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Crystal structure of poly[[aqua(μ_2-pyrazine-κ^2N:N')(μ_2-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylato-κ^2O^1:O^4)copper(II)] hemihydrate]

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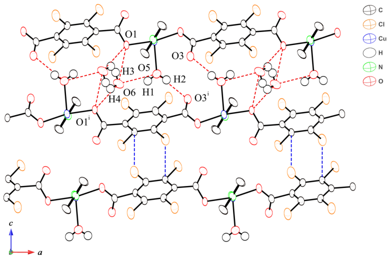
The asymmetric unit of the title compound, $\{[Cu_2(C_8Cl_4O_4)_2(C_4H_4N_2)_2(H_2O)_2]\cdot H_2O\}_n$ or $\{[Cu_2(Cl_4bdc)_2(pyz)_2(H_2O)_2]\cdot H_2O\}_n$ comprises of a Cu^{II} ion, one tetrachlorobenzenedicarboxylate ion (Cl_4bdc^{2-}), one pyrazine ligand (pyz), and one and a half water molecules. The Cu^{II} ion exhibits a five-coordinated square-pyramidal geometry with a CuN_2O_3 coordination environment comprising two oxygen atoms of the Cl_4bdc^{2-} ligands, one oxygen atom of a water molecule, and two nitrogen atoms of the pyz ligands. The carboxylate group is almost perpendicular to the benzene ring and shows monodentate coordination to the Cu^{II} ion. The Cu^{II} ions of these units are bridged by both the Cl_4bdc^{2-} and pyz ligands to form two-dimensional (2D) layers, which are linked by alternating hydrogen-bonding and C—Cl···π interactions to yield a three-dimensional network.



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1. Chemical context

Metal–organic frameworks (MOFs) or coordination polymers (CPs) consist of infinite assemblies of metal ions bridged by organic linkers such as benzendicarboxylate dianions and are attracting much interest due to their applications, for example in gas adsorption, and their optical and magnetic properties (Eddaoudi *et al.*, 2002; Cheetham *et al.*, 1999; Lacroix & Nakatani, 1997; Kitagawa *et al.*, 2004; Kurmoo, 2009). We have prepared electrode materials using a benzendicarboxylate dianion and its analogues (Ogihara *et al.*, 2014, 2023; Yasuda & Ogihara, 2014; Ozawa *et al.*, 2018; Mikita *et al.*, 2020), and also magnetic materials that involve polycarboxylates in which the number of carboxylate groups and the distances between them are systematically varied (Kumagai *et al.*, 2001, 2002, Kurmoo *et al.*, 2001, 2003, 2005). The selection of metal ions and appropriate bridging ligands is fundamental for the development of a rational synthetic method to prepare these functional materials. We have reported the fine tuning of crystal structures and the properties of these materials, where not only are the metal ions systematically changed, but also the halogen atoms attached to the benzene ring of benzenedicarboxylate dianions (R_4bdc^{2-}; R = H, F, Cl, Br) with pyrazine (pyz) or 4,4′-bipyridine (bpy) as co-bridging ligands (Kumagai *et al.*, 2012, 2021). Among the M/Br_4bdc^{2-}/pyz (M = Co^{II}, Cu^{II}, Zn^{II}) systems, the Cu^{II} compound showed a different structure and water adsorption/desorption properties due to the different coordination geometry around the Cu^{II} ion (Kumagai *et al.*, 2021). In this contribution, we focus on the use of the Cl_4bdc^{2-} dianion and pyz as a co-bridging ligand in the synthesis of a Cu^{II}–Cl_4bdc^{2-} dianion system to

