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Bis(3-aminopyridine-κ*N*)(4,4′-dimethyl-2,2′-bipyridine-κ²*N*,*N*′)(perchlorato-κ*O*)copper(II) perchlorate

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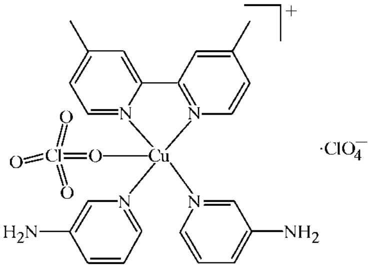
The title compound, $[Cu(ClO_4)(C_5H_6N_2)_2(C_{12}H_{12}N_2)]ClO_4$, was prepared by *in situ* partial ligand substitution between 3-aminopyridine and 4,4′-dimethyl-2,2′-bipyridine at room temperature. The central copper(II) ion is five-coordinated by one bidentate 4,4′-dimethyl-2,2′-bipyridine molecule, two monodentate pyridine-coordinated 3-aminopyridine molecules and one apical O atom from the perchlorate counter-ion. Intermolecular N—H···O and C—H···O hydrogen-bonding interactions form a hydrogen-bond-sustained network.

Comment

The rational design and synthesis of coordination complexes are of continuing interest for developing new functional molecular-based materials (Robson *et al.*, 1992). A commonly used strategy is preparing the metal complexes with mixed functional ligands in order to tune precisely their chemical and physical properties. Some weakly coordinated ligands can cap or preoccupy certain coordination sites of the central metal ions, and they can be replaced by a variety of bridging groups capable of stronger coordination ability in the subsequent synthesis (Huang *et al.*, 2003, 2006). However, owing to the different coordination abilities of the ligands, it is difficult to obtain the desired complexes in many cases (Huang & Ogawa, 2006*b*). We report here the title copper(II) complex, (I), having monodentate and bidentate ligands in the molecular structure simultaneously, which can be synthesized in a very facile way by *in situ* partial ligand substitution between 3-aminopyridine and 4,4′-dimethyl-2,2′-bipyridine at room temperature. The Cambridge Structural Database (Version 5.26; Allen, 2002) contains no previous structural reports of compounds in which 4,4′-dimethyl-2,2′-bipyridine and 3-aminopyridine molecules are coordinated simultaneously to one metal center.

The atom-numbering scheme of (I) at 120 (2) K is shown in Fig. 1, while bond distances and angles related to the copper(II) center are given in Table 1. The coordination configuration of the Cu^{II} center is a slightly distorted five-coordinate square pyramid, which has a τ value of 0.134 (Addison *et al.*, 1984). Two N atoms from one bidentate 4,4′-dimethyl-2,2′-bipyridine molecule and two monodentate pyridine-coordinated 3-aminopyridine molecules constitute the basal plane, with Cu—N bond lengths in the range 1.983 (2)–2.013 (2) Å. Atom O1 from one perchlorate counter-ion occupies the apical position, the Cu—O bond length being 2.396 (2) Å. The other perchlorate anion is believed to be uncoordinated since the shortest distance between the O atom and the central copper ion is 3.192 (3) Å (Cu1···O7). Neither of the perchlorate anions in (I) is disordered at 120 (2) K. Comparison with the related data for the same complex at 291 (2) K [Cu—N = 1.980 (3)–2.012 (3) Å, Cu—O = 2.433 (3) Å for the coordinated perchlorate anion, and a shortest Cu···O separation between the uncoordinated



(I)

