

## (Benzoato- $\kappa$ O)bis(1,10-phenanthroline- $\kappa^2$ N,N')copper(II) chloride benzoic acid disolvate

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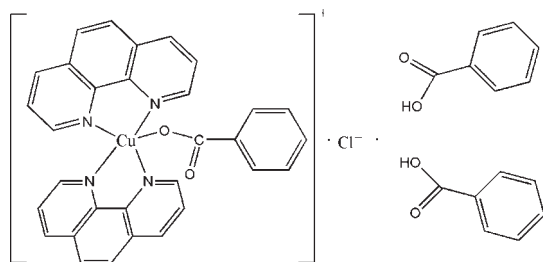
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; disorder in main residue;  $R$  factor = 0.038;  $wR$  factor = 0.101; data-to-parameter ratio = 12.1.

In the title complex,  $[\text{Cu}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{Cl}\cdot 2\text{C}_6\text{H}_5\text{COOH}$ , the  $\text{Cu}^{\text{II}}$  ion is coordinated by one carboxylate O atom from a benzoate anion and four N atoms from two phenanthroline ligands in a distorted five-coordinate trigonal-bipyramidal  $\text{CuON}_4$  chromophore. The  $\text{Cu}^{2+}$  and the  $\text{Cl}^-$  ion are imposed by a twofold rotation axis which also bisects the equally disordered benzoate anion. In the crystal, the molecules are assembled into chains along  $[010]$  by  $\text{C}-\text{H}\cdots\text{Cl}$ ,  $\text{O}-\text{H}\cdots\text{Cl}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions. The resulting chains are further connected into two-dimensional supramolecular layers parallel to  $[100]$  by inter-chain  $\pi\cdots\pi$  stacking interactions [centroid-centroid distance =  $3.823$  (5) Å] between the phenanthroline ligands and the benzoic acid molecules, and by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions. Strong  $\pi\cdots\pi$  stacking interactions between adjacent phenanthroline ligands [ $3.548$  (4) Å] assemble the layers into a three-dimensional supramolecular architecture.

### Related literature

For copper-aromatic acid coordination polymers, see: Li *et al.* (2006); Devereux *et al.* (2007). For related structures, see: Mao *et al.* (2001). For the  $\tau$  parameter, see: Addison *et al.* (1984).



### Experimental

#### Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{Cl}\cdot 2\text{C}_7\text{H}_6\text{O}_2$	$\beta = 113.86$ (3) $^\circ$
$M_r = 824.74$	$V = 3922.1$ (14) Å <sup>3</sup>
Monoclinic, $C2/c$	$Z = 4$
$a = 16.724$ (3) Å	Mo $K\alpha$ radiation
$b = 19.288$ (4) Å	$\mu = 0.68$ mm <sup>-1</sup>
$c = 13.295$ (3) Å	$T = 293$ K
	$0.35 \times 0.31 \times 0.28$ mm

#### Data collection

Rigaku R-Axis RAPID diffractometer	15193 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	3449 independent reflections
$T_{\text{min}} = 0.710$ , $T_{\text{max}} = 0.750$	2623 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.101$	$\Delta\rho_{\text{max}} = 0.33$ e Å <sup>-3</sup>
$S = 1.08$	$\Delta\rho_{\text{min}} = -0.45$ e Å <sup>-3</sup>
3449 reflections	
286 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5A}\cdots\text{Cl}$	0.96	2.94	3.728 (4)	140
$\text{O3}-\text{H31}\cdots\text{Cl}$	0.85 (4)	2.20 (4)	3.051 (3)	177 (4)
$\text{O3}-\text{H31}\cdots\text{Cl}^{\text{i}}$	0.85 (4)	2.20 (4)	3.051 (3)	177 (4)
$\text{C24}-\text{H24A}\cdots\text{O4}^{\text{ii}}$	0.93	2.49	3.355 (5)	155
$\text{C8}-\text{H8A}\cdots\text{O3}^{\text{iii}}$	0.93	2.47	3.307 (4)	149
$\text{C10}-\text{H10A}\cdots\text{O1}^{\text{iv}}$	0.93	2.53	3.275 (7)	138
$\text{C12}-\text{H12A}\cdots\text{O1}^{\text{iv}}$	0.93	2.30	3.106 (7)	146

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2032).

