic pseudo-symmetry in a 0.560(1) to 0.440(1) ratio (see the X-ray diffraction experimental section for technical details of structure solution and refinement).



**Fig. 1**  
Asymmetric unit of [Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub>]Cl<sub>2</sub>·5H<sub>2</sub>O with atom labels and 50% probability displacement ellipsoids for non-H atoms. The dashed lines indicate weak Cu–O interactions.

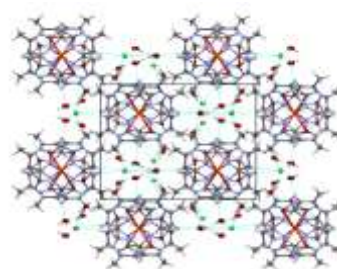


**Fig. 2**  
Partial packing view with water and chlorine atoms filling a channel extending down the *c*-axis highlighted to show the pseudo-symmetry. In the hypothetical orthorhombic setting a glide plane would run vertically through the center of the channel relating atoms on the left half of the channel to those on the right (O5 to O9, Cl1 to O8, and Cl2 to O6).

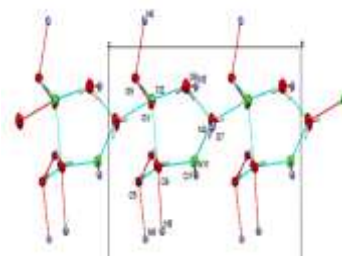
In the atomic arrangement of this complex, the Cu(II) atom is coordinated in a square planar fashion by four nitrogen atoms N1, N4, N7 and N10 each belonging to one 2-amino-6-methylpyrimidin-4-(1*H*)-one ligand molecule. The Cu–N distances are Cu1–N1 = 1.997(3), Cu1–N4 = 2.026(3), Cu1–N7 = 2.014(3) and Cu1–N10 = 2.018(3) Å. The square planar coordination sphere around the metal is augmented by four weakly bound keto oxygen atoms of the organic ligands (Fig. 1). The corresponding Cu–O distances Cu1–O1 = 2.807(6), Cu1–O2 = 2.786(4), Cu1–O3 = 2.783(4) and Cu1–O4 = 2.822(6) Å are however much longer than the Cu–N distances (Table 2). It should also be pointed out that the oxygen atoms act as acceptors of N–H···O hydrogen bonds (*vide infra*), which saturate the valences of the oxygen atoms. The Cu–O distances in the Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub> cations should thus be regarded as a sign of very weak interactions rather than actual metal-oxygen bonds, and the potentially bidentate ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one is here acting only in a monodentate fashion.

The crystal structure is organized in regions of cationic complexes that alternate with channels filled with the chlorine anions and the solvate water molecules. The cations are arranged in infinite pillars of individual complexes that interdigitate with their neighbors in the *c*-axis direction. Formation of the infinite chains is guided by shape recognition. Alternating molecules are rotated by 89.6°, which allows the methyl groups of the organic ligands to point into the voids between the aromatic rings of the next molecule. No strong directional forces are involved in the interactions between neighboring cationic complexes within these chains and no  $\pi$ - $\pi$  stacking interactions between the organic rings or C–H··· $\pi$  interactions towards them are observed. In the direction of the *a* and *b* axes the infinite chains alternate with channels filled with the chlorine anions and the interstitial water molecules (Figure 3). The water and chlorine atoms within the channels are tightly hydrogen bonded with each other through a range of strong O–H···O and O–H···Cl hydrogen bonds, which arranges the atoms in the channels into five-atom rings of each two chlorine atoms and three of the five interstitial water molecules (O6, O67 and O8). The two remaining interstitial water molecules (O5 and O9) connect to the Cl<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> rings through each one single O–H···O and O–H···Cl bond. Each of these Cl<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> assemblies is in turn connected with its counterparts along the direction of the channel rings (the *c*-direction), leading in total to an arrangement of chlorine ions and water molecules filling the channels as shown in Figure 4. The tight network of hydrogen bonds is however not limited to interactions between the water molecules and chlorine ions, but through N–H···O and N–H···Cl hydrogen bonds that originate from the ligands of the cations and O–H···O hydrogen bonds from the water molecules to the keto oxygen atoms the metal complexes are incorporated into the H-bonding network. For numerical details of the hydrogen bonding interactions and symmetry codes, see Table 3.

