data reports

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Crystal structure of bis[μ-methoxy-(pyridin-2-yl)methanolato-κ³N,O:O]-bis[chloridocopper(II)]

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The racemic title compound, [Cu₂(C₇H₈NO₂)₂Cl₂], is composed of dinuclear molecules in which methoxy(pyridin-2-yl)methanolate ligands bridge two symmetry-related Cu^{II} ions. Each Cu^{II} ion is coordinated in a square-planar geometry by one Cl atom, the N and O atoms of the bidentate ligand and the bridging O atom of the centrosymmetrically related bidentate ligand. The separation between the two Cu^{II} atoms is 3.005 (1) Å. In the crystal, non-classical C—H···O hydrogen bonds, weak π–π stacking [centroid–centroid distance = 4.073 (1) Å] and weak electrostatic Cu···Cl interactions [3.023 (1) Å] link the dinuclear molecules into chains running parallel to the *b* axis. These chains are further connected by weak C—H···Cl hydrogen bonds directed approximately along the *a* axis, forming a three-dimensional supramolecular network.

1. Related literature

For related structures and applications of transition metal compounds with the methoxy-2-pyridylmethanolate ligand, see: Pijper *et al.* (2010); Mondal *et al.* (2009); Drew *et al.* (2008); Wang *et al.* (2003); Guidote *et al.* (2001).
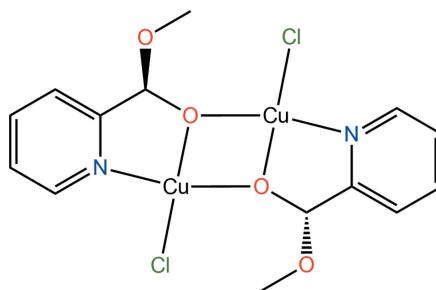
2. Experimental

2.1. Crystal data

[Cu₂(C₇H₈NO₂)₂Cl₂]
$M_r = 474.29$
Monoclinic, $P2_1/n$
$a = 10.5568\ (14)$ Å
$b = 4.0728\ (6)$ Å
$c = 19.257\ (3)$ Å
$\beta = 95.280\ (3)°$

$V = 824.5\ (2)$ Å³
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.92$ mm^{-1}
$T = 298$ K
$0.16 \times 0.10 \times 0.06$ mm

2.2. Data collection

Bruker D8 QUEST CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
$T_{min} = 0.645$, $T_{max} = 0.745$

7703 measured reflections
1485 independent reflections
1030 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.04$
1485 reflections

110 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl1^i	0.93	2.90	3.756 (6)	154
C3—H3···O2^{ii}	0.93	2.65	3.517 (7)	156
C6—H6···O2^{iii}	0.98	2.59	3.548 (8)	165

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

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010), *enCIFer* (Allen *et al.*, 2004) and *OLEX2* (Dolomanov *et al.*, 2009).

Acknowledgements

Supporting information for this paper is available from the IUCr electronic archives (Reference: CQ2013).

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supporting information

Crystal structure of bis[*μ*-methoxy(pyridin-2-yl)methanolato-*κ*³*N,O:O*]bis[chloridocopper(II)]

Sujirat Boonlue, Anchalee Sirikulkajorn and Kittipong Chainok

### S1. Synthesis and crystallization

The title compound was obtained unexpectedly from the reaction of copper(I) chloride and 4-iodo-*N*-(2-pyridylmethylene)aniline in a mixed solvent of acetonitrile and dichloromethane. Typically, a solution of 4-iodo-*N*-(2-pyridylmethylene)aniline (61.6 mg, 0.2 mmol) in dry dichloromethane (2 ml) was placed in a test tube. A mixture of acetonitrile and dichloromethane solution (6 ml, 1:1, v/v) was carefully added on the top. A solution of CuCl (19.8 mg, 0.2 mmol) in dry acetonitrile (2 ml) was then carefully layered on the top of the acetonitrile/dichloromethane mixed solution. After slow diffusion at room temperature for 2 days, pale-green plate shaped crystals of the title compound were obtained.