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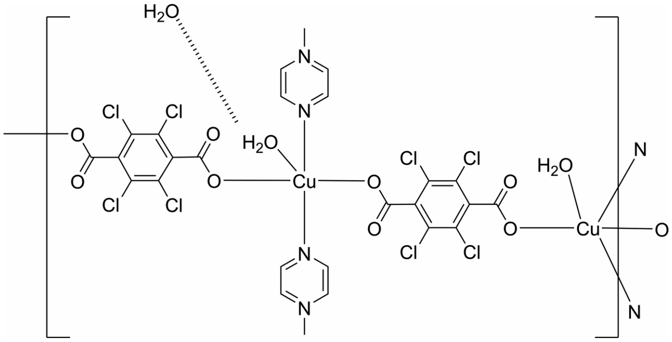
observe the structural change that results from the substitution of Br$_4$bdc^{2-} for Cl$_4$bdc^{2-}. Here, we report on the single-crystal structure of [Cu$_2$(Cl$_4$bdc)$_2$(pyz)$_2$(H$_2$O)$_2$](H$_2$O).



2. Structural commentary

The asymmetric unit of the title compound, [Cu$_2$(Cl$_4$bdc)$_2$(pyz)$_2$(H$_2$O)$_2$](H$_2$O), consists of one Cu^{II} ion, one Cl$_4$bdc^{2-} dianion, one pyz ligand, one water molecule coordinated by the metal and ahalf water molecule of crystallization. The key feature of the structure is a two-dimensional (2D) coordination polymer in which CuN$_2$O$_3$ square pyramids bridged by Cl$_4$bdc^{2-} and pyz ligands are arranged in a lyaer, as shown in Fig. 1. The Cu^{II} ion is penta-coordinated with a square-pyramidal geometry. Pairs of Cl$_4$bdc^{2-} and pyz ligands are coordinated *trans* to each other to give the basal plane of the pyramid, while the coordinated water molecule occupies the apical position. The carboxylate group exhibits monodentate coordination, and the dihedral angle between the benzene ring and the carboxylate group is roughly orthogonal [C6—C1—C7—O1 105.5 (3)°]. We have recently reported a series of 2D layer compounds involving M^{II} cations (M = Co, Cu, Zn), the tetrabromobenzenedicarboxylate ligand (Br$_4$bdc^{2-}) and pyz as co-bridging ligands (Kumagai *et al.*, 2021). While the metal ions exhibit octahedral coordination environments in these complexes, the Cu^{II} ion of the title compound has a square-pyramidal geometry. The 2D layers of [M(Br$_4$bdc)(pyz)(H$_2$O)] (M = Co, Zn) include pyz molecules between the layers to give [M(Br$_4$bdc)(pyz)(H$_2$O)$_2$](pyz) by hydrogen-bonding and π–π stacking interactions. On the other hand, the [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] layers contain water molecules due to elongation of the Cu—O(H$_2$O) bond, which prevents the π–π stacking interactions of the pyz molecules. The Cu—O(H$_2$O) bond length of 2.301 (2) Å in the title compound is longer than that of [M(Br$_4$bdc)(pyz)(H$_2$O)$_2$] [M = Co 2.096 (4) Å, Zn 2.090 (3) Å], but shorter than that in [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] [2.487 (4) Å]. The Cu—N bond lengths of 2.015 (2) and 2.019 (2) Å are similar to that in [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] [2.012 (3) Å]. The Cu···Cu separations defined by Cu–Cl$_4$bdc^{2-}–Cu connectivity and Cu–pyz–Cu connectivity within the chain are 10.98 and 6.78 Å, respectively. While the Cu···Cu distance in Cu–pyz–Cu is similar to that in [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] (6.79 Å), the separation for Cu–Cl$_4$bdc^{2-}–Cu is slightly shorter than that in [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] (11.14 Å). It has been reported that the synthesis of metal complexes using Cl$_4$bdc^{2-} gives different structures depending on the synthetic conditions employed (Chen *et al.*, 2011, 2014). The title compound was synthesized by the same procedure as that used for the synthesis of the M/Br$_4$bdc^{2-}/pyz (M = Co^{II}, Cu^{II}, Zn^{II}) systems; therefore, it is considered that the structural differences are attributable to the halogen atoms attached to the benzene ring. A similar coordination network, [Cu(Cl$_4$bdc)(dioxane)(H$_2$O)$_2$]·(dioxane), with dioxane as co-bridging ligand instead of pyz, has previously been synthesized using different synthetic conditions (He *et al.*, 2009). The Cu^{II} ion exhibits an octahedral coordination environment and an almost rectangular 2D framework with dimensions of *ca*. 11.1 × 7.9 Å defined by the Cu···Cu separation. Although the Cu···Cu distance for Cu–Cl$_4$bdc^{2-}–Cu in [Cu(Cl$_4$bdc)(dioxane)(H$_2$O)$_2$] is similar to that for the title compound, the Cu···Cu distance for Cu–dioxane–Cu is longer than that for Cu–pyz–Cu due to the large Cu—O(dioxane) bond length of 2.575 (2) Å.