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**supplementary materials**

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## (Benzoato- $\kappa O$ )bis(1,10-phenanthroline- $\kappa^2 N, N'$ )copper(II) chloride benzoic acid disolvate

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### Comment

Over the past decades, vast efforts have been dedicated to rational design and synthesis of copper-aromatic-acid coordination polymers, due to their potential applications in medicine, electronics, magnetism, catalysis, gas storage, etc... It is well known that aromatic carboxylic acids, such as *p*-phthalic acid (Li *et al.*, 2006) and salicylic acid (Devereux *et al.*, 2007), were used to construct coordination polymers with copper salts and exhibited interesting electrochemical properties. In the present contribution, we report a new copper coordination complex,  $[\text{Cu}(\text{phen})_2(\text{C}_6\text{H}_5\text{COO})]_2(\text{C}_6\text{H}_5\text{COOH})\cdot\text{Cl}$ , resulting from self-assembly of  $\text{Cu}^{\text{II}}$  ions, phenanthroline ligands and benzoic acid molecules.

The crystal structure of the title complex consists of  $[\text{Cu}(\text{phen})_2(\text{C}_6\text{H}_5\text{COO})]^+$  cations, free benzoic acid molecules and uncoordinated  $\text{Cl}^-$  anions in a ratio 1:2:1. The  $\text{Cu}^{\text{II}}$  ion is coordinated by one carboxylate O atom from a benzoate anion and four N atoms from two phenanthroline ligands to complete a distorted five-coordinate trigonal bipyramidal  $\text{CuON}_4$  chromophore. The equatorial positions of the  $\text{Cu}^{\text{II}}$  ion are occupied by one O atom and two N atoms from different phen molecules, and the axial ones by the other two N atoms. The Addison's  $\tau$  value of 0.53 ( $\tau = 0$  for an ideal square pyramid and  $\tau = 1$  for an ideal trigonal bipyramid) speaks for a trigonal bipyramid character with a '3+2' coordination type (Addison *et al.*, 1984), which is similar to that of Cu atom in the literature (Mao *et al.*, 2001). The dihedral angle between the benzene ring plane and the carboxylate plane of the coordinated benzoic ion is  $14.4(1)^\circ$ , which is larger than the dihedral angle in the free benzoic acid molecule ( $6.5(6)^\circ$ ). In addition, the  $\text{Cu}^{\text{II}}$  ions and the benzoate ligands are crystallographically imposed by 2-fold rotation axes. The molecules are assembled into one-dimensional chains along [010] direction through hydrogen bonds interactions (C5–H5A...Cl, O3–H3A...Cl, C24–H24A...O4, C8–H8A...O3). The resulting chains are further connected into two-dimensional supramolecular layers parallel to [100] by interchain  $\pi\cdots\pi$  stacking interactions ( $3.823(5)$  Å) between the phenanthroline ligands and the molecular benzoic acid, and by hydrogen bonding interactions (C10–H10A...O1, C12–H12A...O1). Furthermore, on the basis of strong  $\pi\cdots\pi$  stacking interactions between interlayer adjacent phenanthroline ligands ( $3.548(4)$  Å), the layers are assembled into a three-dimensional supramolecular architecture.

### Experimental

Dropwise addition of 2.0 mL (1.0 M) NaOH to a stirred aqueous solution of 0.1708 g (1.001 mmol)  $\text{CuCl}_2\cdot\text{H}_2\text{O}$  in 10.0 mL  $\text{H}_2\text{O}$  afforded a blue precipitate, which was separated by centrifugation and washed with distilled water for 5 times. The gathered precipitate was then transferred into a solution of benzoic acid (0.2448 g, 2.0049 mmol) and 1,10-phenanthroline (0.1986 g, 1.002 mmol) in a mixed solvent composed of 10.0 mL  $\text{H}_2\text{O}$  and 10.0 mL ethanol to yield a blue suspension. The mixture was then stirred for further 30 min. After filtration, the filtrate was kept at room temperature and afforded a small amount of blue crystalline blocks after 20 days.

