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Aquadichloro(di-2-pyridyldiazene)-copper(II) monohydrate

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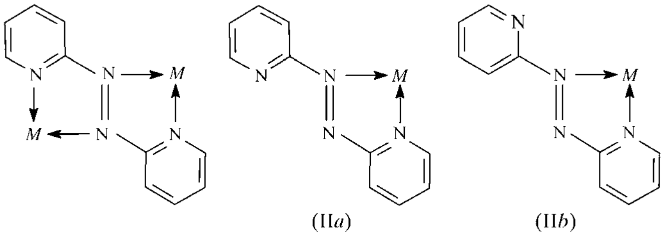
The crystal structure of the mononuclear title complex, $[CuCl_2(C_{10}H_8N_4)(H_2O)]\cdot H_2O$, shows an *s-cis*/*E*/*s-trans*-configured di-2-pyridyldiazene ligand, with the square-pyramidal Cu^{II} ion coordinated to one pyridyl and one diazene N atom together with two Cl atoms and one aqua ligand. The crystal packing involves both hydrogen-bonding and π–π interactions. The solvent water molecule links three monomers to one another through hydrogen-bonding interactions in which two monomers are linked *via* chloro ligands and the third *via* the aqua ligand. Face-to-face and weak slipped π–π interactions also occur between di-2-pyridyldiazene moieties, and these interactions are responsible for the interchain packing.

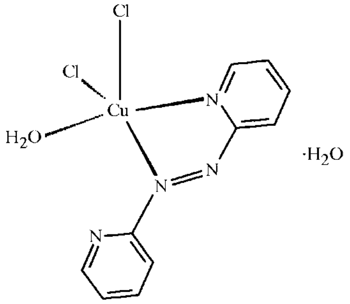
Comment

Non-covalent interactions, particularly versatile hydrogen bonds (Desiraju, 2000; Steiner & Desiraju, 1998; Bertolasi *et al.*, 2001; Mathew *et al.*, 2002), play vital roles in constructing organic and inorganic supramolecular architectures. During the past few years, several types of non-covalent interactions, such as π–π stacking interactions (Harrowfield, 1996; Roesky & Andruh, 2003), weak coordination interactions (Grove *et al.*, 2001) and electrostatic interactions (Reddy *et al.*, 1993; Dong *et al.*, 1999), have been recognized and used in constructing extended networks of supramolecular architectures. These types of interactions have attracted particular attention in fields such as developing new functional materials, crystal engineering, molecular recognition and self-assembly of organometallic compounds (Desiraju, 1996; Braga *et al.*, 1998). Organic molecules containing two donor N atoms, such as pyrazine, bipyridine and dipyridyldiazene, have been employed extensively for this purpose, and a number of extended structures with diverse topologies have been synthesized (Li *et al.*, 2001; Moliner *et al.*, 1999; Wong *et al.*, 2000). The di-2-pyridyldiazene (2,2′-azobispyridine, abpy) ligand, which is known to form an unusual complex (Baldwin *et al.*, 1969), was selected for the present study. The abpy ligand has several different coordination modes involving five-membered chelate-ring formation (N/N/C/N/*M*), as shown in the first scheme below. When one 2-pyridyl ring remains uncoordinated, because of the repulsion effects between diazene N-atom lone pairs and *ortho*-CH or pyridyl N-atom lone pairs, a singly chelating complex can form, as in (II*a*) or (II*b*).



(II*a*) (II*b*)

In the present study, apby is used as the building block and an interesting supramolecular architecture, (I), containing the Cu^{II} complex, corresponding to (II*b*) in the scheme above, is obtained.