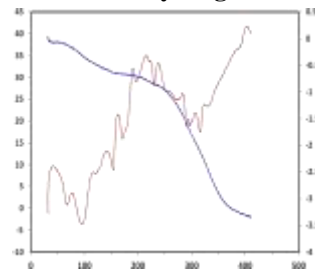
Within the organic ligand 2-amino-6-methylpyrimidin-4-(1*H*)-one, an examination of the bond length data shows that C4–O1 [1.243(4) Å], C9–O2 [1.260(4) Å], C14–O3 [1.251(4) Å] and C19–O4 [1.241(4) Å] can be attributed as having clear double bond character. This confirms that the title compound is present as the keto tautomer 2-amino-6-methylpyrimidin-4-(1*H*)-one rather than in the enol form 2-amino-6-methyl-4-pyrimidinol.



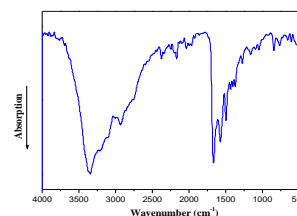
**Fig. 3**  
Crystal packing arrangement of [Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub>]Cl<sub>2</sub>.5H<sub>2</sub>O. The dotted lines indicate hydrogen bonds.



**Fig. 4**  
Arrangement of water and chlorine atoms in the channels along the *c*-axis direction. View down the *b*-axis. The dotted lines indicate hydrogen bonds.



**Fig. 5**  
DTA and TGA curves of [Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub>]Cl<sub>2</sub>.5H<sub>2</sub>O with rising temperature.



**Fig. 6**  
IR absorption spectrum of [Cu(C<sub>5</sub>H<sub>7</sub>N<sub>3</sub>O)<sub>4</sub>]Cl<sub>2</sub>.5H<sub>2</sub>O.

This observation agrees with the literature which shows that in polar solvents the quinonic form is more stable than the phenolic one [19]. The C–N bond distances of the NH<sub>2</sub> groups are 1.333(5) Å [N3–C1], 1.324(5) Å [N6–C6], 1.342(4) Å [N11–C9] and 1.336(5) Å [N12–C16] which are short for C–N single bonds, but still not quite as contracted as one would expect for a fully established C=N double bond. These bond length features are consistent with an imino resonance form as it is commonly found for a C–N single bond involving sp<sup>2</sup> hybridized C and N atoms [20, 21]. In agreement with this, the amino groups are not pyramidal but the electron density of the hydrogen atoms of the amino groups was found to be in plane with the 2-amino-6-methylpyrimidin-4-(1*H*)-one skeleton (in the

final crystal structure refinement the H atoms were placed in calculated positions assuming perfectly  $sp^2$  hybridized N atoms).

#### Thermal analysis

Two curves, corresponding to Differential Thermal Analysis, DTA, and Thermal Gravimetric Analyses, TGA, measured in open air, are given in Fig. 5. The DTA curve shows that the compound undergoes a series of endothermic transformations. The four first peaks, which occur between 65.9 and 151.4 °C, correspond to the complete dehydration of the compound. They are accompanied by the weight loss observed in the TGA curve. From the latter, we deduced a departure of five water molecules (weight loss calculated: 12.41%, experimentally observed in the TGA curve: 12.82%). Then the organic groups start to decompose over a wide temperature range (170-420 °C). This is also confirmed by the significant weight loss observed in the TGA. A black deposit of carbon is obtained at the end of the experiment.

#### IR spectroscopy investigations

The IR spectrum of crystalline  $[Cu(C_5H_7N_3O)_4]Cl_2 \cdot 5H_2O$  is shown in Fig. 6. The most representative and characteristic vibrational modes of this compound can be compared to those of similar compounds [22-24].