## Refinement

H atoms bonded to C atoms were placed in geometrically calculated positions and were refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . The H atom attached to O3 was found in a difference Fourier map and was refined using a riding model, with the O—H bond distance fixed as initially found and with  $U_{\text{iso}}(\text{H})$  value set at  $1.2 U_{\text{eq}}(\text{O})$ .

## Figures

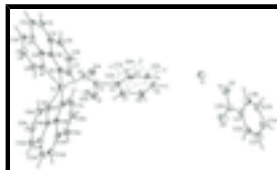


Fig. 1. ORTEP view of the title compound. The displacement ellipsoids are drawn at the 20% probability level.



Fig. 2. The three-dimensional structure of the title complex through  $\pi \cdots \pi$  stacking and hydrogen bond interactions.

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### Crystal data

$[\text{Cu}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{Cl}\cdot 2\text{C}_7\text{H}_6\text{O}_2$	$F(000) = 1700$
$M_r = 824.74$	$D_x = 1.397 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 15193 reflections
$a = 16.724 (3) \text{ \AA}$	$\theta = 3.2\text{--}25.0^\circ$
$b = 19.288 (4) \text{ \AA}$	$\mu = 0.68 \text{ mm}^{-1}$
$c = 13.295 (3) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 113.86 (3)^\circ$	Block, blue
$V = 3922.1 (14) \text{ \AA}^3$	$0.35 \times 0.31 \times 0.28 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku R-Axis RAPID diffractometer	3449 independent reflections
Radiation source: fine-focus sealed tube graphite	2623 reflections with $I > 2\sigma(I)$
Detector resolution: 0 pixels $\text{mm}^{-1}$	$R_{\text{int}} = 0.029$
$\omega$ scans	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 3.2^\circ$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -19 \rightarrow 17$
$T_{\text{min}} = 0.710$ , $T_{\text{max}} = 0.750$	$k = -22 \rightarrow 22$
	$l = -15 \rightarrow 15$

15193 measured reflections

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.101$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 3.5087P]$
3449 reflections	where $P = (F_o^2 + 2F_c^2)/3$
286 parameters	$(\Delta/\sigma)_{\max} = 0.001$
0 restraints	$\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu	0.5000	0.26282 (3)	0.2500	0.05651 (17)	
N1	0.40747 (13)	0.19982 (11)	0.12871 (18)	0.0554 (5)	
N2	0.40438 (13)	0.26263 (12)	0.30525 (18)	0.0565 (5)	
O1	0.4521 (4)	0.3849 (3)	0.1410 (5)	0.090 (2)	0.50
O2	0.5351 (3)	0.3568 (3)	0.3129 (5)	0.0600 (12)	0.50
C1	0.5000	0.4012 (3)	0.2500	0.0678 (11)	
C2	0.5084 (4)	0.47718 (18)	0.2698 (3)	0.0556 (17)	0.50
C3	0.4829 (4)	0.5284 (3)	0.1894 (2)	0.0788 (19)	0.50
H3A	0.4598	0.5159	0.1131	0.095*	0.50
C4	0.4907 (5)	0.5979 (2)	0.2196 (3)	0.075 (3)	0.50
H4A	0.4731	0.6333	0.1641	0.090*	0.50
C5	0.5240 (5)	0.61615 (16)	0.3302 (4)	0.084 (3)	0.50
H5A	0.5295	0.6641	0.3511	0.100*	0.50
C6	0.5495 (3)	0.5649 (2)	0.4106 (3)	0.0794 (18)	0.50
H6A	0.5726	0.5775	0.4869	0.095*	0.50
C7	0.5417 (3)	0.49540 (19)	0.3803 (3)	0.0639 (15)	0.50

