metal-organic compounds

Diaquadichlorido[5-(3-pyridinio)tetrazolato-κN^2]copper(II) dihydrate

Bo Wang

Ordered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China
Correspondence e-mail: fudavid88@yahoo.com.cn

The title compound, $[CuCl_2(C_6H_5N_5)_2(H_2O)_2]\cdot 2H_2O$, was synthesized by hydrothermal reaction of $CuCl_2$ with 3-(2H-tetrazol-5-yl)pyridine. The Cu^{II} cation, located on an inversion center, is coordinated by two Cl^- ions, two N atoms from two 5-(3-pyridinio)tetrazolate zwitterions and two O atoms from two water molecules in a distorted octahedral geometry. In the crystal, molecules are linked into a two-dimensional sheet parallel to (001) by N—H⋯N, O—H⋯N, O—H⋯O and O—H⋯Cl hydrogen bonds involving the pyridinium N atom, the Cl atoms and the coordinated and free water molecules. The latter are disordered over two positions in a 0.54:0.46 ratio.

Related literature

For general background to metal-organic coordination compounds, see: Chen *et al.* (2000, 2001); Fu & Xiong (2008); Fu *et al.* (2007); Liu *et al.* (1999); Xie *et al.* (2002, 2003); Zhang *et al.* (2001); Zhao *et al.* (2004). For related structures, see: Wang *et al.* (2005); Fu *et al.* (2008).
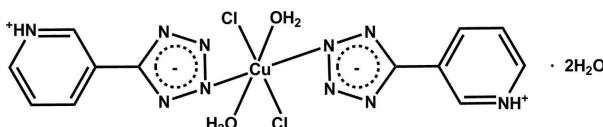
Experimental

Crystal data

$[CuCl_2(C_6H_5N_5)_2(H_2O)_2]\cdot 2H_2O$
M_r = 500.80
Triclinic, $P\bar{1}$
a = 6.5484 (13) Å
b = 8.3348 (17) Å
c = 9.1215 (18) Å
α = 99.54 (3)°
β = 110.22 (3)°

γ = 91.73 (3)°
V = 458.64 (19) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.53 mm^{-1}
T = 298 K
$0.15 \times 0.10 \times 0.10$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 T_{min} = 0.85, T_{max} = 1.00
 (expected range = 0.729–0.858)

4880 measured reflections
2103 independent reflections
1953 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.114
S = 1.31
2103 reflections

142 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯N4^i	0.86	1.96	2.763 (4)	155
O1W—H11W⋯O2WA	0.85	1.91	2.663 (7)	146
O1W—H11W⋯O2WB	0.85	2.08	2.779 (9)	139
O1W—H12W⋯Cl1^{ii}	0.85	2.42	3.233 (3)	161
O2WA—H1WA⋯N2	0.85	2.07	2.906 (8)	168
O2WB—H1WB⋯Cl1^i	0.85	2.46	3.259 (9)	156

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2471).

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supporting information

Diaquadichlorido[5-(3-pyridinio)tetrazolato-*κN*²]copper(II) dihydrate

Bo Wang

S1. Comment

The construction of metal-organic coordination compounds has attracted much attention owing to the potential functions, such as permittivity, fluorescence, magnetism and optical properties. (Chen *et al.*, 2000; Chen *et al.*, 2001; Fu *et al.*, 2007; Fu & Xiong 2008; Liu *et al.*, 1999; Xie *et al.*, 2003; Xie *et al.*, 2002; Zhang *et al.*, 2001; Zhao *et al.*, 2004) Tetrazole compounds are a class of excellent ligands for the construction of novel metal-organic frameworks, because of its various coordination modes. (Wang, *et al.* 2005; Fu *et al.*, 2008). We report here the crystal structure of the title compound, Diaqua-dichlorido[pyridinio-3-(2*H*-tetrazolato)-*κN*] copper(II) dihydrate.