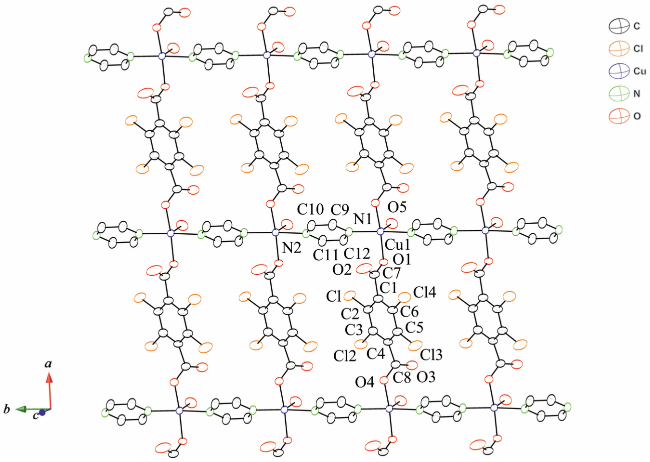


Figure 1
The two-dimensional layered structure of the title compound with the atom-labelling scheme and 50% probability displacement ellipsoids. Hydrogen atoms and the water molecules of crystallization are omitted for clarity.

3. Supramolecular features

There are two types of interactions between the 2D networks in the crystal structure, namely hydrogen-bonding and other C—Cl···π interactions. The hydrogen-bonding interactions involve water molecules and carboxylate groups. The coordinated water molecules act as hydrogen-bonding donors and the non-coordinated oxygen atoms of the carboxylate groups of the Cl$_4$bdc^{2-} ligands in the adjacent 2D layer act as hydrogen-bonding acceptors (Fig. 2, Table 1). The coordinated water molecules also act as hydrogen-bonding donors for the water molecules of crystallization. These molecules, in turn, form hydrogen-bonding interactions with the coordinated oxygen atoms of the Cl$_4$bdc^{2-} ligands in the adjacent 2D layers. The other characteristic feature of the structure is C—Cl···π interactions between the 2D layers. The distances

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1···O6	0.79 (2)	2.11 (3)	2.781 (7)	143 (4)
O5—H2···O3^{i}	0.82 (2)	2.03 (3)	2.827 (3)	163 (5)
O6—H3···O1	0.82 (2)	2.04 (5)	2.763 (6)	147 (8)
O6—H4···O1^{i}	0.82 (2)	2.07 (4)	2.843 (6)	156 (10)

Symmetry code: (i) $-x, -y+1, -z+1$.

Cl3···C6^{ii} [3.370 (3) Å, symmetry code: (ii) $-x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{3}{2}$] and Cl3···centroid of the phenyl ring [3.745 (9) Å] are indicative of C—Cl···π interactions (Gilday *et al.*, 2015). The layers are thus alternately stacked by hydrogen-bonding and C—Cl···π interactions to form a 3D network. The 2D layers in [Cu(Br$_4$bdc)(pyz)(H$_2$O)$_2$] form a 3D network solely by hydrogen-bonding interactions *via* water molecules between the 2D layers in which Cu^{II} ions exhibit an octahedral coordination geometry. Chemical modification by replacement of the halogen atoms results not only in different coordination geometries of the Cu^{II} ions, but also in different inter-layer interactions.

