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# Bis(2-chloro-5-methylpyridine-$\kappa N$)-bis(nitrato-$\kappa^2 O,O'$)copper(II)

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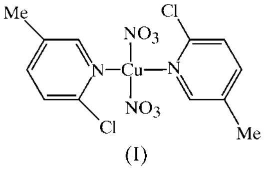
In the molecule of the title compound, $[Cu(NO_3)_2(C_6H_6ClN)_2]$, the Cu atom lies on an inversion centre and is six-coordinated by two pyridine N atoms and four nitrate O atoms in *trans* positions. The nitrate acts as an unsymmetrical bidentate ligand. The coordination geometry is octahedral, with the Cu—N and the two Cu—O distances being 1.9939 (16), 2.0246 (16) and 2.4866 (19) Å, respectively. There are five types of C—H···O hydrogen bonds. Two of these generate two-dimensional molecular networks in the direction of the *a* axis, and the others connect adjacent molecular networks.

## Comment

2-Chloro-5-methylpyridine can form a complex with $CuCl_2 \cdot 2H_2O$ [dichlorobis(2-chloro-5-methylpyridine-$\kappa N$)copper(II); Xuan *et al.*, 2003]. In recent work, we have found that it can also form the title complex, (I), with $Cu(NO_3)_2$, but the melting point of this complex is much higher than that of the chloro complex. In order to study the specific structural features of complex (I), we have performed an X-ray structural analysis, and the results are presented here.



(I)

The molecular structure of (I) is shown in Fig. 1. The Cu atom lies on a crystallographic inversion centre, so the N1—Cu—N1$^i$, O2—Cu—O2$^i$ and O3—Cu—O3$^i$ angles are 180° [symmetry code: (i) $-x, 1-y, -z$]. The two pyridine rings are coplanar in the molecule of (I) because of crystallographic symmetry, but they are twisted from the Cu/N1/O2 plane, with an O1—Cu—N1—C1 torsion angle of 113.70 (15)°. The title complex forms a distorted octahedral structure, with Cu—N1, Cu—O1 and Cu—O3 distances of 1.9939 (16), 2.0246 (16) and 2.4866 (19) Å, respectively, N1—Cu—O1 and N1—Cu—O3 angles of 88.23 (6) and 92.80 (7)°, respectively, and O3—N2—O1—Cu and N1—Cu—O1—N2 torsion angles of −5.1 (2) and −91.88 (33)°, respectively. The Cu—N1 and Cu—O1 bond distances (Table 1) agree with the corresponding values for other Cu$^{II}$ complexes (Zavalij *et al.*, 2002), but Cu—O3 is 0.46 Å longer than Cu—O1. The N2—O1 bond is longer than N2—O3, so the nitrate is unsymmetrical. The nitrate groups act as bidentate ligands, just as they do in other metal complexes (Freire *et al.*, 2001; Yoshida *et al.*, 2001; Sommerer *et al.*, 1994), but in (I) they are unsymmetrical bidentate ligands. The nitrate bite angle is 55.49 (7)°.

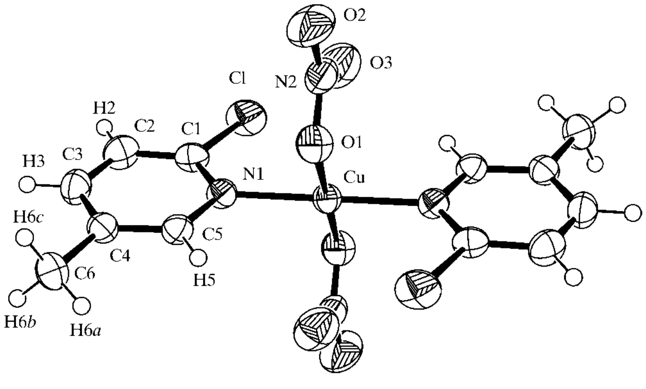


**Figure 1**
A view of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Analysis of the short intermolecular contacts (Nardelli, 1995; Desiraju, 1996) in (I) shows that there are five types of C—H···O hydrogen-bonding interactions (Table 2), and the nitrate group acts as a C—H···O acceptor. A detailed analysis of the crystal packing shows that two types of hydrogen bonds [*viz.* C2···O2($x, \frac{3}{2}-y, z-\frac{1}{2}$) and C2···O1($x, \frac{3}{2}-y, z-\frac{1}{2}$)] generate two-dimensional networks in the direction of the *a*

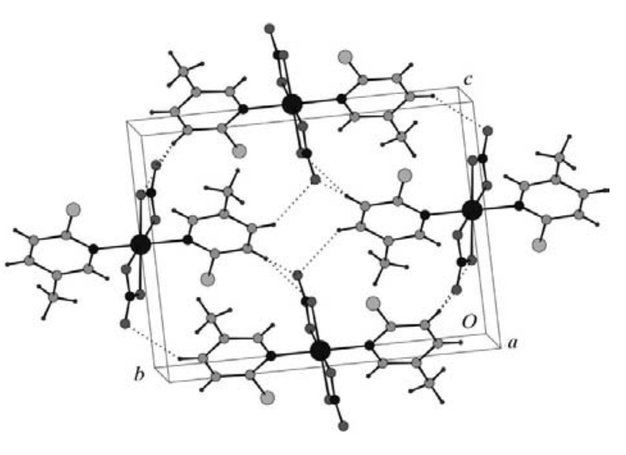


**Figure 2**
The packing diagram of (I), viewed along the *a* axis. Some C—H···O interactions are indicated by dotted lines.

