Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Aqua(4′-hydroxy-2,2′;6′,6″-terpyridyl)copper(II) bis(perchlorate)

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Key indicators

Single-crystal X-ray study
T = 158 K
Mean σ(C–C) = 0.012 Å
R factor = 0.058
wR factor = 0.137
Data-to-parameter ratio = 9.6

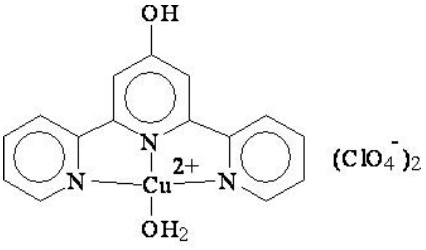
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 9 August 2005
Accepted 16 August 2005
Online 27 August 2005

In the title compound, $[Cu(C_{15}H_{11}N_3)(H_2O)](ClO_4)_2$, the 4′-hydroxyterpyridine and water molecule are coordinated in the Cu equatorial plane and the two perchlorate ions are semicoordinate in the axial positions. The crystal structure is stabilized by hydrogen bonds between the 4′-hydroxy group, the coordinated water molecule and the perchlorate ions, forming two-dimensional sheets.

Comment

We are interested in the synthesis of stable, chelated metal–organic fragments for applications to molecular magnetism. Ligands such as terpyridine, suitably substituted in the 4, 4′ and/or 4″ positions, are potential candidates for this work and we have previously reported on the structures of a series of 4′-methylsulfanyl complexes (Jeitler *et al.*, 2003). The related compound 4′-hydroxyterpyridine and its derivatives have the same potential to chelate metals in a robust fashion (Fallahpour *et al.*, 1999; Chow *et al.*, 2003; Liu *et al.*, 2001) and could further bridge metal sites through deprotonation of the hydroxy group. Most interesting from the point of view of molecular magnetism is the spin crossover behavior exhibited by the complex $[Co(4'\text{-hydroxyterpyridine})_2](ClO_4)_2$ (Gaspar *et al.*, 2001). Thus, we prepared a series of 4′-hydroxyterpyridine metal complexes and were able to obtain crystals of the title compound, (I).



(I)

The Cu^{II} complex is pseudo-square-planar (Fig. 1) with the three terpyridyl N atoms and the O atom from a coordinated water molecule occupying the equatorial plane. The bond lengths and angles between the Cu and N atoms are similar to those observed by Rojo *et al.* (1987) in a dimeric CuBr(terpyridyl) complex. The mean deviation of the ligands from the coordination plane is 0.05 Å. The individual rings within the terpyridine ligand itself are also planar (mean deviations of atoms within a ring range 0.004–0.008 Å) and the rings are twisted with respect to each other [N1—N7 rings = 4.8 (4)° and N7–N17 rings = 8.8 (4)°]. The perchlorate ions are semicoordinate in the axial positions with Cu—O distances of Cu—O1 = 2.494 (8) Å and Cu—O8 = 2.591 (6) Å, and an

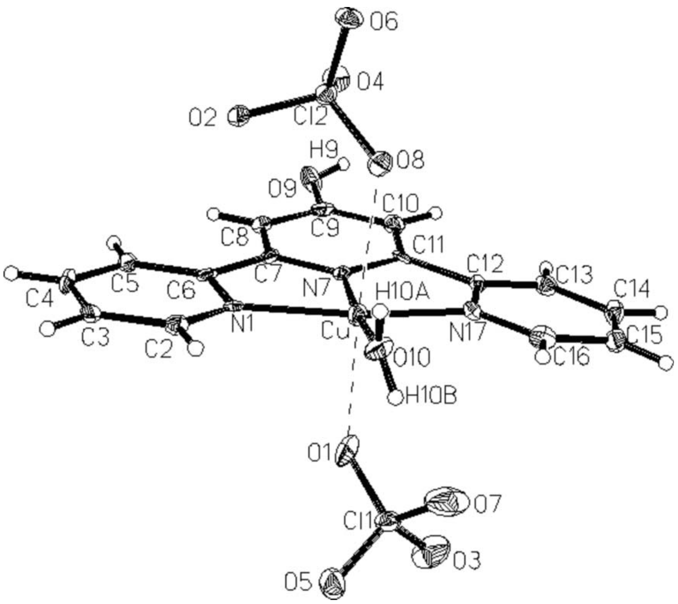


Figure 1
The asymmetric unit of (I), showing 30% probability displacement ellipsoids. For clarity, only the H atoms whose positions were refined are labeled.