## supplementary materials

H7A	0.5593	0.4600	0.4358	0.077*	0.50
C8	0.4095 (2)	0.16743 (16)	0.0414 (2)	0.0694 (8)	
H8A	0.4614	0.1678	0.0313	0.083*	
C9	0.3373 (2)	0.13300 (16)	-0.0355 (3)	0.0791 (9)	
H9A	0.3417	0.1106	-0.0950	0.095*	
C10	0.2608 (2)	0.13242 (17)	-0.0231 (3)	0.0794 (9)	
H10A	0.2123	0.1097	-0.0742	0.095*	
C11	0.25483 (17)	0.16598 (14)	0.0667 (2)	0.0620 (7)	
C12	0.17667 (18)	0.16982 (17)	0.0868 (3)	0.0790 (9)	
H12A	0.1260	0.1485	0.0379	0.095*	
C13	0.17515 (18)	0.20324 (17)	0.1738 (3)	0.0773 (9)	
H13A	0.1231	0.2055	0.1835	0.093*	
C14	0.25144 (16)	0.23560 (14)	0.2524 (2)	0.0596 (7)	
C15	0.25428 (19)	0.27038 (17)	0.3459 (3)	0.0726 (8)	
H15A	0.2041	0.2741	0.3596	0.087*	
C16	0.3303 (2)	0.29866 (18)	0.4164 (3)	0.0773 (9)	
H16A	0.3330	0.3211	0.4796	0.093*	
C17	0.40467 (19)	0.29405 (17)	0.3938 (3)	0.0728 (8)	
H17A	0.4565	0.3138	0.4430	0.087*	
C18	0.32904 (15)	0.23281 (13)	0.2352 (2)	0.0502 (6)	
C19	0.33051 (15)	0.19836 (13)	0.1411 (2)	0.0509 (6)	
C20	0.6442 (2)	0.89663 (16)	0.5209 (3)	0.0723 (8)	
C21	0.6652 (2)	0.94046 (15)	0.6202 (3)	0.0673 (8)	
C22	0.7514 (2)	0.9571 (2)	0.6830 (3)	0.0868 (10)	
H22A	0.7949	0.9405	0.6626	0.104*	
C23	0.7738 (3)	0.9976 (2)	0.7744 (3)	0.1056 (12)	
H23A	0.8322	1.0083	0.8157	0.127*	
C24	0.7114 (3)	1.0223 (2)	0.8054 (4)	0.1033 (12)	
H24A	0.7268	1.0498	0.8680	0.124*	
C25	0.6259 (3)	1.0067 (2)	0.7445 (4)	0.1094 (14)	
H25A	0.5833	1.0236	0.7662	0.131*	
C26	0.6014 (2)	0.96621 (18)	0.6513 (3)	0.0901 (11)	
H26A	0.5427	0.9564	0.6100	0.108*	
Cl	0.5000	0.80270 (7)	0.2500	0.0916 (4)	
O4	0.69924 (15)	0.87024 (14)	0.4972 (2)	0.1004 (8)	
O3	0.55968 (17)	0.88975 (14)	0.4593 (2)	0.0977 (8)	
H31	0.544 (3)	0.867 (2)	0.400 (3)	0.117*	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu	0.0442 (3)	0.0686 (3)	0.0647 (3)	0.000	0.0303 (2)	0.000
N1	0.0514 (12)	0.0577 (13)	0.0631 (13)	0.0028 (10)	0.0293 (11)	-0.0023 (11)
N2	0.0457 (11)	0.0689 (14)	0.0605 (13)	-0.0025 (10)	0.0274 (11)	-0.0060 (11)
O1	0.074 (3)	0.099 (5)	0.066 (4)	0.006 (3)	-0.003 (3)	-0.021 (3)
O2	0.048 (3)	0.066 (3)	0.065 (3)	-0.003 (2)	0.021 (3)	-0.001 (2)
C1	0.043 (2)	0.069 (3)	0.090 (4)	0.000	0.025 (2)	0.000
C2	0.036 (3)	0.071 (3)	0.057 (5)	0.001 (4)	0.015 (4)	0.008 (3)