The Cu^{II} cation, located on an inversion center, is coordinated by two Cl⁻ ions, two N atoms from two pyridinio-4-(2H-tetrazolate) zwitterions and two O atoms from two water molecules in a distorted octahedral geometry. The pyridine N atom of the organic ligand is protonated. The pyridinium and tetrazolate rings are essentially coplanar, with a dihedral angle of 0.76 (1)°. The geometric parameters of the tetrazolate ring are comparable to those in related molecules (Wang, *et al.* 2005; Fu *et al.*, 2008).

The molecules are linked into a two-dimensional sheet parallel to the (0 0 1) plane by intermolecular N—H···N, O-H···N, O-H···O and O-H···Cl hydrogen bonds involving the pydine nitrogen and the coordinated and free water molecules. (Table 1 and Fig.2).

S2. Experimental

A mixture of 3-(2*H*-tetrazol-5-yl)pyridine (0.2 mmol), CuCl$_2$ (0.4 mmol), distilled water (1 ml) and a few drops of HCl (6 mol/L) was sealed in a glass tube and maintained at 323 K. Blue block-shaped crystals suitable for X-ray analysis were obtained after 3 d.

S3. Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å and N—H = 0.86 Å with $U_{iso}(H) = 1.2U_{eq}(C$ or N). H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O-H= 0.85 (1)Å and H···H= 1.39 (2)Å) with $U_{iso}(H) = 1.5U_{eq}(O)$. In the last stage of refinement, these H atoms were treated as riding on their parent O atom.

The free water molecule was found to be roughly staistically disoredered over two positions. H atoms for this disordered molecules were treated as above.
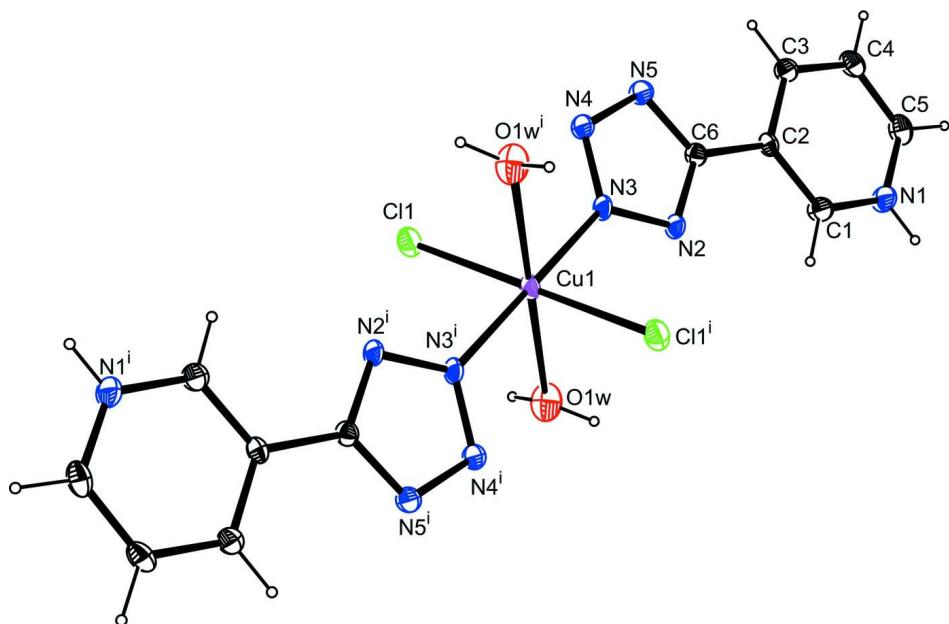
Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small sphere of arbitrary radii. Free water molecules have been omitted for clarity. [Symmetry codes: (i) -x+1, -y+1, -z+1].
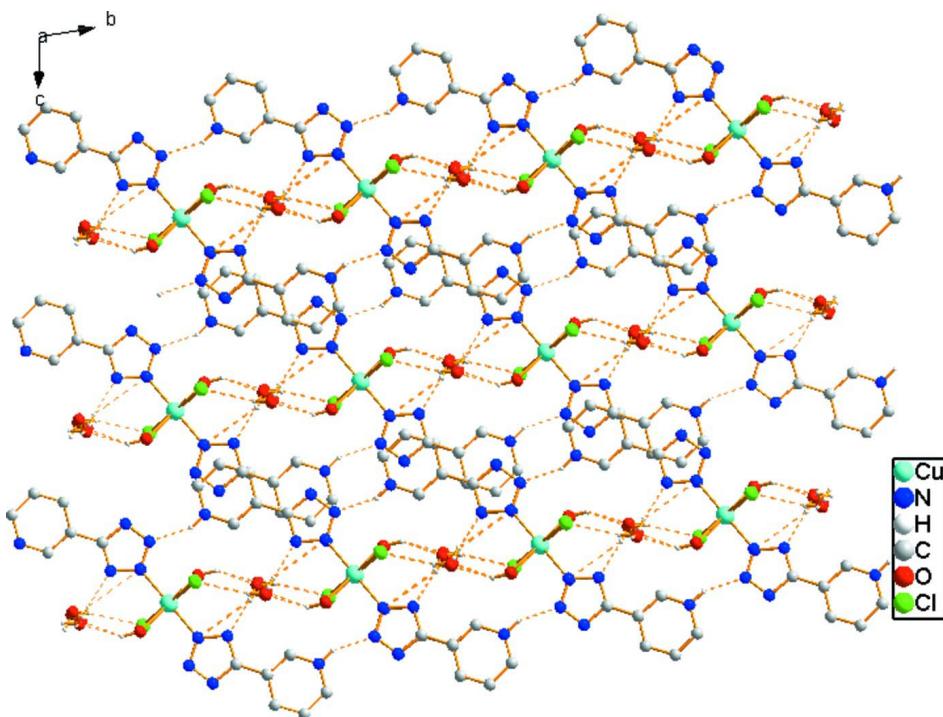
Figure 2

