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# (Benzoato-$\kappa^2O,O'$)chlorido(di-2-pyridylamine-$\kappa^2N,N'$)copper(II)

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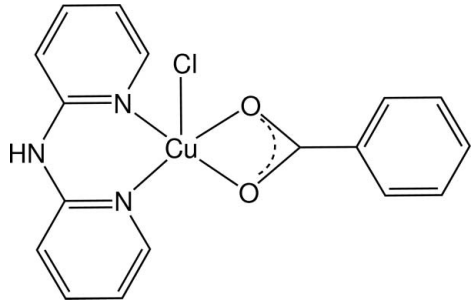
Key indicators: single-crystal X-ray study; $T$ = 123 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.025; $wR$ factor = 0.072; data-to-parameter ratio = 15.9.

In the title complex, $[Cu(C_7H_5O_2)Cl(C_{10}H_9N_3)]$, the Cu atom has a distorted $CuN_2O_2Cl$ square-pyramidal geometry defined by one $N,N'$-bidentate 2,2′-bipyridylamine (bpa) molecule, one $O,O'$-bidentate benzenecarboxylate (BA) anion and one chloride ion, the latter in the apical position. The complete molecule is generated by mirror symmetry with the NH group of bpa, the Cu atom, three C atoms of BA and the Cl atom lying on the mirror plane. The complexes are connected to each other by N—H···Cl hydrogen bonds and $\pi$–$\pi$ stacking interactions between adjacent heterocyclic rings, with distances between the ring centroids of 3.592 (4) and 3.468 (4) Å.

## Related literature

For related literature, see: Brophy *et al.* (1999); Kelland (2005); Li *et al.* (2005); Mao *et al.* (2004); Ranford *et al.* (1993); Selvakumar *et al.* (2006); Wang & Okabe (2005); Youngme *et al.* (1999, 2004).




## Experimental

### Crystal data

$[Cu(C_7H_5O_2)Cl(C_{10}H_9N_3)]$
$M_r$ = 391.31
Orthorhombic, *Pnma*
$a$ = 19.31 (2) Å
$b$ = 11.77 (1) Å
$c$ = 6.958 (6) Å
$V$ = 1581 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.57 mm$^{-1}$
$T$ = 123.1 K
0.40 × 0.40 × 0.10 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR* : Higashi,1995)
$T_{min}$ = 0.587, $T_{max}$ = 0.840
15128 measured reflections
1893 independent reflections
1746 reflections with $F^2 > 2\sigma(F^2)$
$R_{int}$ = 0.015

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.072
$S$ = 1.12
1893 reflections
119 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.34 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.17 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cu1—Cl1 | 2.502 (3) | Cu1—N1 | 1.963 (1) |
| Cu1—O1 | 2.046 (1) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H5···Cl1$^{i}$ | 0.86 | 2.3 | 3.144 (2) | 168 |

Symmetry code: (i) $x, y, z+1$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997), and *PLATON* (Spek, 2003); software used to prepare material for publication: *CrystalStructure*.

The authors thank Kinki University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2414).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m1756-m1757 [ **doi:10.1107/S1600536807023495** ]

# (Benzoato-$\kappa^2O,O'$)chlorido(di-2-pyridylamine-$\kappa^2N,N'$)copper(II)

**N. Okabe, A. Tsuji and M. Yodoshi**

## Comment

The construction of novel Cu(II) complexes are important for the development of new therapeutic drug design, because some Cu(II) complexes of 1,10-phenanthroline have antitumor activity (Selvakumar *et al.*, 2006; Li *et al.*, 2005; Kelland, 2005; Ranford *et al.*, 1993).

In a previous study, we have reported the structure of the ternary Cu(II) complex with 2,2'-bipyridylamine (bpa) and *p*-hydroxybenzenecarboxylate (*p*-HB) (Wang & Okabe, 2005) in which the bpa ligand has been used as the bidentate N-donor ligand and *p*-HB as the bidentate O-donor. In this study, we report the structure of the Cu(II) complex with bpa and benzenecarboxylate (BA), (I).