4. Database survey

A search of the SciFinder database for structures with Cl$_4$bdc^{2-}, pyz ligands, and Cu^{II} ions resulted in no complete matches. A search of the Web of Science database for the keywords 2,4,5,6-tetrachloro-1,3-benzenedicarboxylic acid and copper led to two publications that include dimethylformamide (FUDPUQ), pyridine (XUWRAJ, FUDPIE) and dioxane (FUDPOK) as co-ligands (He *et al.*, 2009; Zheng *et al.*, 2009).

5. Synthesis and crystallization

An aqueous solution (5 mL) of copper(II) nitrate trihydrate (0.24 g, 1.0 mmol) was transferred to a glass tube, and an ethanol–water (1:1) mixture (5 mL) of 2,3,5,6-tetrachlorobenzenedicarboxylic acid (0.30 g, 1.0 mmol), NaOH (0.16 g, 2.0 mmol), and pyrazine (0.08 g, 1.0 mmol) was poured into the glass tube without the two solutions being mixed. Blue crystals began to form at ambient temperature in 1 week. One of these crystals was used for X-ray diffraction analysis.

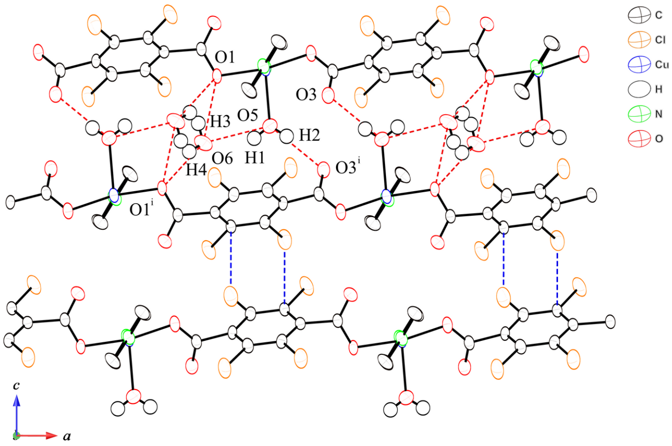


Figure 2
View of inter-molecular hydrogen-bonding and C—Cl···π interactions along the *b* axis, represented by red and blue dashed lines, respectively.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Cu$_2$(C$_8$Cl$_4$O$_4$)$_2$(C$_4$H$_4$N$_2$)$_2$-(H$_2$O)$_2$]·H$_2$O
M_r	945.07
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, *b*, *c* (Å)	10.975 (3), 6.7837 (15), 21.803 (4)
β (°)	90.222 (14)
V (Å^3)	1623.3 (6)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	2.03
Crystal size (mm)	0.20 × 0.20 × 0.20
Data collection	
Diffractometer	Rigaku Mercury70
Absorption correction	Multi-scan (*REQAB*; Rigaku, 2008)
T_{min}, T_{max}	0.429, 0.666
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15268, 3684, 3391
R_{int}	0.030
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.109, 1.18
No. of reflections	3684
No. of parameters	242
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.49, −0.67

Computer programs: *CrystalClear* (Rigaku, 2008), *SIR92* (Altomare *et al.*, 1994), *SHELXL2018/3* (Sheldrick, 2015) and *Yadokari-XG 2009* (Wakita, 2009).

6. Refinement

The crystal data, data collection, and structure refinement details are summarized in Table 2. The hydrogen atoms attached to water molecules were extracted from difference-Fourier maps and refined isotropically. Other hydrogen atoms were located at ideal positions and were refined using a riding model.

