# metal-organic compounds

# Chloridotetrakis(pyridine-4-carbalde-hyde-$\kappa N$)copper(II) chloride

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In the molecular structure of the title compound, [CuCl(C$_6$H$_5$-NO)$_4$]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 C—H···Cl interaction is also present.

## Related literature

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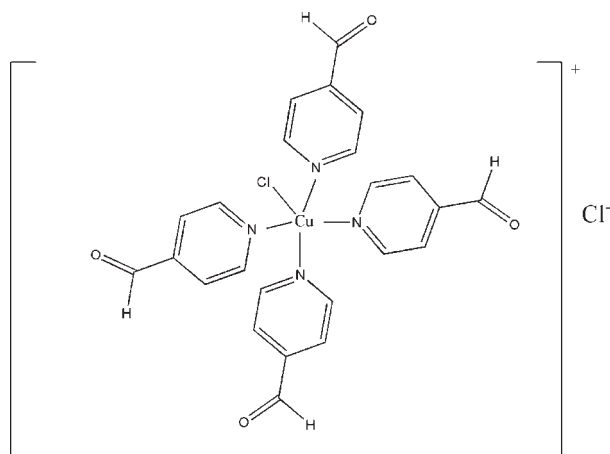


## Experimental

### Crystal data

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

$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.12 mm$^{-1}$
$T$ = 296 K
0.38 × 0.21 × 0.18 mm

### Data collection

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

9150 measured reflections
1126 independent reflections
1083 reflections with $I > 2\sigma(I)$
$R_{int}$ = 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
$\Delta\rho_{max}$ = 0.56 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.48 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
| --- | --- | --- | --- | --- |
| C5—H5···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*.

## References

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Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
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**supplementary materials**

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

**X.-J. Meng, S.-H. Zhang, G.-G. Yang, X.-R. Huang and Y.-M. Jiang**

### 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 $[CoBr_2(C_5H_4N\text{-}CHO)_4]$ (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 $[CuCl(OCHC_5H_4N)_4]Cl$, 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 $[CuCl(C_5H_4N\text{-}CHO)_4]^+$ 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)

### Experimental

For the preparation of the title compound, a solution of $CuCl_2 \times 2\ H_2O$ (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 compoound were obtained with a yield of 70%.

### 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 $U_{iso}(H) = 1.2U_{eq}(C)$.
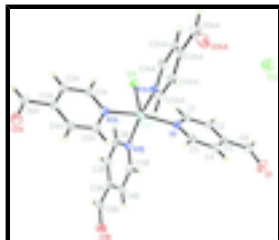
# supplementary materials

**Figures**



Fig. 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, $z$.
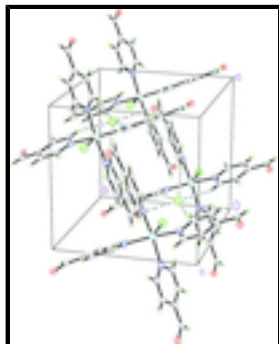


Fig. 2. 2-D network, as viewed down the $c$ axis. Dashed lines indicate hydrogen bonds.

## Chloridotetrakis(pyridine-4-carbaldehyde-κ*N*)copper(II) chloride

*Crystal data*

| | |
|---|---|
| [CuCl(C$_6$H$_5$NO)4]Cl | $Z = 2$ |
| $M_r = 562.88$ | $F_{000} = 574$ |
| Tetragonal, $P4/n$ | $D_x = 1.490$ Mg m$^{-3}$ |
| Hall symbol: -P 4a | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 10.5035$ (3) Å | Cell parameters from 1162 reflections |
| $b = 10.5035$ (3) Å | $\theta = 2.6–25.1°$ |
| $c = 11.3751$ (6) Å | $\mu = 1.12$ mm$^{-1}$ |
| $\alpha = 90°$ | $T = 296$ K |
| $\beta = 90°$ | Block, blue |
| $\gamma = 90°$ | $0.38 \times 0.21 \times 0.18$ mm |
| $V = 1254.94$ (8) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 1126 independent reflections |
| Radiation source: fine-focus sealed tube | 1083 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.017$ |
| $T = 296$ K | $\theta_{max} = 25.1°$ |
| phi and ω scans | $\theta_{min} = 2.6°$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -12 \rightarrow 12$ |
| $T_{min} = 0.675$, $T_{max} = 0.825$ | $k = -12 \rightarrow 12$ |

9150 measured reflections                   $l = -12 \rightarrow 13$

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | H-atom parameters constrained |
| $wR(F^2) = 0.114$ | $w = 1/[\sigma^2(F_o{}^2) + (0.091P)^2 + 0.4771P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1126 reflections | $\Delta\rho_{max} = 0.56$ e Å$^{-3}$ |
| 82 parameters | $\Delta\rho_{min} = -0.48$ e Å$^{-3}$ |
| 13 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| 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 (Å$^2$)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, °)*

| | | | |
|---|---|---|---|
| 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, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C5—H5···Cl2 | 0.93 | 2.84 | 3.732 (2) | 160 |

**Fig. 1**

**Fig. 2**