(I)

The asymmetric unit of the title complex consists of one $[CuCl_2(C_{10}H_8N_4)(H_2O)]$ unit and a solvent water molecule. The Cu^{II} ion is coordinated in a distorted square-pyramidal mode to two N atoms (one pyridyl and one diazene N) of the abpy ligand, one chloro ligand and one water molecule in the basal plane, with a second chloro ligand in the apical position (Fig. 1 and Table 1). The abpy ligand adopts an *s-cis*/*E*/*s-trans* conformation. The second pyridyl N atom is not coordinated to the Cu^{II} ion but is the acceptor in a strong intramolecular hydrogen bond with the coordinated water molecule (Table 2).

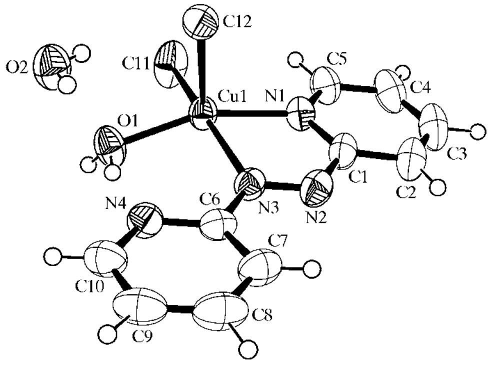


Figure 1
A view of the copper coordination of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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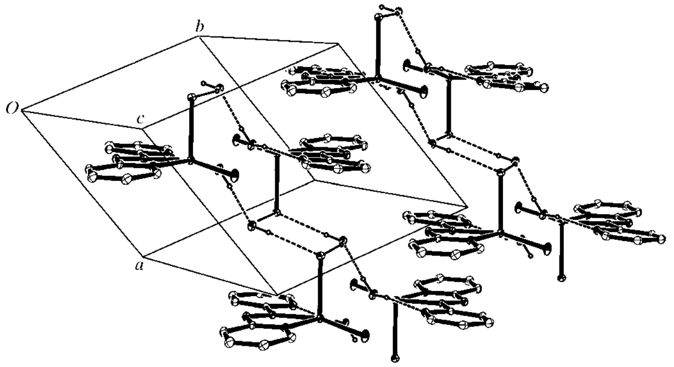

Figure 2
The hydrogen-bonding (dashed lines) and π–π interactions, with 10% probability displacement ellipsoids.

The stabilizing effect of the formation of this hydrogen bond is probably largely responsible for the abpy ligand adopting conformation (II*b*), with a dihedral angle between the coordinated and uncoordinated pyridyl planes of 7.03 (2)°. Hartmann *et al.* (2000) reported that the N=N distance [1.272 (9) Å] in the abpy ligand in an Re complex deviates significantly from that in free abpy [1.246 (2) Å; Bock *et al.*, 1998], while the Re—N distance is shorter [2.143 (5) Å]. Hartmann *et al.* (2000) also attributed the shortening of the Re—N bond length and the extension of the N=N bond length to the effect of substantial π back donation from the metal ion centers into the π^*(abpy) orbital. This effect, nevertheless, is not observed to be significant in the present complex [N=N = 1.254 (3) Å], because of the high effective charge of the Cu^{II} ion.

Both intermolecular hydrogen-bonding and π–π interactions combine to stabilize the extended structure (Fig. 2). The water molecule of crystallization links three monomers to one another, acting as a hydrogen-bond donor to chloro ligands of two monomers and as a hydrogen-bond acceptor to the coordinated water molecule of a third monomer (Table 2). These interactions are responsible for forming a ladder-type structure (Fig. 2). The abpy moieties are also subject to π–π non-covalent interactions, which are either strong face-to-face interactions [$Cg1\cdots Cg3$ = 3.415 (3) Å; $Cg1$ is the center of the chelate ring and $Cg3$ is the center of the uncoordinated pyridyl ring] or weak slipped interactions [$Cg2\cdots Cg3$ = 3.944 (3) Å; $Cg2$ is the center of coordinated pyridyl ring]. These π–π interactions link the hydrogen-bonded chains. The five-membered chelate ring and uncoordinated pyridyl ring are stacked so as to be nearly parallel, with a dihedral angle of 4.68 (2)°. The interplanar separation of these rings is 3.414 (3)–3.404 (3) Å, the closest interatomic distance being C1$\cdots$C10^{iii} of 3.330 (5) Å [symmetry code: (iii) $1 - x$, $-y$, $1 - z$]. The other π–π interaction is between the coordinated and uncoordinated pyridyl rings. The interplanar separation of these rings range from 3.464 (3) to 3.232 (3) Å, the closest interatomic distance being C1$\cdots$C10^{iii} of 3.330 (5) Å. Thus, an extensive network of hydrogen bonds and π–π stacking interactions stabilizes the crystal structure and forms an infinite three-dimensional lattice.