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supporting information

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Crystal structure of poly[[aqua(μ_2-pyrazine-κ^2N:N')(μ_2-2,3,5,6-tetrachloro-benzene-1,4-dicarboxylato-κ^2O^1:O^4)copper(II)] hemihydrate]

Hitoshi Kumagai, Satoshi Kawata and Nobuhiro Ogihara

Computing details

Poly[[aqua(μ_2-pyrazine-κ^2N:N')(μ_2-2,3,5,6-tetrachlorobenzene-1,4-dicarboxylato-κ^2O^1:O^4)copper(II)] hemihydrate]

Crystal data

$[Cu_2(C_8Cl_4O_4)_2(C_4H_4N_2)_2(H_2O)_2]\cdot H_2O$
M_r = 945.07
Monoclinic, $P2_1/n$
a = 10.975 (3) Å
b = 6.7837 (15) Å
c = 21.803 (4) Å
β = 90.222 (14)°
V = 1623.3 (6) Å^3
Z = 2
$F(000)$ = 936
D_x = 1.934 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.7107 Å
Cell parameters from 4544 reflections
θ = 1.9–30.1°
μ = 2.03 mm^{-1}
T = 293 K
Prism, colorless
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku Mercury70 diffractometer
Detector resolution: 7.314 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 2008)
T_{min} = 0.429, T_{max} = 0.666
15268 measured reflections
3684 independent reflections
3391 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.5°, θ_{min} = 1.9°
h = −14→13
k = −8→8
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.109
S = 1.18
3684 reflections
242 parameters
5 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 1.5531P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

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	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Cu1	0.27764 (2)	0.62427 (4)	0.61712 (2)	0.01913 (11)	
Cl1	−0.09180 (7)	0.98567 (12)	0.58342 (4)	0.0420 (2)	
Cl2	−0.37150 (7)	0.92147 (13)	0.56485 (4)	0.0442 (2)	
Cl3	−0.34867 (7)	0.25931 (14)	0.69731 (4)	0.0493 (2)	
Cl4	−0.07035 (7)	0.31868 (14)	0.71717 (4)	0.0443 (2)	
O1	0.10094 (16)	0.6243 (3)	0.60367 (9)	0.0232 (4)	
O2	0.0908 (2)	0.7070 (5)	0.70164 (10)	0.0573 (8)	
O3	−0.49156 (19)	0.4414 (4)	0.56869 (10)	0.0404 (5)	
O4	−0.55433 (17)	0.6298 (3)	0.64610 (9)	0.0256 (4)	
O5	0.2948 (2)	0.6265 (4)	0.51195 (10)	0.0379 (5)	
O6	0.0506 (6)	0.5848 (12)	0.4800 (3)	0.0692 (19)	0.5
N1	0.27784 (19)	0.9216 (3)	0.62098 (10)	0.0217 (4)	
N2	0.27117 (19)	1.3279 (3)	0.62254 (10)	0.0222 (4)	
C1	−0.0938 (2)	0.6454 (4)	0.64777 (11)	0.0247 (5)	
C2	−0.1622 (2)	0.7822 (4)	0.61483 (12)	0.0259 (5)	
C3	−0.2862 (2)	0.7553 (4)	0.60668 (12)	0.0265 (5)	
C4	−0.3430 (2)	0.5911 (4)	0.63065 (12)	0.0231 (5)	
C5	−0.2765 (2)	0.4576 (4)	0.66547 (12)	0.0259 (5)	
C6	−0.1519 (2)	0.4851 (4)	0.67378 (11)	0.0252 (5)	
C7	0.0433 (2)	0.6632 (4)	0.65330 (12)	0.0258 (5)	
C8	−0.4746 (2)	0.5481 (4)	0.61336 (12)	0.0239 (5)	
C9	0.3304 (3)	1.0246 (4)	0.66616 (13)	0.0296 (6)	
H9	0.370398	0.957881	0.697589	0.036*	
C10	0.3264 (3)	1.2270 (4)	0.66709 (12)	0.0278 (6)	
H10	0.362814	1.294764	0.699390	0.033*	
C11	0.2177 (3)	1.2256 (4)	0.57790 (13)	0.0298 (6)	
H11	0.177402	1.292424	0.546606	0.036*	
C12	0.2209 (3)	1.0233 (4)	0.57707 (13)	0.0289 (6)	
H12	0.182535	0.955829	0.545269	0.035*	
H1	0.239 (3)	0.641 (6)	0.4894 (16)	0.044 (11)*	
H2	0.361 (3)	0.605 (8)	0.495 (2)	0.082 (18)*	
H3	0.035 (8)	0.592 (14)	0.5168 (12)	0.06 (3)*	0.5
H4	−0.003 (7)	0.515 (16)	0.465 (4)	0.09 (4)*	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01352 (17)	0.01482 (18)	0.02901 (18)	−0.00014 (10)	−0.00327 (11)	0.00023 (10)
Cl1	0.0272 (4)	0.0395 (4)	0.0592 (5)	−0.0092 (3)	−0.0032 (3)	0.0149 (3)