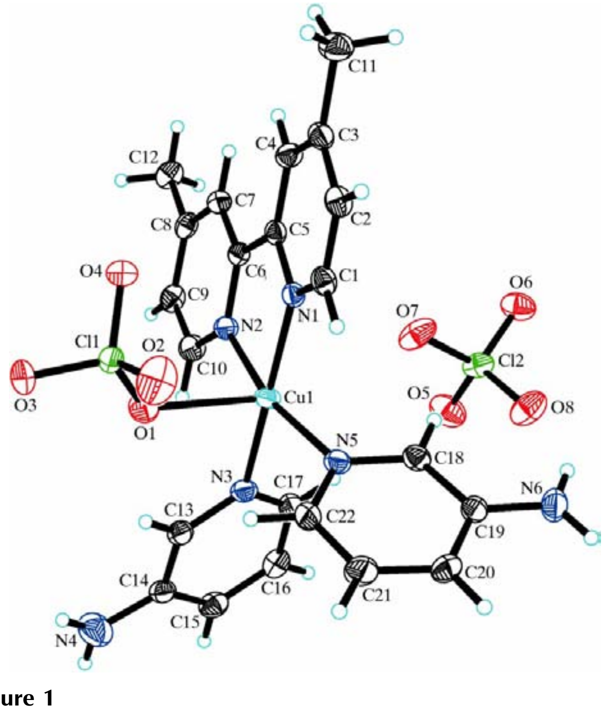


Figure 1
A drawing of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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perchlorate anion and the Cu^{II} center of 3.179 (5) Å for Cu1···O7] shows that the square pyramid around the copper(II) center in (I) is slightly compressed when the temperature is decreased, but the geometries of the basal N_4 plane are almost unchanged.

The two pyridine rings of the 4,4′-dimethyl-2,2′-bipyridine molecule are essentially coplanar, with a torsion angle of 7.2 (2)°, which is analogous to those in our previous reports (Huang & Ogawa, 2006*a*; Qian & Huang, 2006). The dihedral angles between the 4,4′-dimethyl-2,2′-bipyridine least-squares plane and the two 3-aminopyridine molecular planes in (I) are 77.5 (2) and 76.2 (2)°, while the two 3-aminopyridine molecular planes are nearly perpendicular to one another, with a dihedral angle of 93.6 (2)° in order to minimize the steric hindrance.

Versatile hydrogen-bonding interactions are another remarkable structural feature of the title compound. In the crystal structure, every molecule is connected to six adjacent perchlorate groups besides the coordinated one by means of intermolecular N—H···O and C—H···O hydrogen-bonding contacts (Fig. 2 and Table 2). The donors come from the H atoms of the amine groups in the 3-aminopyridine ligands, as well as the pyridyl H atoms of 4,4′-dimethyl-2,2′-bipyridine and 3-aminopyridine, while the acceptors are the O atoms of the perchlorate anions. As a result, two kinds of neighbouring eight-membered $ClO_2H_2C_2N$ hydrogen-bond rings are formed. Furthermore, all the molecules in (I) pack along the crystallographic *b* axis, forming a hydrogen-bond-sustained supramolecular framework.

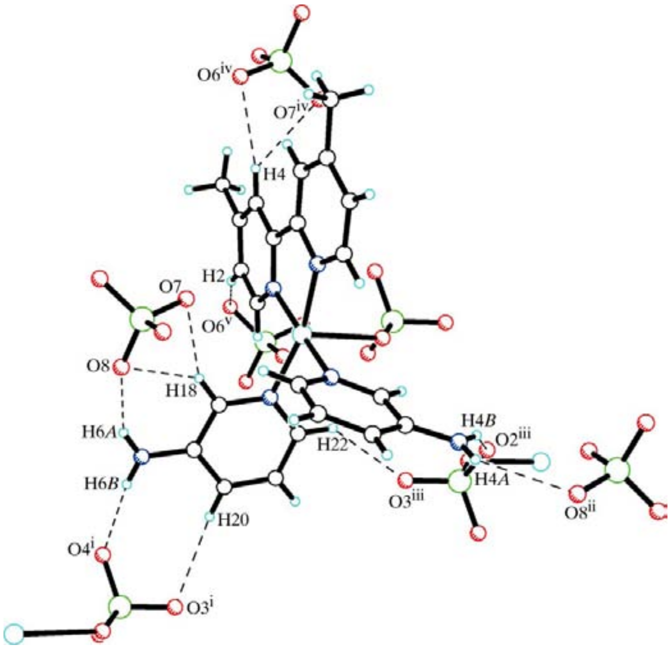

Figure 2
A perspective view of the intermolecular hydrogen-bond contacts between neighbouring molecules in (I). Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z$; (v) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