The central Cu atom in (I) (Fig. 1) has a square-pyramidal $CuN_2O_2Cl$ geometry. Each Cu atom is coordinated by two N atoms from one bpa and two O atoms from one BA and one chloride anion. The bond distances and angles around the Cu atom indicate that the coordination geometry is a slightly distorted square pyramidal (Table 1).

In the complex molecule, the two pyridine rings of the bpa ligand are related by mirror symmetry and distinguished as Ring I (N1/C1—C5) and Ring II ($N1^i$/$C1^i$—$C5^i$) [symmetry code: (i)($x$, 1/2 − $y$, $z$)]. Four ligand atoms (N1, $N1^i$,O1 and $O1^i$) are neary coplanar, and the Cu atom deviates from the mean square plane towards the apical Cl atom by 0.2986 (1) Å. The bite angle N1—Cu1—$N1^i$ is in the range normally observed for the Cu(II) bpa complexes (Wang & Okabe, 2005; Youngme *et al.*, 1999, 2004) The Cu—Cl distance is intermediate between the known values from 2.336 (2) to 2.733 (2) Å (Mao *et al.*, 2004; Brophy *et al.*, 1999). The long Cu—Cl bond distance is explained by the well known Jahn-Teller effect. The molecular structure of (I) is similar to that of the Cu(II) complex with bpa and *p*-HB (Wang & Okabe, 2005), although the hydrogen bonding and the packing modes of these are different to each other.

As shown in Figs. 2a and 2 b, the crystal structure of (I) is stabilized by hydrogen bonds (Table 2) and by two kinds of π-π stacking interactions with distances between the centroids of the aromatic rings, 3.592 (4) Å between *Cg*1 (Ring I) and *Cg*3 (Ring II) at ($x$, $y$, 1 + $z$) and 3.468 (4) Å between *Cg*2 (N1/C5/N2/$C5^i$/$N1^i$/Cu1) [symmetry code: (i) ($x$, 1/2 − $y$, $z$)] and *Cg*4 (BA) at (1 − $x$, 1 − $y$, 1 − $z$).

## Experimental

2,2'-Bipyridylamine (5.0 mg, 0.03 mol) dissolved in 90%(*v*/*v*) methanol-water solution (2 ml) was reacted with benzoic acid (3.6 mg, 0.03 mol), dissolved in the same solution (2 ml) for 5 min at room temperature. This was followed by the addition of $CuCl_2{\cdot}2H_2O$ (5.0 mg, 0.03 mol) dissolved in $H_2O$ (1 ml) and reacted for 15 min at room temperature. After several days green plates of (I) appeared from the mother liquor.

### Refinement

All H atoms were located from the difference Fourier maps, and then were placed in idealized positions and treated as riding, with C—H = 0.93 Å, N—H = 0.86Å and $U_{iso}$(H) = 1.2$U_{eq}$(C,*N*).

### Figures

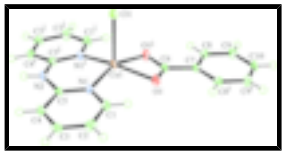

Fig. 1. View of (I) with the atomic numbering-scheme and displacement ellipsoid drawn at the 50% probability level (arbitrary spheres for the H atoms). Symmetry code: (i) *x*, 1/2 − *y*, *z*.

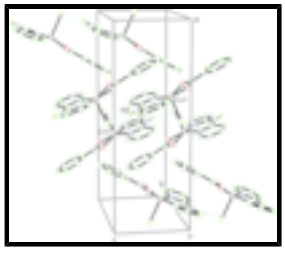

Fig. 2. A view of the N—H···Cl hydrogen bonds (dashed lines) between the adjacent molecules of (I)

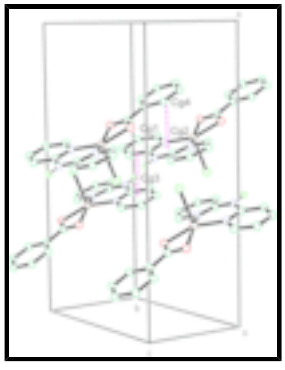

Fig. 3. A view of the π-π stacking interaction in (I). See the text for the ring designations.