The crystal packing of the title compound, viewed along the *c* axis, showing the two dimensionnal hydrogen-bonded network. H atoms not involved in hydrogen bonding (dashed line) have been omitted for clarity.

Diaquadichlorido[5-(3-pyridinio)tetrazolato-*κN²*]copper(II) dihydrate

Crystal data

[CuCl₂(C₆H₅N₅)₂(H₂O)₂]·2H₂O	$Z = 1$
$M_r = 500.80$	$F(000) = 255$
Triclinic, $P\overline{1}$	$D_x = 1.813$ Mg m⁻³
Hall symbol: -P 1	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$a = 6.5484$ (13) Å	Cell parameters from 1953 reflections
$b = 8.3348$ (17) Å	$\theta = 3.1$–27.5°
$c = 9.1215$ (18) Å	$\mu = 1.53$ mm⁻¹
$\alpha = 99.54$ (3)°	$T = 298$ K
$\beta = 110.22$ (3)°	Block, blue
$\gamma = 91.73$ (3)°	0.15 × 0.10 × 0.10 mm
$V = 458.64$ (19) Å³	

Data collection

Rigaku Mercury2 diffractometer	4880 measured reflections
Radiation source: fine-focus sealed tube	2103 independent reflections
Graphite monochromator	1953 reflections with $I > 2\sigma(I)$
Detector resolution: 13.6612 pixels mm⁻¹	$R_{int} = 0.037$
CCD profile fitting scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$h = -8 \rightarrow 8$
	$k = -10 \rightarrow 10$
$T_{min} = 0.85$, $T_{max} = 1.00$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.114$	
$S = 1.31$	H-atom parameters constrained
2103 reflections	$w = 1/[\sigma^2(F_o^2) + 1.0933P]$
142 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.33$ e Å⁻³
	$\Delta\rho_{min} = -0.43$ 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.

Refinement. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2sigma(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.5000	0.5000	0.5000	0.02259 (18)	
N1	0.2750 (6)	−0.3207 (4)	0.0634 (4)	0.0311 (7)	
H1	0.3009	−0.3948	0.1211	0.037*	

