Redetermination of [bis(2-pyridyl)amine-N,N']copper(II) diperchlorate

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In the crystal structure of the title complex, $[Cu(C_{10}H_9N_3)_2](ClO_4)_2$, the Cu^{II} center is four-coordinated by the nitrogen donors of the pyridine rings of the ligand, bis(2-pyridyl)amine. The crystal structure reveals that the CuN_4 coordination sphere has a distorted tetrahedral coordination geometry with a crystallographic C_2 axis through the Cu^{II} center. The perchlorate anions link the complex cations to form a chain structure through C—H$\cdots$O close contacts and N—H$\cdots$O hydrogen bonds.

Comment

Ligands containing aromatic nitrogen heterocycles, such as pyridine, 2,2'-bipyridine and 1,10-phenanthroline, have given a great impetus to metal coordination chemistry. Bis(2-pyridyl)amine has attracted a great interest in the molecular self-assembling processes that lead to macromolecular architectures (Cotton *et al.*, 1997, 1998; Gornitzka & Stalke, 1998) and three different coordination modes were found for this ligand (see below).

trans-trans   cis-trans   cis-cis
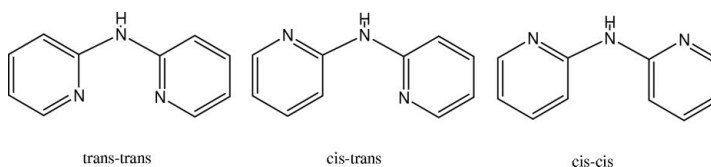
A structure analysis of the title complex, (I), was performed early in 1971 (Johnson *et al.*, 1971). The structure was refined to $R = 0.094$ using 1167 visually estimated intensities which were not corrected for absorption and the s.u.'s reported were 0.01 Å for bond lengths and 1° for bond angles.

(I)
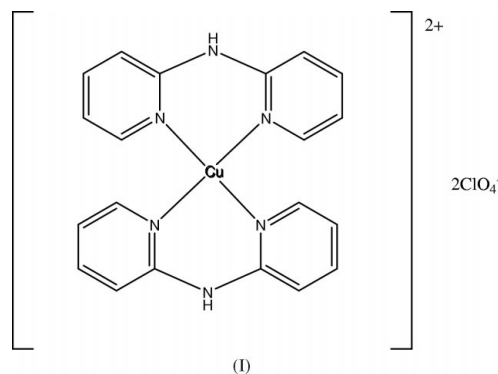
We have now redetermined the structure of (I) using CCD data. Not only is the structure reported here more aprecisely determined but some of the parameters, such as unit-cell dimensions, bond lengths and intramolecular interactions,
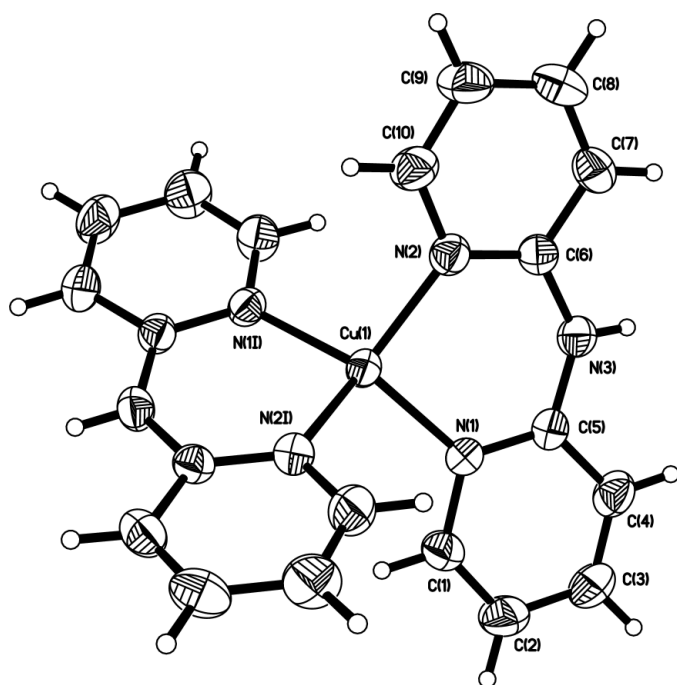
Figure 1
View of the complex cation with 50% probability ellipsoids. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$].

show significant differences from those reported earlier.

The structure (I) consists of discrete $[Cu(C_{10}H_9N_3)_2]^{2+}$ cations and perchlorate anions. The Cu^{II} center lies on the crystallographic twofold rotation axis. The Cu^{II} atom is four coordinated and bonded in a bidentate fashion to two pyridine rings of the ligand by *trans–trans* mode (Fig. 1). The coordination geometry of Cu^{II} could be best described as distorted tetrahedron. The degree of distortion from planar towards tetrahedral can be reflected by the dihedral angle between the N1—Cu—N2 and N1^i—Cu1—N2^i planes, 54.9 (4)° [symmetry code: (i) $-x, y, -z + \frac{1}{2}$]. The Cu—N bond distances (Table 1) are almost equivalent [1.971 (2) and 1.977 (2) Å], which are similar to the value of the analogous complexes (Ray *et al.*, 1982; Rodig *et al.*, 1981; Spodine *et al.*, 1996).