### (Benzoato-κ$^2$*O*,*O*')chlorido(di-2-pyridylamine- κ$^2$*N*,*N*')copper(II)

*Crystal data*

| | |
|---|---|
| $[Cu(C_7H_5O_2)Cl(C_{10}H_9N_3)]$ | $F_{000}$ = 796.0 |
| $M_r$ = 391.31 | $D_x$ = 1.644 Mg m$^{-3}$ |
| Orthorhombic, *Pnma* | Mo *K*α radiation<br>λ = 0.7107 Å |
| Hall symbol: -P 2ac 2n | Cell parameters from 13658 reflections |
| *a* = 19.31 (2) Å | θ = 3.1–27.5º |
| *b* = 11.77 (1) Å | μ = 1.57 mm$^{-1}$ |
| *c* = 6.958 (6) Å | *T* = 123.1 K |
| *V* = 1581 (3) Å$^3$ | Plate, green |
| *Z* = 4 | 0.40 × 0.40 × 0.10 mm |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 1746 reflections with $F^2 > 2.0\sigma(F^2)$ |
| Detector resolution: 10.00 pixels $mm^{-1}$ | $R_{int} = 0.015$ |
| ω scans | $\theta_{max} = 27.5°$ |
| Absorption correction: multi-scan (ABSCOR : Higashi,1995) | $h = -25\rightarrow25$ |
| $T_{min} = 0.587$, $T_{max} = 0.840$ | $k = -15\rightarrow15$ |
| 15128 measured reflections | $l = -8\rightarrow9$ |
| 1893 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.025$ | $w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 1.7191P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.072$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.12$ | $\Delta\rho_{max} = 0.34$ e Å$^{-3}$ |
| 1893 reflections | $\Delta\rho_{min} = -1.17$ e Å$^{-3}$ |
| 119 parameters | Extinction correction: none |

*Special details*

**Geometry**. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

**Refinement**. Refinement using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on $F^2$. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.61824 (1) | 0.2500 | 0.18707 (4) | 0.0144 (1) |
| Cl1 | 0.50045 (3) | 0.2500 | 0.03740 (8) | 0.0198 (1) |
| O1 | 0.67196 (6) | 0.3426 (1) | −0.0121 (2) | 0.0190 (3) |
| N1 | 0.60171 (7) | 0.3723 (1) | 0.3734 (2) | 0.0148 (3) |
| N2 | 0.5622 (1) | 0.2500 | 0.6194 (3) | 0.0166 (4) |
| C1 | 0.61517 (9) | 0.4801 (2) | 0.3141 (3) | 0.0201 (4) |
| C2 | 0.6049 (1) | 0.5735 (2) | 0.4273 (3) | 0.0238 (4) |
| C3 | 0.57907 (9) | 0.5576 (1) | 0.6132 (3) | 0.0210 (4) |
| C4 | 0.56524 (9) | 0.4495 (2) | 0.6754 (2) | 0.0183 (3) |
| C5 | 0.57716 (8) | 0.3570 (1) | 0.5513 (2) | 0.0146 (3) |
| C6 | 0.6903 (1) | 0.2500 | −0.0902 (3) | 0.0153 (4) |
| C7 | 0.7299 (1) | 0.2500 | −0.2737 (3) | 0.0144 (4) |
| C8 | 0.74776 (9) | 0.1475 (1) | −0.3616 (3) | 0.0178 (3) |
| C9 | 0.78256 (9) | 0.1476 (1) | −0.5363 (3) | 0.0203 (3) |
| C10 | 0.7993 (1) | 0.2500 | −0.6228 (4) | 0.0208 (5) |

