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Chloridotetrakis(pyridine-4-carbaldehyde- κ N)copper(II) chlorideXiu-Jin Meng,^a Shu-Hua Zhang,^b Ge-Ge Yang,^a Xue-Ren Huang^a and Yi-Min Jiang^{a,b*}

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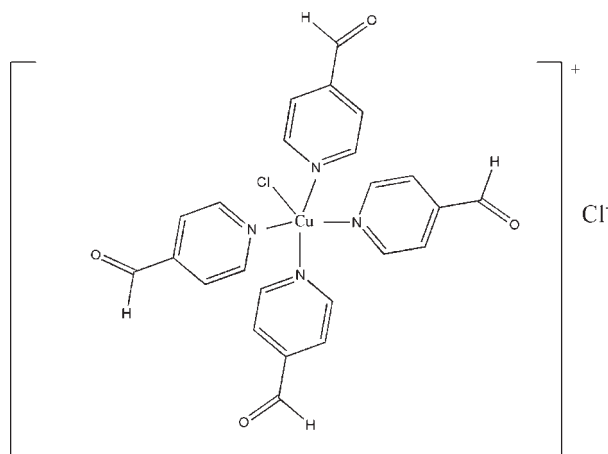
Received 17 August 2009; accepted 13 October 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.033; wR factor = 0.114; data-to-parameter ratio = 13.7.

In the molecular structure of the title compound, $[\text{CuCl}(\text{C}_6\text{H}_5\text{NO})_4]\text{Cl}$, the Cu^{II} atom is coordinated by four N atoms of four pyridine-4-carboxaldehyde ligands and one chloride anion in a slightly distorted square-pyramidal coordination geometry. There is also a non-coordinating Cl^- anion in the crystal structure. The Cu^{II} atom and both Cl atoms are situated on fourfold rotation axes. A weak $\text{C}-\text{H}\cdots\text{Cl}$ interaction is also present.

Related literature

For other compounds with pyridine-4-carboxaldehyde ligands, see: Rivera & Sheldrick (1977); Choi & Wong (1999); Briand *et al.* (2007); Sie *et al.* (2008).



Experimental

Crystal data

$[\text{CuCl}(\text{C}_6\text{H}_5\text{NO})_4]\text{Cl}$
 $M_r = 562.88$
 Tetragonal, $P4/n$
 $a = 10.5035$ (3) Å
 $c = 11.3751$ (6) Å
 $V = 1254.94$ (8) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.12$ mm⁻¹
 $T = 296$ K
 $0.38 \times 0.21 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.675$, $T_{\text{max}} = 0.825$

9150 measured reflections
 1126 independent reflections
 1083 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.114$
 $S = 1.03$
 1126 reflections
 82 parameters

13 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5}\cdots\text{Cl2}$	0.93	2.84	3.732 (2)	160

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2137).

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supporting information

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Chloridotetrakis(pyridine-4-carbaldehyde- κ N)copper(II) chloride**Xiu-Jin Meng, Shu-Hua Zhang, Ge-Ge Yang, Xue-Ren Huang and Yi-Min Jiang****S1. Comment**

Only one structurally characterized coordination compound with pyridine-4-carboxaldehyde acting as the ligand has been reported up to now. In that article, pyridine-4-carboxaldehyde and CoBr_2 form $[\text{CoBr}_2(\text{C}_5\text{H}_4\text{N-CHO})_4]$ (Rivera *et al.* 1977). This compound is highly related to the title compound. In addition, three crystal structures with pyridine-4-carboxaldehyde acting as independent components were reported (Choi *et al.* 1999; Briand *et al.* 2007; Sie *et al.* 2008).

In the cation of the title compound $[\text{CuCl}(\text{OCHC}_5\text{H}_4\text{N})_4]\text{Cl}$, the Cu^{II} centre is coordinated to four N atoms from four pyridine-4-carboxaldehyde ligands and one chloro ligand. Cu exhibits a slightly distorted square-pyramidal coordination geometry. Another non-coordinating chloride anion is observed in the crystal structure. The $[\text{CuCl}(\text{C}_5\text{H}_4\text{N-CHO})_4]^+$ ion has a perfect C_4 symmetry with the direction of the C_4 axis being collinear with the Cu1—Cl1 direction. Cu1, Cl1 and Cl2 are all situated on the same crystallographic 4-fold rotoinversion axis. In the cation therefore all Cu—N bond lengths and angles are equivalent.