Cl2	0.0246 (4)	0.0445 (5)	0.0635 (5)	0.0030 (3)	−0.0061 (3)	0.0237 (4)
Cl3	0.0308 (4)	0.0530 (5)	0.0641 (5)	−0.0112 (3)	−0.0074 (4)	0.0311 (4)
Cl4	0.0297 (4)	0.0493 (5)	0.0539 (5)	0.0032 (3)	−0.0152 (3)	0.0175 (4)
O1	0.0121 (8)	0.0272 (10)	0.0302 (9)	0.0003 (6)	−0.0014 (7)	−0.0035 (7)
O2	0.0293 (12)	0.115 (2)	0.0270 (10)	−0.0183 (14)	−0.0058 (9)	−0.0104 (13)
O3	0.0232 (10)	0.0596 (15)	0.0383 (11)	−0.0023 (10)	−0.0007 (8)	−0.0149 (11)
O4	0.0152 (8)	0.0243 (10)	0.0371 (10)	0.0004 (7)	−0.0032 (7)	−0.0024 (7)
O5	0.0334 (12)	0.0501 (14)	0.0302 (11)	0.0059 (10)	0.0029 (9)	0.0006 (9)
O6	0.052 (3)	0.119 (6)	0.036 (3)	−0.019 (4)	−0.012 (2)	−0.021 (3)
N1	0.0211 (11)	0.0159 (10)	0.0282 (11)	−0.0002 (8)	−0.0051 (8)	0.0002 (8)
N2	0.0203 (10)	0.0165 (10)	0.0299 (11)	−0.0012 (8)	−0.0042 (8)	0.0014 (8)
C1	0.0153 (11)	0.0380 (15)	0.0209 (11)	−0.0011 (10)	−0.0011 (9)	−0.0031 (10)
C2	0.0171 (12)	0.0313 (14)	0.0293 (12)	−0.0034 (10)	0.0022 (9)	0.0011 (10)
C3	0.0195 (12)	0.0288 (14)	0.0312 (13)	0.0022 (10)	−0.0034 (10)	0.0021 (10)
C4	0.0117 (11)	0.0312 (14)	0.0264 (12)	0.0004 (9)	0.0008 (9)	−0.0009 (10)
C5	0.0170 (12)	0.0333 (14)	0.0274 (12)	−0.0018 (10)	0.0010 (9)	0.0037 (11)
C6	0.0148 (11)	0.0358 (15)	0.0249 (12)	0.0018 (10)	−0.0015 (9)	0.0018 (10)
C7	0.0143 (11)	0.0370 (15)	0.0261 (12)	−0.0030 (10)	−0.0017 (9)	0.0007 (11)
C8	0.0154 (11)	0.0272 (13)	0.0290 (12)	−0.0005 (10)	−0.0032 (9)	0.0032 (10)
C9	0.0359 (15)	0.0220 (13)	0.0308 (13)	−0.0010 (11)	−0.0131 (11)	0.0036 (10)
C10	0.0334 (14)	0.0216 (13)	0.0284 (12)	−0.0032 (11)	−0.0099 (11)	0.0005 (10)
C11	0.0350 (15)	0.0206 (13)	0.0335 (13)	−0.0004 (11)	−0.0173 (11)	0.0023 (10)
C12	0.0317 (14)	0.0201 (13)	0.0348 (14)	−0.0006 (11)	−0.0143 (11)	0.0010 (10)

