metal-organic papers

Bis(di-2-pyridylamine)copper(I) perchlorate benzene solvate

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In the title Cu^I complex, $[Cu(C_{10}H_9N_3)_2]ClO_4 \cdot C_6H_6$, the coordination of the metal ion is tetrahedral, surrounded by two bidentate di-2-pyridylamine ligands, and coordinated by four N atoms from pyridine rings. The Cu^I—N bond lengths are shorter than those reported for Cu^{II}—N. In this structure, the two ligand molecules are approximately orthogonal.

Comment

The ligand di-2-pyridylamine (dpa) has been used widely to form transition metal complexes. With copper(II) the structures of mononuclear compounds have been reported {for example $[Cu(dpa)_2](NO_3)_2$ (Rodig *et al.*, 1981; Blake *et al.*, 1995) and $[Cu(dpa)_2(OH)_2(H_2O)]Cl_2 \cdot 2H_2O$ (Wu *et al.*, 1992)}. In recent years, increasing attention has been paid to the dpa ligand because it has been used as a basic material for the formation of polymeric chain complexes (Shieh *et al.*, 1997; Cotton *et al.*, 1998; Lai *et al.*, 1999; Peng *et al.*, 2000; Li *et al.*, 2003). In the context of our current work concerning the synthesis and characterization of transition metal polynuclear compounds using multidentate N-donor groups as ligands, copper(I) complexes with the dpa ligand have been examined. We report here the structure of the title compound, (I). As shown in Fig. 1, the coordination of the metal ion is tetrahedral. The Cu^I cation is surrounded by two bidentate di-2-pyridylamine ligands, and coordinated by four N atoms from pyridine rings. The structure of the title complex is similar to
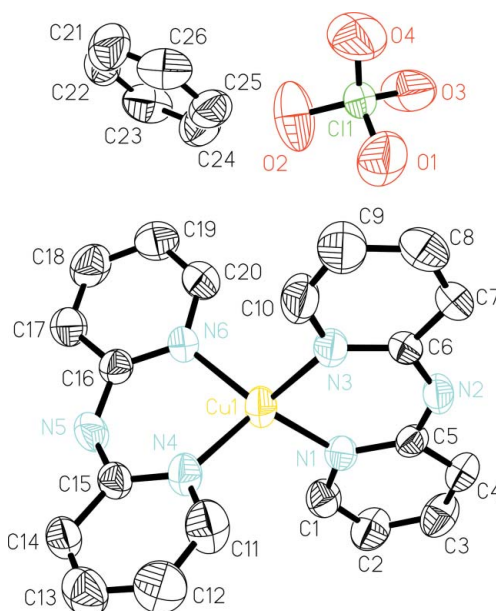

Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted.

that of bis-[di-2-pyridylamine]copper(II) (Rodig *et al.*, 1981; Blake *et al.*, 1995). The Cu—N bond lengths (Table 1) are a little longer than those of bis-[di-2-pyridylamine]copper(II), because of the larger size of copper(I). The dihedral angle, Φ, which defines the distortion between tetrahedral and square-planar geometries (Rodig *et al.*, 1981) [Φ = 0° for square planar and 90° for tetrahedral] is 85.3 (5)°, significantly different from the results of Rodig *et al.* (1981) [58.8 (4)°] and Blake *et al.* (1995) [54.8 (4)°]; the two dpa ligand molecules are approximately orthogonal, the dihedral angle between the least-squares planes of the two ligands being 83.8 (5)°. The two pyridine rings of one dpa ligand, forming a dihedral angle of 1.9 (3)°, are nearly coplanar, while the dihedral angle between the two pyridine rings of the other dpa ligand is 14.4 (5)°.

(I)
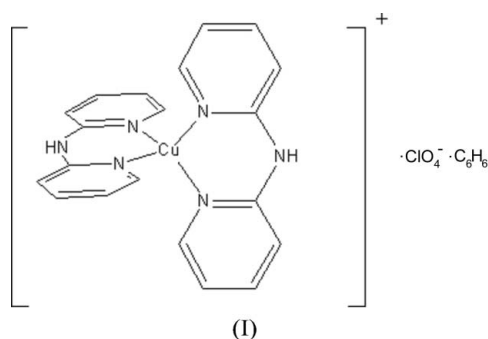
The perchlorate anion balances the charge of the cation. The anions play an important role in the three-dimensional crystal network through hydrogen bonds (Table 2).

Experimental

CuClO4 (0.25 g) and di-2-pyridylamine (dpa, 0.18 g) were dissolved in a mixed solvent of acetonitrile and benzene (1:1, 10 ml) in a nitrogen atmosphere. The resulting solution was poured into a Pyrex glass tube with vitamin C (0.02 g), and then the tube was evacuated and sealed off at the end. The sealed Pyrex glass tube was heated in an oven at 363 K. After two days single crystals of the title complex were obtained.

Crystal data

$[Cu(C_{10}H_9N_3)_2]\cdot ClO_4{}^-\cdot C_6H_6$	$Z = 8$
$M_r = 583.50$	$D_x = 1.447$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.2353 (9)$ Å	$\mu = 0.96$ mm^{-1}
$b = 22.1952 (14)$ Å	$T = 273 (2)$ K
$c = 18.3608 (15)$ Å	Needle, green
$\beta = 112.578 (1)°>$	$0.21 \times 0.08 \times 0.05$ mm
$V = 5356.6 (6)$ Å^3	

Data collection

Bruker APEX-II area-detector diffractometer	32478 measured reflections
φ and ω scans	6623 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	3296 reflections with $I > 2\sigma(I)$
$T_{min} = 0.824$, $T_{max} = 0.958$	$R_{int} = 0.088$
	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.035P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.050$	$+ 1.0071P]$
$wR(F^2) = 0.122$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
6623 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
331 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.990 (3)	Cu1—N3	2.011 (3)
Cu1—N4	2.007 (3)	Cu1—N6	2.016 (3)
N1—Cu1—N4	118.04 (12)	N1—Cu1—N6	125.76 (12)
N1—Cu1—N3	94.04 (13)	N4—Cu1—N6	92.39 (13)
N4—Cu1—N3	116.16 (13)	N3—Cu1—N6	112.23 (13)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H2···O1^i	0.86	2.26	3.108 (4)	168
N5—H5···O3^{ii}	0.86	2.21	3.043 (4)	163

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

H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H and N—H distances of 0.93 and 0.86 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *APEX2*; software used to prepare material for publication: *APEX2*.

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