Several donor CH functions and the chloride acceptor groups participate in the observed hydrogen bonding pattern forming a two-dimensional network in the *ab* plane (Fig. 2)

S2. Experimental

For the preparation of the title compound, a solution of $\text{CuCl}_2 \times 2 \text{H}_2\text{O}$ (0.08524 g, 0.5 mmol) in H_2O (5 ml) was slowly added over a period of 2 h to a solution of *L*-Cysteic acid (0.094 g, 0.5 mmol), KOH (0.056 g, 1 mmol), pyridine-4-carboxaldehyde (0.06 ml, 0.6 mmol) and NaBH_4 (0.03028 g, 0.8 mmol) in methanol (20 ml) resulting in a blue solution that was stirred for another 4 h at 298 K. Then, the solution was left to evaporate slowly at room temperature. After ten days, blue block crystals of the title compound were obtained with a yield of 70%.

S3. Refinement

H atom bonded to C atom were positioned geometrically with the C—H distance of 0.9303 Å, and treated as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

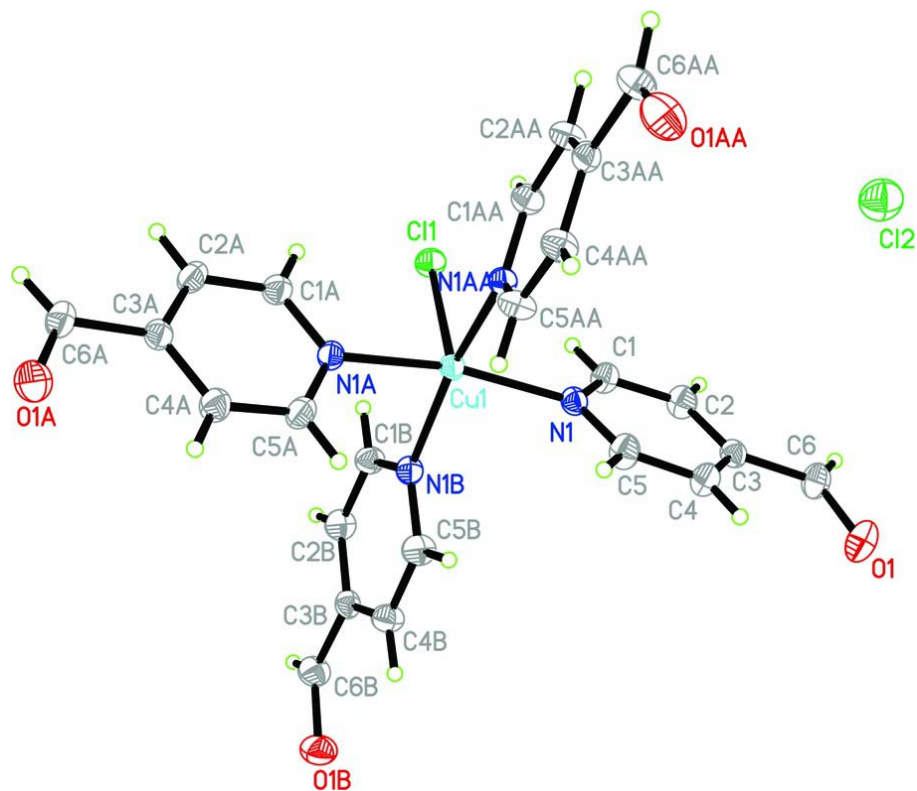


Figure 1

Ellipsoid plot (30% probability) of the title compound showing the numbering scheme. Dashed lines indicate hydrogen bonds. Symmetry code: 1# $-x + 1/2, y + 1/2, z$.