The perchlorate anions act as bridges to link the complex cations through N—H···O hydrogen bonds and C—H···O close contacts, forming a chain structure, as shown in Fig. 2. The C(N)···O and H···O separations, and the bond angles are listed in Table 2, which are in the normal range of the weak interactions (Sasada, 1984; Desiraju, 1991). Furthermore, the complex cations of (I) are stacked in the *b* direction with the closest approach between the pyridine rings of 4.112 (4) Å, indicating no significant π–π-stacking interactions.

Experimental

The title complex was synthesized by mixing Cu(ClO$_4$)$_2$·6H$_2$O (0.37 g, 1.0 mmol) and bis(2-pyridyl)amine (0.34 g, 2.0 mmol) in methanol (20 ml). The reaction mixture was filtered and left to stand at room temperature. Blue single crystals [yield: 360 mg (60%)] suitable for X-ray analysis were obtained by slow evaporation of the solvent.

Crystal data

$[Cu(C_{10}H_9N_3)_2](ClO_4)_2$	$D_x = 1.717$ Mg m^{-3}
$M_r = 604.87$	Mo Kα radiation
Monoclinic, $C2/c$	Cell parameters from 4478
$a = 9.416$ (3) Å	reflections
$b = 12.955$ (4) Å	$\theta = 2.1$–25.0°
$c = 19.748$ (6) Å	$\mu = 1.22$ mm^{-1}
$\beta = 103.792$ (3)°	$T = 298$ (2) K
$V = 2339.5$ (11) Å^3	Prism, blue
$Z = 4$	$0.35 \times 0.30 \times 0.25$ mm

Data collection

CCD diffractometer	1790 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.068$
Absorption correction: by integration (Bruker, 1998)	$\theta_{max} = 25.0°$
	$h = -11 \rightarrow 11$
$T_{min} = 0.674$, $T_{max} = 0.750$	$k = -9 \rightarrow 15$
4515 measured reflections	$l = -23 \rightarrow 23$
1983 independent reflections	

Refinement

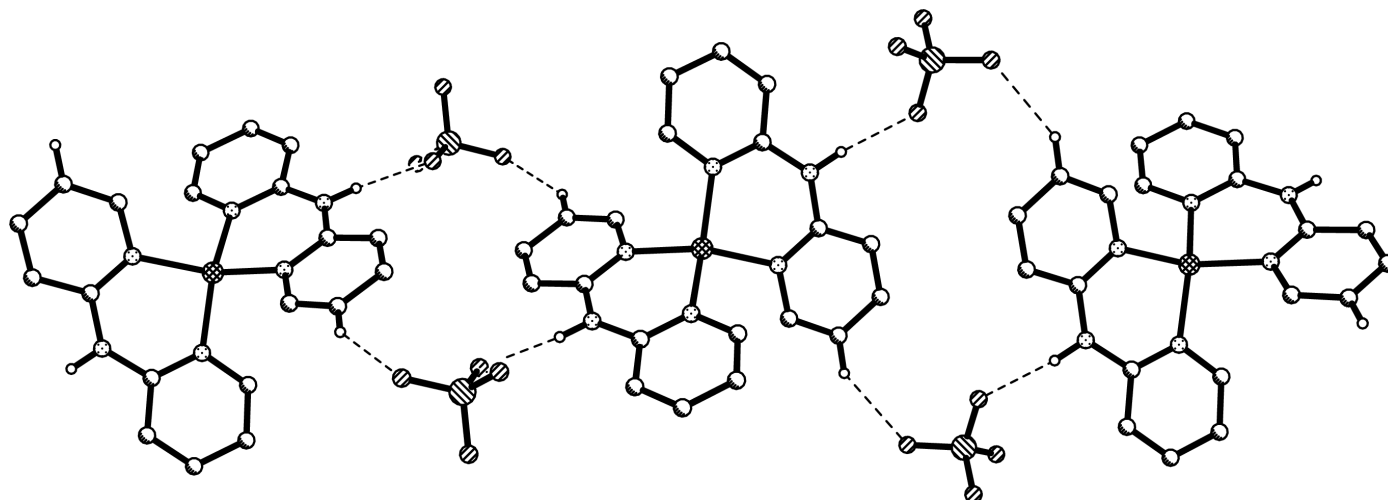|	
Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0612P)^2$
$R(F) = 0.043$	$+ 0.9728P]$
$wR(F^2) = 0.108$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
1983 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
169 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Figure 2
View of the chain structure of the complex cations and perchlorate anions.

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.971 (2)	Cu1—N2	1.977 (2)
N1^i—Cu1—N1	142.90 (13)	N1—Cu1—N2	94.09 (9)
N1^i—Cu1—N2	98.90 (9)	N2—Cu1—N2^i	138.37 (13)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$B\cdots$O3	0.86	2.11	2.963 (6)	174
C9—H9$A\cdots$O2	0.96	2.48	3.331 (5)	149

H atoms were located by geometry and used in the structure-factor calculations.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: XP (Bruker, 1998).

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