Geometric parameters (Å, º)

Cu1—O4^{i}	1.9475 (19)	N1—C9	1.336 (3)
Cu1—O1	1.9603 (18)	N2—C11	1.330 (3)
Cu1—N2^{ii}	2.015 (2)	N2—C10	1.332 (3)
Cu1—N1	2.019 (2)	C1—C6	1.383 (4)
Cu1—O5	2.301 (2)	C1—C2	1.392 (4)
Cl1—C2	1.725 (3)	C1—C7	1.514 (3)
Cl2—C3	1.724 (3)	C2—C3	1.384 (4)
Cl3—C5	1.710 (3)	C3—C4	1.381 (4)
Cl4—C6	1.722 (3)	C4—C5	1.387 (4)
O1—C7	1.283 (3)	C4—C8	1.520 (3)
O2—C7	1.211 (3)	C5—C6	1.392 (3)
O3—C8	1.227 (3)	C9—C10	1.374 (4)
O4—C8	1.260 (3)	C9—H9	0.9300
O5—H1	0.791 (19)	C10—H10	0.9300
O5—H2	0.82 (2)	C11—C12	1.373 (4)
O6—H3	0.82 (2)	C11—H11	0.9300
O6—H4	0.82 (2)	C12—H12	0.9300
N1—C12	1.334 (3)		

O4^{i}—Cu1—O1	169.61 (8)	C4—C3—Cl2	118.9 (2)
O4^{i}—Cu1—N2^{ii}	91.93 (8)	C2—C3—Cl2	120.9 (2)
O1—Cu1—N2^{ii}	88.49 (8)	C3—C4—C5	119.8 (2)

O4^{i}—Cu1—N1	88.08 (8)	C3—C4—C8	119.4 (2)
O1—Cu1—N1	90.41 (8)	C5—C4—C8	120.5 (2)
N2^{ii}—Cu1—N1	173.91 (9)	C4—C5—C6	119.9 (2)
O4^{i}—Cu1—O5	104.00 (9)	C4—C5—Cl3	119.49 (19)
O1—Cu1—O5	86.33 (8)	C6—C5—Cl3	120.6 (2)
N2^{ii}—Cu1—O5	93.91 (9)	C1—C6—C5	120.4 (2)
N1—Cu1—O5	91.99 (9)	C1—C6—Cl4	120.08 (19)
C7—O1—Cu1	111.38 (16)	C5—C6—Cl4	119.5 (2)
C8—O4—Cu1^{iii}	117.82 (17)	O2—C7—O1	124.9 (2)
Cu1—O5—H1	124 (3)	O2—C7—C1	120.9 (2)
Cu1—O5—H2	121 (4)	O1—C7—C1	114.2 (2)
H1—O5—H2	115 (5)	O3—C8—O4	127.3 (2)
H3—O6—H4	105 (5)	O3—C8—C4	116.8 (2)
C12—N1—C9	117.3 (2)	O4—C8—C4	115.9 (2)
C12—N1—Cu1	119.10 (18)	N1—C9—C10	121.3 (2)
C9—N1—Cu1	123.59 (18)	N1—C9—H9	119.4
C11—N2—C10	117.6 (2)	C10—C9—H9	119.4
C11—N2—Cu1^{iv}	119.57 (18)	N2—C10—C9	121.2 (2)
C10—N2—Cu1^{iv}	122.65 (18)	N2—C10—H10	119.4
C6—C1—C2	119.2 (2)	C9—C10—H10	119.4
C6—C1—C7	119.3 (2)	N2—C11—C12	121.4 (2)
C2—C1—C7	121.5 (2)	N2—C11—H11	119.3
C3—C2—C1	120.4 (2)	C12—C11—H11	119.3
C3—C2—Cl1	119.8 (2)	N1—C12—C11	121.3 (2)
C1—C2—Cl1	119.8 (2)	N1—C12—H12	119.4
C4—C3—C2	120.2 (2)	C11—C12—H12	119.4