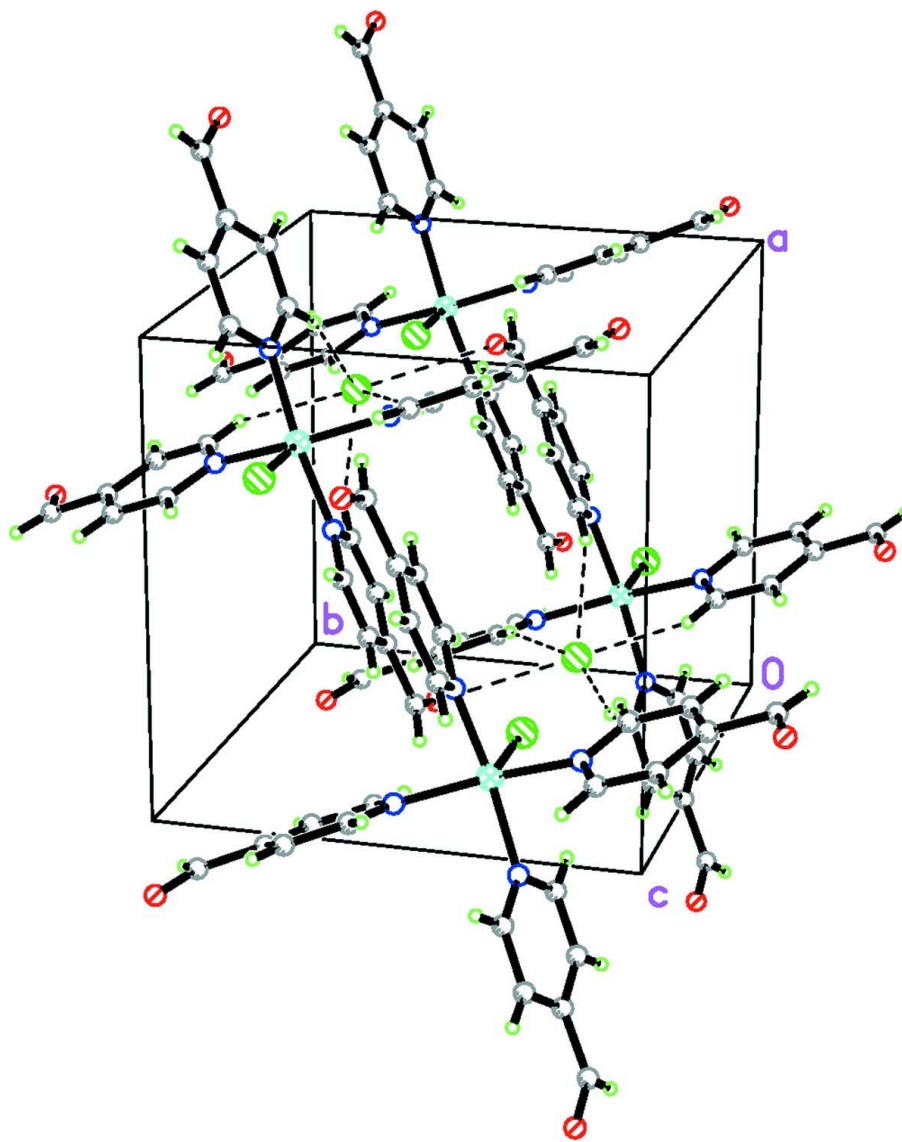


Figure 2

2-D network, as viewed down the *c* axis. Dashed lines indicate hydrogen bonds.

Chloridotetrakis(pyridine-4-carbaldehyde- κN)copper(II) chloride

Crystal data

[CuCl(C₆H₅NO)₄]Cl

$M_r = 562.88$

Tetragonal, *P4/n*

Hall symbol: -P 4a

$a = 10.5035 (3) \text{ \AA}$

$c = 11.3751 (6) \text{ \AA}$

$V = 1254.94 (8) \text{ \AA}^3$

$Z = 2$

$F(000) = 574$

$D_x = 1.490 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1162 reflections

$\theta = 2.6\text{--}25.1^\circ$

$\mu = 1.12 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, blue

$0.38 \times 0.21 \times 0.18 \text{ mm}$

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 phi and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.675$, $T_{\max} = 0.825$