- In the high-frequency region, the very large band spreading between 3600 and 2500  $cm^{-1}$  corresponds to the valence vibrations of C-H, O-H and N-H groups interconnected by a system of hydrogen bonds in the crystal [25].
- The intense band at 1679  $cm^{-1}$  can be attributed to the C=O groups of the organic ligand [26], further supporting the presence of the 2-amino-6-methylpyrimidin-4-(1H)-one rather than the 2-amino-6-methyl-4-pyrimidinol starting material tautomer.
- Bands in the 1620 - 1100  $cm^{-1}$  region correspond to the N-H and O-H bending vibrations and to the valence vibrations of C=C, C-C, C=N and C-N groups [27].
- The observed bands in the range 1000 - 600  $cm^{-1}$  can be assigned to the  $CH_3$  and  $NH_2$  groups and to the skeleton of the amino-pyrimidione rings symmetric, asymmetric, stretching and deformation modes [28, 29].

#### Conclusions

A new Cu(II) complex with the potentially bidentate ligand 2-amino-6-methylpyrimidin-4-(1H)-one was synthesized and characterized by various physico-chemical methods. The monoclinic solid state structure exhibits substantial pseudosymmetry emulating an orthorhombic *Pccn* setting which is broken only by ordering of solvate water and chlorine anions in channels stretching along the *c*-axis of the unit cell. X-ray analysis reveals the Cu(II) atom to be square planar four-coordinated by four 2-amino-6-methylpyrimidin-4-(1H)-one ligands which do coordinate in a monodentate rather than bidentate fashion in this compounds. The presence of an intense band, in the IR spectrum, at 1679  $cm^{-1}$ , attributed to the C=O group, indicates presence of the keto tautomer 2-amino-6-methylpyrimidin-4-(1H)-one rather than the enol tautomer 2-amino-6-methyl-4-pyrimidinol. When heated, the title compound loses the five crystallization water molecules and then undergoes decomposition of the organic entity.

#### Supplementary material

Crystallographic data for the title compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-847478). These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12,

Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; mailto: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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**Table 1**  
**Crystallographic data and refinement details of the title compound**

Empirical formula	C <sub>20</sub> H <sub>28</sub> CuN <sub>12</sub> O <sub>4</sub> ·5(H <sub>2</sub> O)·2(Cl)
Formula weight	725.06
Temperature (K)	100
Crystal system	Monoclinic,
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	15.304 (4)
<i>b</i> (Å)	13.528 (3)
<i>c</i> (Å)	15.071 (4)
$\beta$ (°)	90.120 (5)
Mo K $\alpha$ radiation, $\lambda$ (Å)	0.71073
<i>V</i> (Å <sup>3</sup> )	3120.0 (13)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (Mg·m <sup>-3</sup> )	1.544
Crystal size (mm <sup>3</sup> )	0.19 × 0.15 × 0.06
Absorption correction	multi-scan
$\theta$ range for data collection (°)	2.4–30.7
Absorption coefficient (mm <sup>-1</sup> )	0.94
<i>F</i> (000)	1508
Reflections collected	28185
Independent reflections ( <i>R</i> <sub>int</sub> )	8298 (0.040)
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	6831
Goodness-of-fit -on <i>F</i> <sup>2</sup>	1.04
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.045, <i>wR</i> <sub>2</sub> = 0.111
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.060, <i>wR</i> <sub>2</sub> = 0.1021
Largest difference peak and hole (eÅ <sup>-3</sup> )	1.57 and -0.81