C3	0.051 (4)	0.108 (6)	0.068 (4)	0.009 (4)	0.014 (3)	0.018 (4)
C4	0.066 (5)	0.059 (4)	0.099 (10)	0.010 (5)	0.031 (7)	0.030 (4)
C5	0.066 (5)	0.062 (4)	0.118 (8)	0.009 (4)	0.033 (6)	-0.016 (5)
C6	0.086 (4)	0.067 (4)	0.077 (4)	0.000 (3)	0.025 (4)	-0.008 (4)
C7	0.065 (4)	0.060 (4)	0.062 (4)	0.000 (3)	0.020 (3)	-0.004 (3)
C8	0.0703 (18)	0.071 (2)	0.077 (2)	0.0054 (16)	0.0401 (17)	-0.0067 (16)
C9	0.088 (2)	0.071 (2)	0.075 (2)	-0.0002 (18)	0.0290 (18)	-0.0246 (17)
C10	0.0640 (19)	0.075 (2)	0.085 (2)	-0.0066 (16)	0.0146 (17)	-0.0168 (18)
C11	0.0550 (16)	0.0535 (16)	0.0726 (19)	-0.0011 (13)	0.0207 (14)	-0.0038 (14)
C12	0.0483 (16)	0.078 (2)	0.105 (3)	-0.0131 (15)	0.0248 (17)	-0.009 (2)
C13	0.0491 (16)	0.081 (2)	0.108 (3)	-0.0054 (15)	0.0388 (18)	0.000 (2)
C14	0.0462 (14)	0.0615 (17)	0.0778 (18)	0.0016 (13)	0.0322 (14)	0.0083 (15)
C15	0.0616 (18)	0.086 (2)	0.090 (2)	0.0066 (16)	0.0514 (18)	0.0042 (18)
C16	0.071 (2)	0.097 (2)	0.080 (2)	0.0014 (18)	0.0474 (18)	-0.0120 (18)
C17	0.0627 (17)	0.093 (2)	0.0726 (19)	-0.0080 (16)	0.0373 (16)	-0.0174 (17)
C18	0.0423 (13)	0.0502 (14)	0.0619 (15)	0.0033 (11)	0.0248 (12)	0.0061 (13)
C19	0.0450 (13)	0.0464 (15)	0.0629 (16)	0.0042 (11)	0.0237 (13)	0.0044 (12)
C20	0.080 (2)	0.0680 (19)	0.093 (2)	0.0097 (16)	0.061 (2)	0.0170 (17)
C21	0.083 (2)	0.0550 (17)	0.088 (2)	0.0119 (15)	0.0592 (19)	0.0123 (15)
C22	0.073 (2)	0.106 (3)	0.093 (3)	0.0252 (19)	0.044 (2)	0.014 (2)
C23	0.089 (3)	0.132 (4)	0.093 (3)	0.011 (2)	0.034 (2)	-0.005 (3)
C24	0.115 (3)	0.106 (3)	0.105 (3)	-0.002 (3)	0.061 (3)	-0.014 (2)
C25	0.115 (3)	0.105 (3)	0.146 (4)	-0.003 (3)	0.093 (3)	-0.031 (3)
C26	0.084 (2)	0.085 (2)	0.129 (3)	-0.0038 (18)	0.072 (2)	-0.016 (2)
Cl	0.0794 (8)	0.0839 (8)	0.1148 (10)	0.000	0.0425 (7)	0.000
O4	0.0964 (16)	0.121 (2)	0.1100 (18)	0.0257 (15)	0.0688 (15)	-0.0062 (15)
O3	0.0869 (17)	0.113 (2)	0.118 (2)	-0.0093 (14)	0.0673 (17)	-0.0255 (16)

*Geometric parameters (Å, °)*

Cu—O2	1.984 (5)	C11—C19	1.399 (4)
Cu—O2 <sup>i</sup>	1.984 (5)	C11—C12	1.438 (4)
Cu—N2 <sup>i</sup>	2.012 (2)	C12—C13	1.334 (4)
Cu—N2	2.012 (2)	C12—H12A	0.9300
Cu—N1	2.110 (2)	C13—C14	1.425 (4)
Cu—N1 <sup>i</sup>	2.110 (2)	C13—H13A	0.9300
N1—C8	1.330 (3)	C14—C15	1.396 (4)
N1—C19	1.362 (3)	C14—C18	1.407 (3)
N2—C17	1.322 (3)	C15—C16	1.352 (4)
N2—C18	1.355 (3)	C15—H15A	0.9300
O1—C1	1.378 (6)	C16—C17	1.395 (4)
O2—C1	1.174 (6)	C16—H16A	0.9300
C1—C2	1.486 (6)	C17—H17A	0.9300
C2—C3	1.3900	C18—C19	1.425 (3)
C2—C7	1.3900	C20—O4	1.200 (3)
C3—C4	1.3900	C20—O3	1.323 (4)
C3—H3A	0.9600	C20—C21	1.485 (4)
C4—C5	1.3900	C21—C22	1.380 (5)