9150 measured reflections
 1126 independent reflections
 1083 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 25.1^\circ$, $\theta_{\min} = 2.6^\circ$
 $h = -12 \rightarrow 12$
 $k = -12 \rightarrow 12$
 $l = -12 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.114$
 $S = 1.03$
 1126 reflections
 82 parameters
 13 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 0.4771P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.7500	0.7500	0.81702 (4)	0.0289 (3)
Cl1	0.7500	0.7500	1.03833 (9)	0.0373 (3)
C1	0.8616 (2)	0.5010 (2)	0.8824 (2)	0.0376 (5)
H1	0.8631	0.5372	0.9570	0.045*
C2	0.9093 (3)	0.3791 (2)	0.8675 (2)	0.0418 (6)
H2	0.9404	0.3342	0.9319	0.050*
C3	0.9109 (2)	0.3241 (2)	0.7569 (2)	0.0342 (5)
C4	0.8612 (3)	0.3938 (2)	0.6653 (2)	0.0411 (6)
H4	0.8601	0.3603	0.5896	0.049*
C5	0.8132 (3)	0.5140 (3)	0.6867 (2)	0.0422 (6)
H5	0.7790	0.5593	0.6240	0.051*
C6	0.9662 (3)	0.1930 (2)	0.7405 (3)	0.0466 (6)
H6	0.9939	0.1428	0.8027	0.056*
N1	0.81319 (18)	0.56845 (17)	0.79272 (17)	0.0320 (4)
O1	0.9721 (2)	0.1535 (2)	0.6224 (2)	0.0598 (6)
Cl2	0.7500	0.7500	0.44844 (12)	0.0562 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0261 (3)	0.0261 (3)	0.0344 (4)	0.000	0.000	0.000
Cl1	0.0410 (4)	0.0410 (4)	0.0299 (5)	0.000	0.000	0.000
C1	0.0418 (13)	0.0357 (12)	0.0354 (11)	0.0033 (10)	-0.0029 (10)	-0.0013 (9)
C2	0.0487 (15)	0.0378 (13)	0.0390 (13)	0.0075 (11)	-0.0068 (10)	0.0066 (10)
C3	0.0288 (11)	0.0306 (11)	0.0434 (12)	-0.0011 (8)	0.0001 (9)	0.0016 (9)
C4	0.0485 (15)	0.0372 (13)	0.0377 (11)	0.0062 (11)	-0.0016 (10)	-0.0031 (10)
C5	0.0527 (16)	0.0355 (13)	0.0385 (13)	0.0079 (11)	-0.0074 (10)	0.0039 (9)
C6	0.0514 (15)	0.0348 (13)	0.0536 (15)	0.0105 (11)	-0.0040 (12)	-0.0009 (11)
N1	0.0314 (10)	0.0282 (9)	0.0364 (9)	0.0000 (7)	-0.0003 (8)	0.0025 (8)
O1	0.0654 (14)	0.0500 (12)	0.0642 (13)	0.0141 (10)	-0.0063 (10)	-0.0171 (10)
Cl2	0.0619 (6)	0.0619 (6)	0.0448 (7)	0.000	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Cu1—N1 ⁱ	2.0380 (19)	C2—H2	0.9300
Cu1—N1	2.0380 (19)	C3—C4	1.377 (3)
Cu1—N1 ⁱⁱ	2.0380 (19)	C3—C6	1.506 (3)
Cu1—N1 ⁱⁱⁱ	2.0380 (19)	C4—C5	1.381 (4)
Cu1—Cl1	2.5175 (11)	C4—H4	0.9300
C1—N1	1.342 (3)	C5—N1	1.335 (3)
C1—C2	1.385 (4)	C5—H5	0.9300
C1—H1	0.9300	C6—O1	1.407 (4)
C2—C3	1.384 (4)	C6—H6	0.9300
N1 ⁱ —Cu1—N1	88.946 (16)	C4—C3—C2	117.5 (2)
N1 ⁱ —Cu1—N1 ⁱⁱ	164.41 (11)	C4—C3—C6	122.6 (2)
N1—Cu1—N1 ⁱⁱ	88.946 (16)	C2—C3—C6	119.9 (2)
N1 ⁱ —Cu1—N1 ⁱⁱⁱ	88.946 (15)	C3—C4—C5	119.4 (2)
N1—Cu1—N1 ⁱⁱⁱ	164.41 (11)	C3—C4—H4	120.3
N1 ⁱⁱ —Cu1—N1 ⁱⁱⁱ	88.946 (16)	C5—C4—H4	120.3
N1 ⁱ —Cu1—Cl1	97.79 (6)	N1—C5—C4	123.4 (2)
N1—Cu1—Cl1	97.79 (6)	N1—C5—H5	118.3
N1 ⁱⁱ —Cu1—Cl1	97.79 (6)	C4—C5—H5	118.3
N1 ⁱⁱⁱ —Cu1—Cl1	97.79 (6)	O1—C6—C3	113.9 (2)
N1—C1—C2	122.2 (2)	O1—C6—H6	123.0
N1—C1—H1	118.9	C3—C6—H6	123.0
C2—C1—H1	118.9	C5—N1—C1	117.4 (2)
C3—C2—C1	120.1 (2)	C5—N1—Cu1	121.56 (16)
C3—C2—H2	120.0	C1—N1—Cu1	120.97 (16)
C1—C2—H2	120.0		

Symmetry codes: (i) $y, -x+3/2, z$; (ii) $-y+3/2, x, z$; (iii) $-x+3/2, -y+3/2, z$.

Hydrogen-bond geometry (Å, °)

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
C5—H5···Cl2	0.93	2.84	3.732 (2)	160