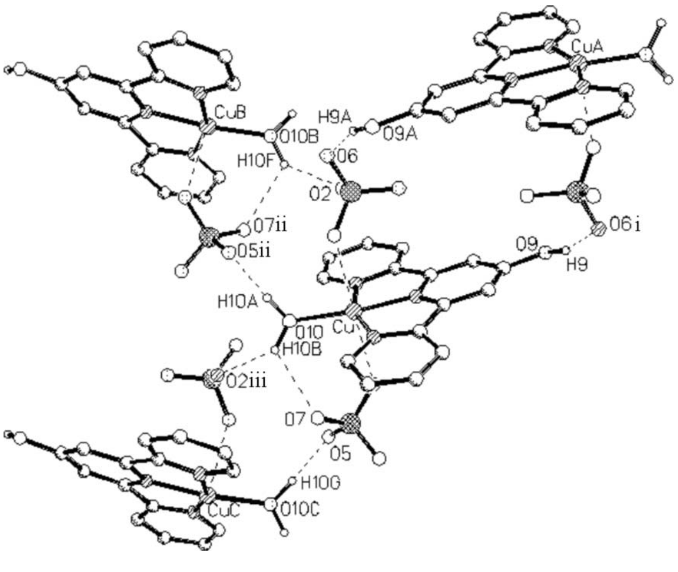


Figure 2
The hydrogen-bonding network in (I), indicated by broken lines. Only H atoms bonded to O atoms are shown. The suffixes *A*, *B* and *C* of the non-H atoms correspond to symmetry codes (i), (ii) and (iii), respectively, in Table 2.

angle of O1—Cu—O8 = 176.1 (3)°. The angle between the O1—O8 vector and the copper equatorial plane is 84.4 (4)°.

The crystal structure is stablized by an extended hydrogen-bonding network that involves the hydroxy and water H atoms and the perchlorate ions (Fig. 2 and Table 2). Inversion-related molecular units are linked into dimers *via* the hydroxy OH group (O9—H9···O6^{i}; see Table 2 for symmetry code). The coordinated water molecule links molecules related by the 2_1 screw axis into chains (O10—H10*A*···O5^{ii} and O10—H10*B*···O2^{iii}). The latter of these is a bifurcated hydrogen bond with H10*B* also forming an intramolecular interaction (O10—H10*B*···O7).

Experimental

A solution of copper(II) perchlorate hexahydrate (0.69 g, 1.86 mmol) in 95% ethanol (5 ml) was added to a hot solution of 4′-hydroxy-2,2′,6′,6″-terpyridine (0.93 g, 3.77 mmol) in 95% ethanol (5 ml). The resulting precipitate of bis(4′-hydroxyterpyridine)copper(II) perchlorate monohydrate was removed by filtration and the filtrate allowed to evaporate slowly at room temperature, resulting in medium blue crystals of (I) (yield 4%). IR (KBr, cm^{-1}): 3271 (*m*), 1607 (*m*), 1518 (*m*), 1487 (*m*), 1086 (*s*), 795 (*m*), 627 (*m*).

Crystal data

$[Cu(C_{15}H_{11}N_3)(H_2O)](ClO_4)_2$
$M_r = 529.72$
Monoclinic, $P2_1/c$
$a = 8.487$ (4) Å
$b = 11.230$ (3) Å
$c = 19.662$ (8) Å
$\beta = 100.19$ (3)°
$V = 1844.4$ (13) Å^3
$Z = 4$
$D_x = 1.908$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 reflections
$\theta = 4.9$–12.2°
$\mu = 1.54$ mm^{-1}
$T = 158$ (2) K
Plate, blue
0.65 × 0.22 × 0.05 mm

Data collection

Siemens P4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Sheldrick, 1985)
$T_{min} = 0.634$, $T_{max} = 0.926$
2982 measured reflections
2788 independent reflections
1455 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 24.0°$
$h = -9 \rightarrow 1$
$k = 0 \rightarrow 12$
$l = -20 \rightarrow 22$
3 standard reflections every 397 reflections intensity decay: 5.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.137$
$S = 0.85$
2788 reflections
289 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N7	1.914 (7)	Cu—N17	2.002 (7)
Cu—O10	1.940 (7)	Cu—N1	2.015 (6)
N7—Cu—O10	173.7 (3)	N7—Cu—N1	80.6 (3)
N7—Cu—N17	80.4 (3)	O10—Cu—N1	100.7 (3)
O10—Cu—N17	98.4 (3)	N17—Cu—N1	161.0 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9···O6^{i}	0.79 (9)	2.00 (9)	2.760 (8)	163 (10)
O10—H10*A*···O5^{ii}	0.79 (9)	1.95 (9)	2.725 (9)	167 (10)
O10—H10*B*···O7	0.80 (9)	2.44 (9)	2.993 (10)	127 (8)
O10—H10*B*···O2^{iii}	0.80 (9)	2.23 (9)	2.864 (9)	136 (9)

Symmetry codes: (i) $-x+1, -y-1, -z+1$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

The X-ray data collection was terminated at $\theta = 24^\circ$ because the crystal was lost due to a failure of the cryosystem prior to completion. H atoms bonded to O atoms were located in difference maps and their positions were refined with the restraint O—H = 0.80 (9) Å. H atoms bonded to C atoms were positioned geometrically at a C—H bond length of 0.95 Å using a riding model. with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,*O*).

Data collection: *XSCANS* (Siemens, 1992); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

MMT is grateful to Professor Ward Robinson and the Chemistry Department at the University of Canterbury for their hospitality during this work.

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