Experimental

All solvents and chemicals were of analytical grade, purchased as commercial chemicals from Aldrich or ACROS, and were used without further purification. Compound (I) was synthesized by *in situ* partial ligand substitution at room temperature. A colorless methanol solution (20 ml) of sixfold 3-aminopyridine (0.282 g, 3.0 mmol) was added to a blue methanol solution (10 ml) of $[Cu(ClO_4)_2]\cdot 6H_2O$ (0.186 g, 0.5 mmol) at room temperature, and then a colourless methanol solution (20 ml) of 4,4′-dimethyl-2,2′-bipyridine (0.092 g, 0.5 mmol) was added to the resulting green mixture. The color of the solution turned quickly from green to brown, which demonstrated the exchange between the monodentate and bidentate ligands. Finally, the mixture was evaporated slowly in air at room temperature to nearly 10 ml, and then microcrystals were collected, washed with acetone and dried *in vacuo* (yield 77%, 0.244 g). FT–IR (KBr pellets, cm^{-1}): 3459 (*s*), 3381 (*s*), 3222 (*w*), 3087 (*m*), 2924 (*m*), 1620 (*s*), 1582 (*s*), 1560 (*m*), 1496 (*s*), 1450 (*s*), 1107 (*vs*), 1088 (*vs*), 803 (*s*), 699 (*m*), 625 (*s*). Elemental analysis calculated for $C_{22}H_{24}Cl_2CuN_6O_8$: C 48.99, H 3.74, N 10.39%; found: C 49.03, H 3.79, N 10.42%. UV–vis (δ_{max}) in methanol: 263, 254, 250, 220 nm. ESI–MS (*m/z*): 534 $[M - ClO_4]^+$. Brown single crystals of (I) suitable for X-ray diffraction determination were grown from methanol by slow evaporation in air at room temperature.

Crystal data

$[Cu(ClO_4)(C_5H_6N_2)_2(C_{12}H_{12}N_2)]$-$ClO_4$
$M_r = 634.91$
Monoclinic, $P2_1/n$
$a = 16.112$ (3) Å
$b = 10.442$ (2) Å
$c = 17.058$ (3) Å
$\beta = 115.67$ (3)°
$V = 2586.6$ (11) Å^3
$Z = 4$
$D_x = 1.630$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.11$ mm^{-1}
$T = 120$ (2) K
Block, brown
0.20 × 0.15 × 0.10 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
$T_{min} = 0.808$, $T_{max} = 0.897$
22276 measured reflections
4949 independent reflections
4665 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.103$
$S = 1.13$
4949 reflections
354 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 5.1887P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.30$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.983 (2)	Cu1—N2	2.013 (2)
Cu1—N3	1.993 (2)	Cu1—O1	2.396 (2)
Cu1—N5	1.997 (2)		
N1—Cu1—N3	174.07 (9)	N5—Cu1—N2	166.06 (9)
N1—Cu1—N5	93.69 (9)	N1—Cu1—O1	91.06 (8)
N3—Cu1—N5	90.58 (9)	N3—Cu1—O1	92.40 (9)
N1—Cu1—N2	81.51 (9)	N5—Cu1—O1	98.15 (9)
N3—Cu1—N2	93.39 (9)	N2—Cu1—O1	95.02 (9)

H atoms were placed in geometrically idealized positions (C—H = 0.93–0.96 Å and N—H = 0.86 Å) and refined as riding atoms [$U_{iso}(H) = 1.5U_{eq}$(N and methyl C) or $1.2U_{eq}$(other C atoms)].

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C22—H22···O3$^{\rm iii}$	0.93	2.35	3.067 (4)	134
C20—H20···O3$^{\rm i}$	0.93	2.54	3.432 (4)	161
C18—H18···O8	0.93	2.41	3.176 (4)	139
C18—H18···O7	0.93	2.36	3.224 (3)	154
C13—H13···O1	0.93	2.40	3.074 (3)	129
C10—H10···N3	0.93	2.60	3.103 (4)	114
C4—H4···O7$^{\rm iv}$	0.93	2.46	3.382 (4)	171
C4—H4···O6$^{\rm iv}$	0.93	2.58	3.263 (4)	130
C2—H2···O6$^{\rm v}$	0.93	2.41	3.313 (4)	164
C1—H1···N5	0.93	2.60	3.093 (4)	114
N6—H6*B*···O4$^{\rm i}$	0.86	2.19	3.037 (4)	169
N6—H6*A*···O8	0.86	2.30	3.057 (4)	146
N4—H4*B*···O2$^{\rm iii}$	0.86	2.42	3.197 (4)	150
N4—H4*A*···O8$^{\rm ii}$	0.86	2.56	3.187 (4)	130

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z$; (iv) $-x+2, -y+1, -z$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3007). Services for accessing these data are described at the back of the journal.

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