## supplementary materials

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C4—H4A	0.9600	C21—C26	1.384 (4)
C5—C6	1.3900	C22—C23	1.363 (5)
C5—H5A	0.9601	C22—H22A	0.9300
C6—C7	1.3900	C23—C24	1.355 (5)
C6—H6A	0.9599	C23—H23A	0.9300
C7—H7A	0.9601	C24—C25	1.361 (5)
C8—C9	1.395 (4)	C24—H24A	0.9300
C8—H8A	0.9300	C25—C26	1.379 (5)
C9—C10	1.356 (4)	C25—H25A	0.9300
C9—H9A	0.9300	C26—H26A	0.9300
C10—C11	1.395 (4)	Cl—Cl <sup>i</sup>	0.000 (3)
C10—H10A	0.9300	O3—H31	0.85 (4)
O2—Cu—O2 <sup>i</sup>	47.8 (3)	C11—C10—H10A	120.1
O2—Cu—N2 <sup>i</sup>	90.69 (16)	C10—C11—C19	117.1 (3)
O2 <sup>i</sup> —Cu—N2 <sup>i</sup>	89.49 (16)	C10—C11—C12	124.5 (3)
O2—Cu—N2	89.49 (16)	C19—C11—C12	118.4 (3)
O2 <sup>i</sup> —Cu—N2	90.69 (16)	C13—C12—C11	121.6 (3)
N2 <sup>i</sup> —Cu—N2	179.80 (13)	C13—C12—H12A	119.2
O2—Cu—N1	148.10 (18)	C11—C12—H12A	119.2
O2 <sup>i</sup> —Cu—N1	101.76 (18)	C12—C13—C14	121.5 (3)
N2 <sup>i</sup> —Cu—N1	99.53 (8)	C12—C13—H13A	119.3
N2—Cu—N1	80.35 (8)	C14—C13—H13A	119.3
O2—Cu—N1 <sup>i</sup>	101.76 (18)	C15—C14—C18	117.5 (3)
O2 <sup>i</sup> —Cu—N1 <sup>i</sup>	148.10 (18)	C15—C14—C13	124.1 (3)
N2 <sup>i</sup> —Cu—N1 <sup>i</sup>	80.35 (8)	C18—C14—C13	118.4 (3)
N2—Cu—N1 <sup>i</sup>	99.53 (8)	C16—C15—C14	119.7 (2)
N1—Cu—N1 <sup>i</sup>	109.69 (12)	C16—C15—H15A	120.2
C8—N1—C19	117.0 (2)	C14—C15—H15A	120.2
C8—N1—Cu	131.86 (18)	C15—C16—C17	119.7 (3)
C19—N1—Cu	110.87 (16)	C15—C16—H16A	120.2
C17—N2—C18	118.3 (2)	C17—C16—H16A	120.2
C17—N2—Cu	127.38 (19)	N2—C17—C16	122.6 (3)
C18—N2—Cu	113.88 (16)	N2—C17—H17A	118.7
C1—O2—Cu	112.8 (4)	C16—C17—H17A	118.7
O2—C1—O1	119.6 (6)	N2—C18—C14	122.3 (2)
O2—C1—C2	127.5 (4)	N2—C18—C19	117.4 (2)
O1—C1—C2	112.6 (4)	C14—C18—C19	120.3 (2)
C3—C2—C7	120.0	N1—C19—C11	123.5 (2)
C3—C2—C1	126.0 (3)	N1—C19—C18	116.7 (2)
C7—C2—C1	113.9 (3)	C11—C19—C18	119.8 (2)
C4—C3—C2	120.0	O4—C20—O3	122.4 (3)
C4—C3—H3A	120.0	O4—C20—C21	122.9 (3)
C2—C3—H3A	120.0	O3—C20—C21	114.6 (3)
C3—C4—C5	120.0	C22—C21—C26	118.6 (3)
C3—C4—H4A	120.0	C22—C21—C20	119.0 (3)
C5—C4—H4A	120.0	C26—C21—C20	122.5 (3)