N2	0.3845 (5)	0.1765 (3)	0.2805 (4)	0.0228 (6)	
N3	0.3946 (5)	0.3381 (3)	0.2979 (3)	0.0226 (6)	
N4	0.3283 (5)	0.3805 (4)	0.1585 (4)	0.0259 (7)	
N5	0.2733 (6)	0.2488 (4)	0.0467 (4)	0.0268 (7)	
C1	0.3091 (7)	−0.1653 (5)	0.1350 (5)	0.0294 (8)	
H1A	0.3598	−0.1385	0.2454	0.035*	
C2	0.2700 (6)	−0.0447 (4)	0.0473 (4)	0.0204 (7)	
C3	0.1941 (6)	−0.0902 (4)	−0.1163 (4)	0.0253 (8)	
H3	0.1656	−0.0105	−0.1792	0.030*	
C4	0.1608 (7)	−0.2512 (5)	−0.1860 (5)	0.0299 (8)	
H4	0.1095	−0.2821	−0.2962	0.036*	
C5	0.2037 (7)	−0.3666 (5)	−0.0919 (5)	0.0325 (9)	
H5	0.1825	−0.4770	−0.1375	0.039*	
C6	0.3097 (6)	0.1261 (4)	0.1255 (4)	0.0203 (7)	
O1W	0.3115 (5)	0.3482 (4)	0.6228 (4)	0.0451 (8)	
H11W	0.3277	0.2489	0.6316	0.068*	
H12W	0.1779	0.3657	0.5974	0.068*	
Cl1	0.19420 (15)	0.63743 (11)	0.40795 (11)	0.0307 (2)	
O2WA	0.2969 (13)	0.0279 (8)	0.5219 (8)	0.0506 (16)	0.54
H1WA	0.3360	0.0607	0.4513	0.076*	0.54
H2WA	0.1618	0.0387	0.5026	0.076*	0.54
O2WB	0.1538 (17)	0.0200 (10)	0.5354 (13)	0.068 (3)	0.46
H1WB	0.2070	−0.0699	0.5168	0.102*	0.46
H2WB	0.0279	0.0002	0.5394	0.102*	0.46

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0278 (3)	0.0148 (3)	0.0195 (3)	0.0024 (2)	0.0043 (2)	−0.0033 (2)
N1	0.044 (2)	0.0169 (15)	0.0295 (17)	0.0012 (13)	0.0103 (15)	0.0029 (13)
N2	0.0311 (16)	0.0122 (13)	0.0221 (15)	0.0027 (11)	0.0069 (13)	0.0005 (11)
N3	0.0298 (16)	0.0125 (13)	0.0230 (15)	0.0038 (11)	0.0074 (13)	0.0001 (11)
N4	0.0378 (18)	0.0158 (14)	0.0215 (15)	0.0019 (12)	0.0086 (13)	0.0007 (11)
N5	0.0393 (18)	0.0169 (14)	0.0205 (15)	−0.0004 (13)	0.0079 (13)	0.0002 (12)
C1	0.042 (2)	0.0195 (18)	0.0226 (18)	−0.0009 (15)	0.0086 (16)	0.0004 (14)
C2	0.0228 (16)	0.0159 (16)	0.0210 (17)	0.0006 (12)	0.0082 (14)	−0.0017 (13)
C3	0.0301 (19)	0.0221 (18)	0.0217 (18)	0.0010 (14)	0.0078 (15)	0.0017 (14)
C4	0.034 (2)	0.027 (2)	0.0216 (18)	−0.0013 (16)	0.0075 (16)	−0.0072 (15)
C5	0.038 (2)	0.0192 (19)	0.035 (2)	−0.0013 (16)	0.0115 (18)	−0.0071 (16)
C6	0.0215 (16)	0.0168 (16)	0.0204 (17)	−0.0006 (12)	0.0064 (13)	0.0005 (13)
O1W	0.0381 (17)	0.0354 (17)	0.061 (2)	−0.0007 (13)	0.0175 (16)	0.0064 (15)
Cl1	0.0299 (5)	0.0288 (5)	0.0287 (5)	0.0066 (4)	0.0074 (4)	−0.0013 (4)
O2WA	0.069 (5)	0.034 (3)	0.051 (4)	0.008 (3)	0.023 (4)	0.007 (3)
O2WB	0.079 (7)	0.028 (4)	0.109 (8)	−0.001 (4)	0.051 (6)	0.009 (4)

Geometric parameters (Å, º)