| | | | | |
|---|---|---|---|---|
| H1 | 0.6322 | 0.4908 | 0.1905 | 0.024* |
| H2 | 0.6148 | 0.6460 | 0.3816 | 0.028* |
| H3 | 0.5714 | 0.6195 | 0.6935 | 0.025* |
| H4 | 0.5481 | 0.4373 | 0.7986 | 0.022* |
| H5 | 0.5391 | 0.2500 | 0.7250 | 0.020* |
| H6 | 0.7363 | 0.0791 | −0.3030 | 0.021* |
| H7 | 0.7945 | 0.0793 | −0.5948 | 0.024* |
| H8 | 0.8221 | 0.2500 | −0.7405 | 0.025* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0185 (2) | 0.0141 (2) | 0.0105 (2) | 0.0000 | 0.0030 (1) | 0.0000 |
| Cl1 | 0.0175 (3) | 0.0296 (3) | 0.0125 (3) | 0.0000 | 0.0023 (2) | 0.0000 |
| O1 | 0.0228 (6) | 0.0191 (6) | 0.0150 (6) | 0.0009 (5) | 0.0050 (5) | −0.0011 (5) |
| N1 | 0.0159 (6) | 0.0150 (6) | 0.0136 (6) | −0.0010 (5) | 0.0010 (5) | −0.0012 (5) |
| N2 | 0.020 (1) | 0.021 (1) | 0.0092 (9) | 0.0000 | 0.0052 (8) | 0.0000 |
| C1 | 0.0234 (9) | 0.0182 (9) | 0.0187 (9) | −0.0028 (6) | 0.0043 (6) | 0.0000 (7) |
| C2 | 0.0264 (9) | 0.0156 (8) | 0.0292 (9) | −0.0030 (7) | 0.0046 (8) | −0.0017 (7) |
| C3 | 0.0201 (8) | 0.0197 (8) | 0.0233 (9) | 0.0006 (7) | −0.0007 (7) | −0.0085 (7) |
| C4 | 0.0167 (7) | 0.0236 (9) | 0.0146 (8) | 0.0020 (6) | −0.0001 (6) | −0.0040 (6) |
| C5 | 0.0124 (7) | 0.0182 (8) | 0.0133 (7) | 0.0000 (6) | −0.0011 (6) | −0.0010 (6) |
| C6 | 0.014 (1) | 0.020 (1) | 0.012 (1) | 0.0000 | −0.0014 (9) | 0.0000 |
| C7 | 0.0120 (9) | 0.018 (1) | 0.013 (1) | 0.0000 | −0.0004 (9) | 0.0000 |
| C8 | 0.0182 (7) | 0.0167 (8) | 0.0185 (8) | −0.0010 (6) | 0.0023 (6) | 0.0009 (7) |
| C9 | 0.0212 (8) | 0.0206 (8) | 0.0190 (8) | 0.0002 (6) | 0.0036 (7) | −0.0053 (7) |
| C10 | 0.020 (1) | 0.030 (1) | 0.012 (1) | 0.0000 | 0.0054 (9) | 0.0000 |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—Cl1 | 2.502 (3) | C3—C4 | 1.370 (3) |
| Cu1—O1 | 2.046 (1) | C3—H3 | 0.9300 |
| Cu1—O1$^{i}$ | 2.046 (1) | C4—C5 | 1.409 (2) |
| Cu1—N1 | 1.963 (1) | C4—H4 | 0.9300 |
| Cu1—N1$^{i}$ | 1.963 (1) | C6—O1$^{i}$ | 1.269 (2) |
| C6—O1 | 1.269 (2) | C6—C7 | 1.488 (3) |
| N1—C1 | 1.359 (2) | C7—C8 | 1.396 (2) |
| N1—C5 | 1.338 (2) | C7—C8$^{i}$ | 1.396 (2) |
| N2—C5 | 1.377 (2) | C8—C9 | 1.389 (2) |
| N2—C5$^{i}$ | 1.377 (2) | C8—H6 | 0.9300 |
| N2—H5 | 0.8600 | C9—C10 | 1.386 (2) |
| C1—C2 | 1.367 (3) | C9—H7 | 0.9300 |
| C1—H1 | 0.9300 | C10—C9$^{i}$ | 1.386 (2) |
| C2—C3 | 1.399 (3) | C10—H8 | 0.9300 |
| C2—H2 | 0.9299 | | |
| Cl1—Cu1—O1 | 100.32 (4) | H2—C2—C1 | 120.7624 |
| Cl1—Cu1—O1$^{i}$ | 100.32 (4) | C4—C3—C2 | 119.0 (2) |