C4—C5—C6	120.0	C23—C22—C21	121.1 (3)
C4—C5—H5A	120.0	C23—C22—H22A	119.5
C6—C5—H5A	120.0	C21—C22—H22A	119.5
C7—C6—C5	120.0	C24—C23—C22	120.3 (4)
C7—C6—H6A	120.0	C24—C23—H23A	119.8
C5—C6—H6A	120.0	C22—C23—H23A	119.8
C6—C7—C2	120.0	C23—C24—C25	119.6 (4)
C6—C7—H7A	120.0	C23—C24—H24A	120.2
C2—C7—H7A	120.0	C25—C24—H24A	120.2
N1—C8—C9	122.9 (3)	C24—C25—C26	121.3 (3)
N1—C8—H8A	118.5	C24—C25—H25A	119.4
C9—C8—H8A	118.5	C26—C25—H25A	119.4
C10—C9—C8	119.6 (3)	C25—C26—C21	119.2 (4)
C10—C9—H9A	120.2	C25—C26—H26A	120.4
C8—C9—H9A	120.2	C21—C26—H26A	120.4
C9—C10—C11	119.9 (3)	C20—O3—H31	119 (3)
C9—C10—H10A	120.1		

Symmetry codes: (i)  $-x+1, y, -z+1/2$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C5—H5A $\cdots$ Cl	0.96	2.94	3.728 (4)	140
O3—H31 $\cdots$ Cl	0.85 (4)	2.20 (4)	3.051 (3)	177 (4)
O3—H31 $\cdots$ Cl <sup>i</sup>	0.85 (4)	2.20 (4)	3.051 (3)	177 (4)
C24—H24A $\cdots$ O4 <sup>ii</sup>	0.93	2.49	3.355 (5)	155
C8—H8A $\cdots$ O3 <sup>iii</sup>	0.93	2.47	3.307 (4)	149
C10—H10A $\cdots$ O1 <sup>iv</sup>	0.93	2.53	3.275 (7)	138
C12—H12A $\cdots$ O1 <sup>iv</sup>	0.93	2.30	3.106 (7)	146

Symmetry codes: (i)  $-x+1, y, -z+1/2$ ; (ii)  $x, -y+2, z+1/2$ ; (iii)  $x, -y+1, z-1/2$ ; (iv)  $-x+1/2, -y+1/2, -z$ .

Fig. 1

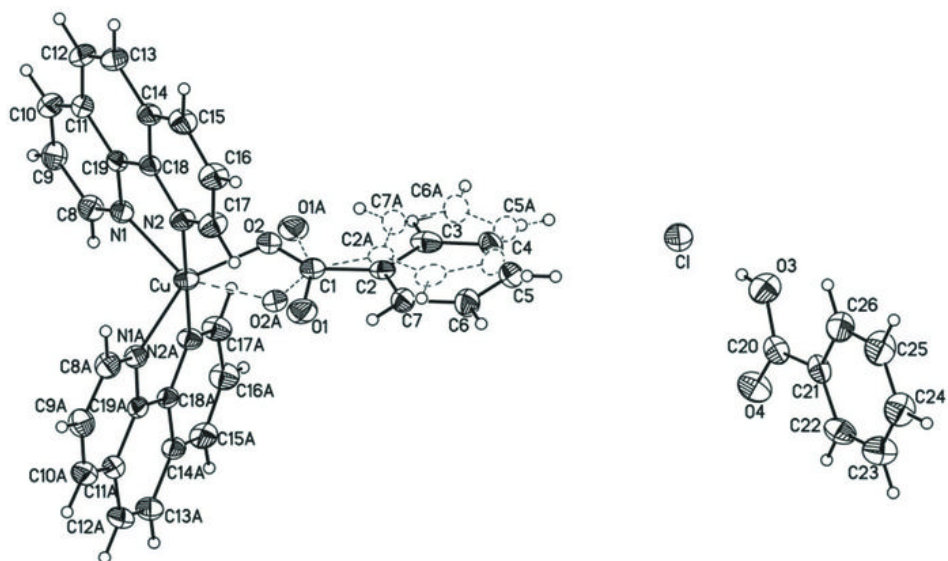


Fig. 2