Cu1—N3^i	1.984 (3)	C2—C3	1.380 (5)
Cu1—N3	1.984 (3)	C2—C6	1.455 (5)
Cu1—Cl1	2.3070 (12)	C3—C4	1.362 (5)
Cu1—Cl1^i	2.3070 (12)	C3—H3	0.9300
Cu1—O1W	2.390 (3)	C4—C5	1.365 (6)
Cu1—O1W^i	2.390 (3)	C4—H4	0.9300
N1—C5	1.312 (5)	C5—H5	0.9300
N1—C1	1.325 (5)	O1W—H11W	0.8509
N1—H1	0.8600	O1W—H12W	0.8482
N2—C6	1.314 (4)	O2WA—H1WA	0.8502
N2—N3	1.326 (4)	O2WA—H2WA	0.8506
N3—N4	1.306 (4)	O2WA—H1WB	0.9761
N4—N5	1.313 (4)	O2WB—H2WA	0.3777
N5—C6	1.327 (5)	O2WB—H1WB	0.8518
C1—C2	1.362 (5)	O2WB—H2WB	0.8501
C1—H1A	0.9300		
N3^i—Cu1—N3	180.000 (1)	C2—C1—H1A	119.9
N3^i—Cu1—Cl1	90.15 (9)	C1—C2—C3	117.9 (3)
N3—Cu1—Cl1	89.85 (9)	C1—C2—C6	120.4 (3)
N3^i—Cu1—Cl1^i	89.85 (9)	C3—C2—C6	121.7 (3)
N3—Cu1—Cl1^i	90.15 (9)	C4—C3—C2	120.3 (4)
Cl1—Cu1—Cl1^i	180.000 (1)	C4—C3—H3	119.8
N3^i—Cu1—O1W	87.13 (12)	C2—C3—H3	119.8
N3—Cu1—O1W	92.87 (12)	C3—C4—C5	119.1 (4)
Cl1—Cu1—O1W	89.21 (9)	C3—C4—H4	120.4
Cl1^i—Cu1—O1W	90.79 (9)	C5—C4—H4	120.4
N3^i—Cu1—O1W^i	92.87 (12)	N1—C5—C4	119.6 (3)
N3—Cu1—O1W^i	87.13 (12)	N1—C5—H5	120.2
Cl1—Cu1—O1W^i	90.79 (9)	C4—C5—H5	120.2
Cl1^i—Cu1—O1W^i	89.21 (9)	N2—C6—N5	112.5 (3)
O1W—Cu1—O1W^i	180.0	N2—C6—C2	124.4 (3)
C5—N1—C1	122.9 (3)	N5—C6—C2	123.2 (3)
C5—N1—H1	118.6	Cu1—O1W—H11W	124.2
C1—N1—H1	118.6	Cu1—O1W—H12W	112.4
C6—N2—N3	103.8 (3)	H11W—O1W—H12W	110.7
N4—N3—N2	109.9 (3)	H1WA—O2WA—H2WA	109.9
N4—N3—Cu1	122.7 (2)	H1WA—O2WA—H1WB	131.0
N2—N3—Cu1	127.4 (2)	H2WA—O2WA—H1WB	64.2
N3—N4—N5	109.5 (3)	H2WA—O2WB—H1WB	97.6
N4—N5—C6	104.4 (3)	H2WA—O2WB—H2WB	122.2
N1—C1—C2	120.2 (4)	H1WB—O2WB—H2WB	109.3
N1—C1—H1A	119.9		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N4ⁱⁱ	0.86	1.96	2.763 (4)	155
O1*W*—H11*W*···O2*WA*	0.85	1.91	2.663 (7)	146
O1*W*—H11*W*···O2*WB*	0.85	2.08	2.779 (9)	139
O1*W*—H12*W*···Cl1ⁱⁱⁱ	0.85	2.42	3.233 (3)	161
O2*WA*—H1*WA*···N2	0.85	2.07	2.906 (8)	168
O2*WB*—H1*WB*···Cl1ⁱⁱ	0.85	2.46	3.259 (9)	156
O2*WB*—H2*WB*···O2*WB*ⁱᵛ	0.85	1.14	1.89 (2)	143

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