| | | | |
|---|---|---|---|
| Cl1—Cu1—N1 | 97.30 (4) | C4—C3—H3 | 120.4892 |
| Cl1—Cu1—N1$^{i}$ | 97.30 (4) | H3—C3—C2 | 120.4784 |
| O1—Cu1—O1$^{i}$ | 64.43 (5) | C5—C4—C3 | 119.5 (2) |
| O1—Cu1—N1 | 97.97 (5) | C5—C4—H4 | 120.2397 |
| O1—Cu1—N1$^{i}$ | 156.99 (5) | H4—C4—C3 | 120.2411 |
| O1$^{i}$—Cu1—N1 | 156.99 (5) | O1$^{i}$—C6—O1 | 118.5 (2) |
| O1$^{i}$—Cu1—N1$^{i}$ | 97.97 (5) | O1$^{i}$—C6—C7 | 120.7 (1) |
| N1—Cu1—N1$^{i}$ | 94.33 (6) | C7—C6—O1i | 120.7 (1) |
| C6—O1—Cu1 | 88.5 (1) | C8—C7—C6 | 120.2 (1) |
| C1—N1—Cu1 | 117.0 (1) | C8—C7—C8$^{i}$ | 119.6 (2) |
| C1—N1—C5 | 118.3 (1) | C8$^{i}$—C7—C6 | 120.2 (1) |
| C5—N1—Cu1 | 124.7 (1) | C9—C8—C7 | 120.2 (2) |
| C5—N2—C5$^{i}$ | 132.5 (2) | C9—C8—H6 | 119.9074 |
| C5—N2—H5 | 113.7538 | H6—C8—C7 | 119.9042 |
| C5$^{i}$—N2—H5 | 113.7538 | C10—C9—C8 | 119.5 (2) |
| C2—C1—N1 | 123.3 (2) | C10—C9—H7 | 120.2314 |
| C2—C1—H1 | 118.3538 | H7—C9—C8 | 120.2290 |
| H1—C1—N1 | 118.3581 | C9$^{i}$—C10—C9 | 120.9 (2) |
| C3—C2—C1 | 118.5 (2) | C9$^{i}$—C10—H8 | 119.5321 |
| C3—C2—H2 | 120.7669 | H8—C10—C9 | 119.5321 |
| Cl1—Cu1—O1—C6 | −94.68 (11) | C1—C2—C3—C4 | 0.1 (2) |
| Cl1—Cu1—N1—C1 | −89.35 (12) | C2—C3—C4—C5 | −0.0 (2) |
| Cu1—O1—C6—C7 | 174.32 (17) | C3—C4—C5—N1 | −0.1 (2) |
| Cu1—N1—C1—C2 | 178.8 (1) | C3—C4—C5—N2 | −179.67 (17) |
| Cu1—N1—C5—N2 | 1.0 (2) | O1—C6—C7—C8 | −177.83 (18) |
| Cu1—N1—C5—C4 | −178.6 (1) | C6—C7—C8—C9 | 177.7 (3) |
| H5—N2—C5—N1 | −168.0 | C7—C8—C9—C10 | −0.1 (2) |
| H5—N2—C5—C4 | 11.6 | C8—C9—C10—H8 | −179.2 |
| N1—C1—C2—C3 | −0.1 (2) | | |

Symmetry codes: (i) *x*, −*y*+1/2, *z*; i.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H5···Cl1$^{ii}$ | 0.86 | 2.3 | 3.144 (2) | 168 |

Symmetry codes: (ii) *x*, *y*, *z*+1.