Experimental

Di-2-pyridyldiazene (abpy) was prepared according to the method of Rivarola *et al.* (1985). Solutions of $CuCl_2\cdot 5H_2O$ (0.12 g, 1 equivalent) in water (20 ml) and abpy (0.1 g, 1 equivalent) in terahydrofuran (THF) were mixed, and the resulting dark-green solution was refluxed for 3 h. After the mixture had cooled to ambient temperature, a dark-green precipitate was obtained, which was filtered off and washed with water. Dark-green crystals suitable for X-ray analysis were obtained by slow evaporation of a THF/H_2O solution over a period of one week (yield 77%).

Crystal data

$[CuCl_2(C_{10}H_8N_4)(H_2O)]\cdot H_2O$
M_r = 354.69
Triclinic, $P\overline{1}$
a = 8.072 (5) Å
b = 8.279 (5) Å
c = 11.327 (5) Å
α = 76.195 (5)°
β = 73.134 (5)°
γ = 74.199 (5)°
V = 686.5 (7) Å^3
Z = 2
D_x = 1.716 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 779 reflections
θ = 2.6–28.8°
μ = 1.98 mm^{-1}
T = 293 (2) K
Prism, dark green
0.42 × 0.33 × 0.21 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
T_{min} = 0.295, T_{max} = 0.477
12 369 measured reflections
3480 independent reflections
2752 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 28.9°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 1.01
3480 reflections
188 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1	2.2433 (14)	Cu1—O1	1.940 (2)
Cu1—Cl2	2.4684 (13)	C5—N1	1.334 (4)
Cu1—N1	1.999 (3)	C10—N4	1.341 (4)
Cu1—N3	2.153 (3)	N2—N3	1.254 (3)
Cl1—Cu1—Cl2	107.93 (4)	Cl2—Cu1—N3	86.39 (7)
Cl1—Cu1—N1	94.94 (9)	Cl2—Cu1—O1	95.40 (8)
Cl1—Cu1—N3	164.56 (6)	N1—Cu1—N3	76.12 (10)
Cl1—Cu1—O1	90.60 (9)	N1—Cu1—O1	159.69 (9)
Cl2—Cu1—N1	101.42 (8)	N3—Cu1—O1	93.81 (11)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H12$\cdots$Cl2^{i}	0.83 (3)	2.39 (3)	3.210 (3)	170 (4)
O1—H10$\cdots$O2^{ii}	0.82 (2)	1.89 (3)	2.710 (4)	172 (4)
O2—H11$\cdots$Cl2	0.80 (3)	2.49 (3)	3.277 (3)	167 (4)
O1—H9$\cdots$N4	0.82 (2)	1.90 (3)	2.689 (3)	161 (4)

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

H atoms on C atoms were placed at calculated positions (C—H = 0.93 Å) and were allowed to ride on their parent atoms [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. Other H atoms were placed from a difference map and were included in the refinement with O—H distances restrained to 0.84 (3) Å. $\Delta\rho_{\rm max}$ and $\Delta\rho_{\rm min}$ are 0.63 and 0.83 Å from atoms N1 and Cu1, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1463). Services for accessing these data are described at the back of the journal.

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