C6—C1—C2—C3	−1.9 (4)	Cl3—C5—C6—Cl4	−0.6 (3)
C7—C1—C2—C3	175.3 (2)	Cu1—O1—C7—O2	4.4 (4)
C6—C1—C2—Cl1	178.7 (2)	Cu1—O1—C7—C1	−174.14 (18)
C7—C1—C2—Cl1	−4.1 (4)	C6—C1—C7—O2	−73.1 (4)
C1—C2—C3—C4	−0.7 (4)	C2—C1—C7—O2	109.7 (4)
Cl1—C2—C3—C4	178.8 (2)	C6—C1—C7—O1	105.5 (3)
C1—C2—C3—Cl2	−178.9 (2)	C2—C1—C7—O1	−71.6 (4)
Cl1—C2—C3—Cl2	0.6 (3)	Cu1^{iii}—O4—C8—O3	−10.5 (4)
C2—C3—C4—C5	3.1 (4)	Cu1^{iii}—O4—C8—C4	168.05 (17)
Cl2—C3—C4—C5	−178.7 (2)	C3—C4—C8—O3	91.6 (3)
C2—C3—C4—C8	−170.9 (2)	C5—C4—C8—O3	−82.4 (3)
Cl2—C3—C4—C8	7.3 (4)	C3—C4—C8—O4	−87.1 (3)
C3—C4—C5—C6	−2.9 (4)	C5—C4—C8—O4	98.9 (3)
C8—C4—C5—C6	171.0 (2)	C12—N1—C9—C10	−0.4 (4)
C3—C4—C5—Cl3	177.6 (2)	Cu1—N1—C9—C10	−179.0 (2)
C8—C4—C5—Cl3	−8.4 (4)	C11—N2—C10—C9	1.5 (4)
C2—C1—C6—C5	2.0 (4)	Cu1^{iv}—N2—C10—C9	−173.5 (2)
C7—C1—C6—C5	−175.2 (2)	N1—C9—C10—N2	−0.8 (5)
C2—C1—C6—Cl4	−177.6 (2)	C10—N2—C11—C12	−1.1 (4)
C7—C1—C6—Cl4	5.2 (3)	Cu1^{iv}—N2—C11—C12	174.1 (2)
C4—C5—C6—C1	0.3 (4)	C9—N1—C12—C11	0.8 (4)

Cl3—C5—C6—C1	179.8 (2)	Cu1—N1—C12—C11	179.5 (2)
C4—C5—C6—Cl4	179.9 (2)	N2—C11—C12—N1	−0.1 (5)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1···O6	0.79 (2)	2.11 (3)	2.781 (7)	143 (4)
O5—H2···O3^{v}	0.82 (2)	2.03 (3)	2.827 (3)	163 (5)
O6—H3···O1	0.82 (2)	2.04 (5)	2.763 (6)	147 (8)
O6—H4···O1^{v}	0.82 (2)	2.07 (4)	2.843 (6)	156 (10)

Symmetry code: (v) −*x*, −*y*+1, −*z*+1.