**Fig. 1**

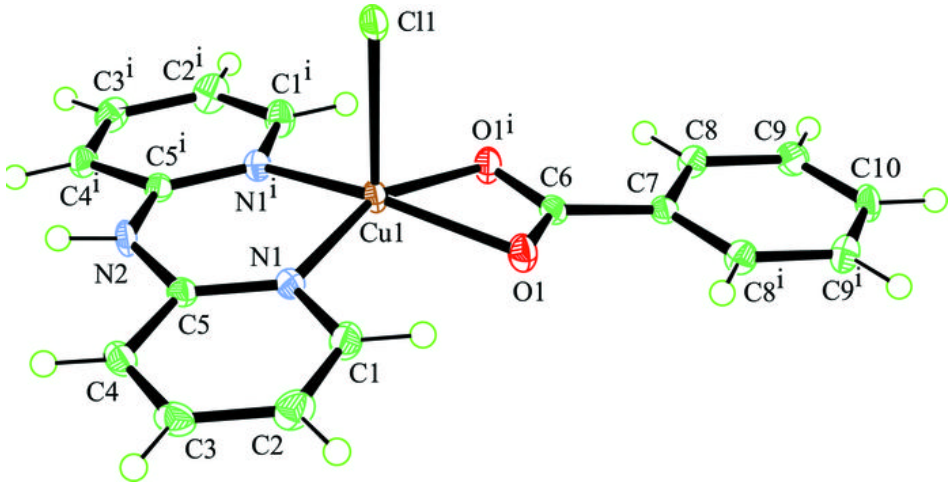
Cl1
C3i
C2i
C1i
O1i
C8
C9
C10
C5i
C6
C7
C4i
N1i
Cu1
N2
N1
O1
C8i
C9i
C5
C1
C4
C3
C2

**Fig. 2**

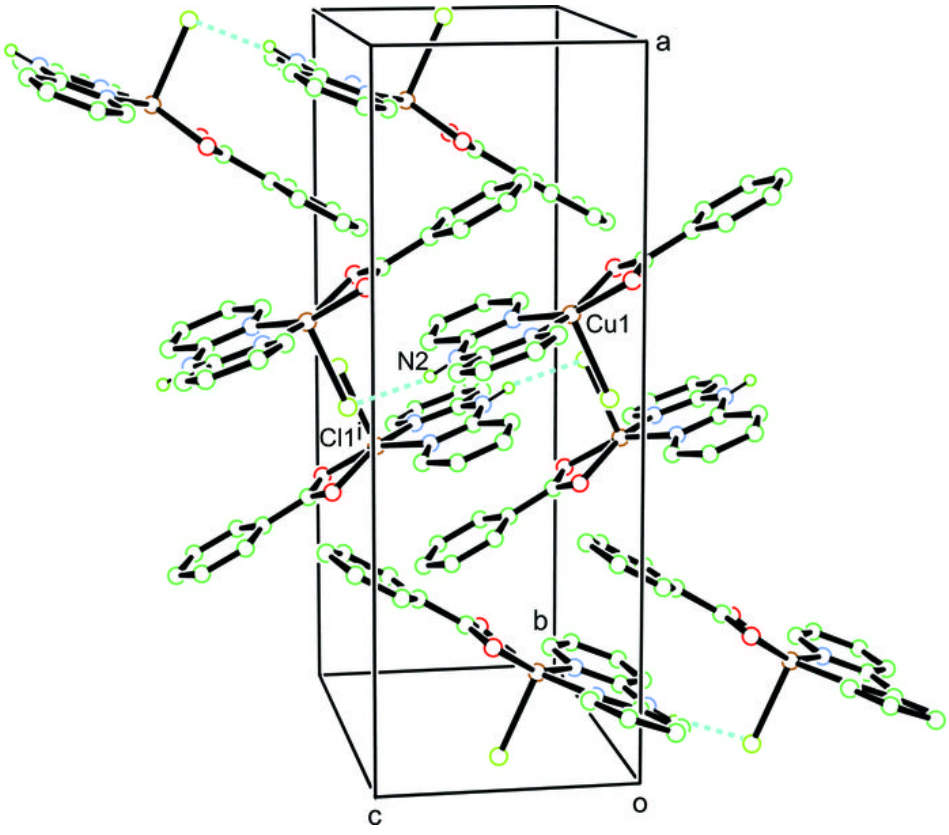

**Fig. 3**