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axis (Fig. 2), and these molecular networks are stacked on top of each other. Three other types of hydrogen bonds [*viz.* C3$\cdots$O2($-x$, $y+\frac{1}{2}$, $\frac{1}{2}-z$), C5$\cdots$O3($x-1$, $y$, $z$) and C6$\cdots$O2($x-1$, $\frac{3}{2}-y$, $z-\frac{1}{2}$)] (Fig. 3) enforce the connection between adjacent molecular networks. Because the centroid–centroid distance between pyridine rings in adjacent molecular networks is 6.6855 Å, any intermolecular forces between these rings should be very weak (Panda *et al.*, 2001). Thus, the C—H$\cdots$O interactions are likely to be the major intermolecular forces, causing the complex molecules to pack in a compact fashion.

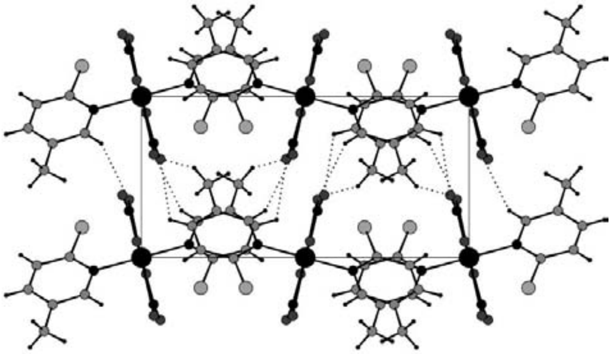

**Figure 3**
The packing diagram of (I), viewed along the *c* axis. Some C—H$\cdots$O interactions are indicated by dotted lines.

In the crystal of (I), every single complex molecule can form ten C—H$\cdots$O hydrogen bonds with neighbouring molecules, but dichlorobis(2-chloro-5-methylpyridine-$\kappa N$)copper(II) can only form six C—H$\cdots$Cl hydrogen bonds. This may be why the melting point of the title complex is much higher than that of the chloro complex.

## Experimental

A solution of 2-chloro-5-methylpyridine (0.8 g, 7.8 mmol) in absolute ethanol (5 ml) was mixed with a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.7 g, 3.3 mmol) in absolute ethanol (5 ml) in a round-bottomed flask. The solution became cloudy after a short time. It was then heated until it became clear, cooled to room temperature and filtered. A single crystal of (I) was obtained from the filtrate after 3 d (m.p. 463 K, decomposition). Analysis calculated for $C_{12}H_{12}CuN_4O_6$: C 32.55, H 2.738, N 12.66%; found: C 32.55, H 2.778, N 12.55%.

*Crystal data*

$[Cu(NO_3)_2(C_6H_6ClN)_2]$
$M_r = 442.7$
Monoclinic, $P2_1/c$
$a = 6.6855$ (2) Å
$b = 13.2221$ (3) Å
$c = 9.9254$ (3) Å
$\beta = 102.5430$ (8)°
$V = 856.43$ (4) Å$^3$
$Z = 2$
$D_x = 1.717$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6378 reflections
$\theta = 2.6$–27.4°
$\mu = 1.62$ mm$^{-1}$
$T = 293$ (2) K
Prism, dark violet
0.40 × 0.25 × 0.23 mm

*Data collection*

Rigaku R-AXIS RAPID CCD area-detector diffractometer
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.621$, $T_{max} = 0.688$
7866 measured reflections
1945 independent reflections
1743 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 27.4°$
$h = -8 \rightarrow 8$
$k = -16 \rightarrow 17$
$l = -12 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R(F) = 0.028$
$wR(F^2) = 0.072$
$S = 1.08$
1945 reflections
117 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 0.4423P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.40$ e Å$^{-3}$
$\Delta\rho_{min} = -0.26$ e Å$^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0063 (12)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu—N1 | 1.9939 (16) | N2—O2 | 1.211 (2) |
| Cu—O1 | 2.0246 (16) | N2—O3 | 1.240 (3) |
| Cu—O3 | 2.4866 (19) | N2—O1 | 1.274 (2) |
| N1—Cu—O1 | 88.23 (6) | O1—Cu—O3 | 55.49 (7) |
| N1—Cu—O3 | 92.80 (7) | | |
| O1—Cu—N1—C1 | 113.70 (15) | N1—Cu—O1—N2 | −91.88 (13) |
| O3—N2—O1—Cu | −5.1 (2) | | |

**Table 2**
Hydrogen-bonding and short-contact geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C2—H2$\cdots$O2$^{i}$ | 0.93 | 2.83 | 3.651 (3) | 147 |
| C2—H2$\cdots$O1$^{i}$ | 0.93 | 2.57 | 3.469 (3) | 162 |
| C3—H3$\cdots$O2$^{ii}$ | 0.93 | 2.78 | 3.587 (3) | 146 |
| C5—H5$\cdots$O3$^{iii}$ | 0.93 | 2.62 | 3.420 (3) | 145 |
| C6—H6*b*$\cdots$O2$^{iv}$ | 0.96 | 2.81 | 3.584 (3) | 138 |
| C5—H5$\cdots$O1 | 0.93 | 2.96 | 3.155 (2) | 93 |
| C3—H3$\cdots$O2$^{iv}$ | 0.93 | 2.76 | 3.188 (3) | 109 |

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

H atoms were included at calculated positions, allowed for as riding and given $U_{iso}$ parameters equal to 1.2 (or 1.5 for methyl H atoms) times the $U_{eq}$ parameters of their parent atoms. C—H distances were restrained to 0.98 Å for methyl H and 0.95 Å for H atoms bonded to atoms C2, C3 and C5.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1150). Services for accessing these data are described at the back of the journal.

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