**Table 2**  
**Selected bond lengths (Å) and angle (°) for the studied compound**

Cu1—N1	1.997 (3)	Cu1—O1	2.807(6)
Cu1—N7	2.014 (3)	Cu1—O2	2.786(4)
Cu1—N10	2.018 (3)	Cu1—O3	2.783(4)
Cu1—N4	2.026 (3)	Cu1—O4	2.822(6)
N1—Cu1—N7	168.63 (11)	O1—Cu1—O4	121.58(8)
N1—Cu1—N10	90.96 (9)	O1—Cu1—O3	67.32(7)
N1—Cu1—N4	89.34 (11)	O1—Cu1—O2	151.24(8)
N4—Cu1—N7	89.93 (11)	O4—Cu1—O3	150.79(7)
N4—Cu1—N10	92.11 (9)	O4—Cu1—O2	66.53(7)
N7—Cu1—N10	168.13 (12)	O3—Cu1—O2	120.70(7)
O1—Cu1—N7	115.95(10)	O3—Cu1—N1	116.17(10)
O1—Cu1—N10	85.53(10)	O3—Cu1—N4	84.7(1)
O1—Cu1—N4	104.35(10)	O3—Cu1—N7	52.99(9)
O1—Cu1—N1	52.79(10)	O3—Cu1—N10	105.46(9)
O2—Cu1—N1	104.66(10)	O4—Cu1—N1	85.75(10)
O2—Cu1—N4	53.19(9)	O4—Cu1—N4	116.02(10)
O2—Cu1—N7	85.42(10)	O4—Cu1—N7	103.32(10)
O2—Cu1—N10	115.25(9)	O4—Cu1—N10	52.28(10)

**Table 3**  
**Hydrogen bond type interactions in the crystal structure of the studied compound.**

<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>
O9—H9A...Cl2	0.91 (2)	2.16 (2)	3.061 (3)	173 (5)
O9—H9B...O3 <sup>i</sup>	0.86 (2)	1.91 (2)	2.769 (4)	173 (5)
O8—H8A...O7	0.89 (2)	1.82 (3)	2.680 (5)	163 (5)
O8—H8B...Cl2	0.86 (2)	2.27 (2)	3.116 (3)	170 (5)
O7—H7A...Cl2 <sup>ii</sup>	0.86 (2)	2.28 (2)	3.116 (3)	165 (5)
O7—H7B...Cl1	0.87 (2)	2.30 (3)	3.084 (3)	151 (5)
O6—H6A...Cl1	0.88 (2)	2.23 (2)	3.089 (4)	164 (5)
O6—H6B...Cl2	0.87 (2)	2.32 (3)	3.136 (3)	156 (5)
O5—H5A...O2	0.83 (2)	1.96 (2)	2.771 (4)	165 (5)
O5—H5B...O6	0.86 (2)	1.97 (3)	2.788 (4)	159 (5)
N12—H12B...Cl1 <sup>iii</sup>	0.88	2.55	3.314 (3)	146
N12—H12A...O3	0.88	2.40	3.199 (4)	150
N12—H12A...O1	0.88	2.34	2.938 (4)	125
N11—H11...Cl1 <sup>iii</sup>	0.88	2.28	3.110 (3)	157
N9—H9D...O6 <sup>iv</sup>	0.88	2.14	2.995 (4)	165
N9—H9C...O2	0.88	2.40	2.983 (4)	124
N9—H9C...O4	0.88	2.32	3.130 (4)	153
N8—H8C...O5 <sup>iv</sup>	0.88	1.85	2.716 (4)	167
N6—H6D...Cl2 <sup>v</sup>	0.88	2.47	3.340 (3)	169
N6—H6C...O3	0.88	2.40	2.992 (4)	125
N6—H6C...O1	0.88	2.40	3.202 (4)	152
N5—H5...O9 <sup>v</sup>	0.88	1.90	2.760 (4)	166
N3—H3B...O7 <sup>vi</sup>	0.88	2.08	2.894 (4)	154
N3—H3A...O4	0.88	2.37	2.953 (4)	124
N3—H3A...O2	0.88	2.33	3.138 (4)	152
N2—H2...O8 <sup>vi</sup>	0.88	1.85	2.731 (4)	175

Symmetry codes: (i)  $x, y+1, z$ ; (ii)  $x, -y+3/2, z-1/2$ ; (iii)  $x, -y+1/2, z+1/2$ ; (iv)  $-x+1, y-1/2, -z+3/2$ ; (v)  $-x, y-1/2, -z+3/2$ ; (vi)  $x, -y+3/2, z+1/2$ .