S2. Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C—H) = 0.93 Å for aromatic CH groups, 0.96 Å for non-aromatic CH groups and 0.98 Å for CH$_3$ groups. The U_{iso} were constrained to be 1.5U_{eq} of the carrier atom for methy H atoms and 1.2U_{eq} for the remaining H atoms.
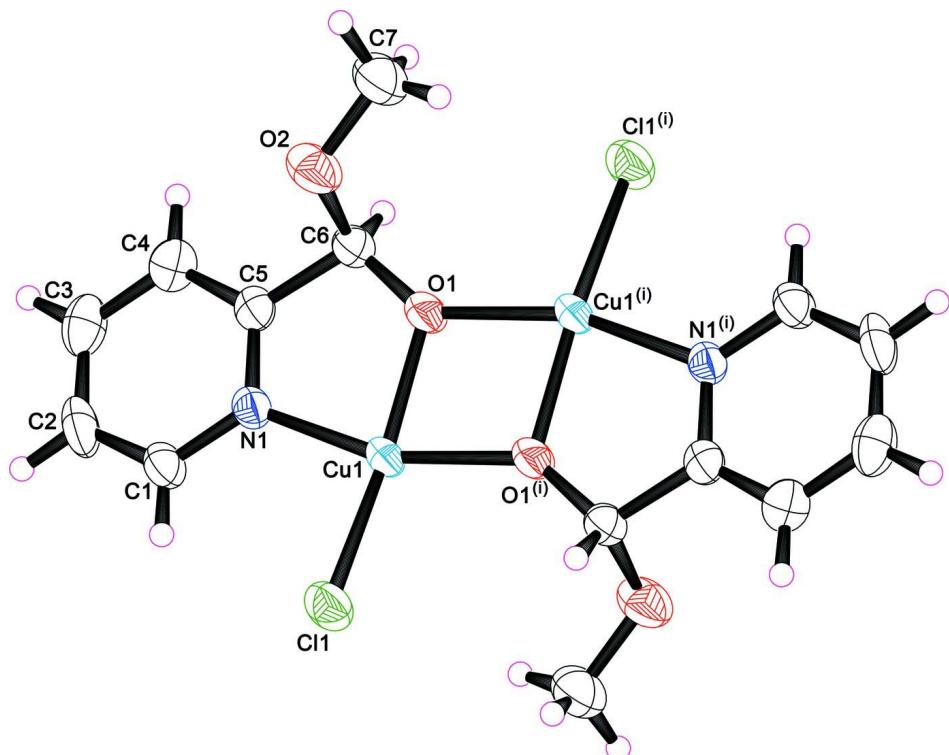
Figure 1

A view of the dinuclear molecule of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.
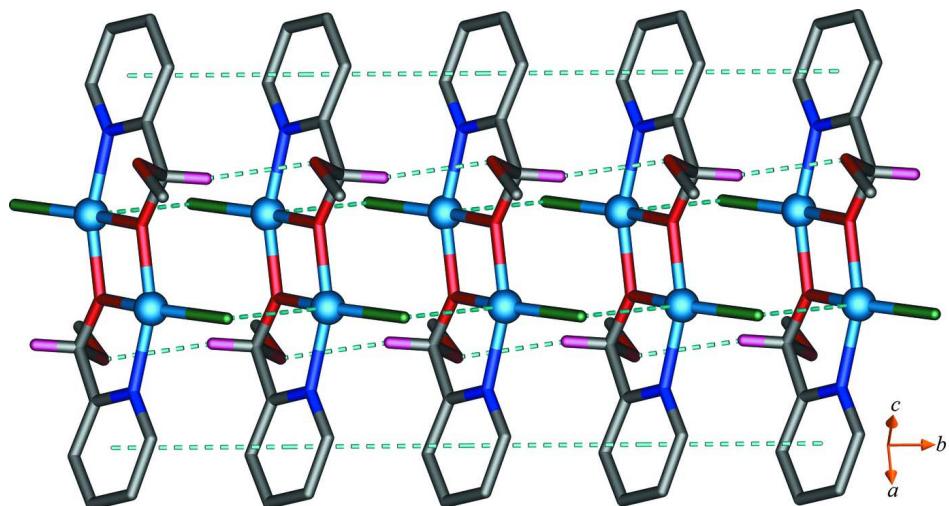
Figure 2

Partial packing diagram of the title compound showing a molecular one-dimensional chain running parallel to the *b* axis assembled from dinuclear molecules linked together through non-classical C—H⋯O hydrogen bonds, weak *π*-*π* stacking and weak electrostatic Cu⋯Cl interactions (dashed lines). Hydrogen atoms not involved in the hydrogen bonding interactions are omitted for clarity.
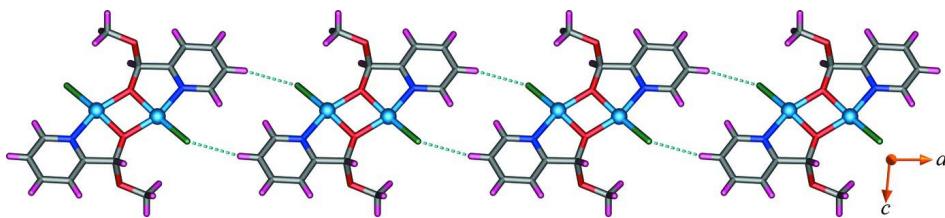
Figure 3

A view of the weak C—H···Cl hydrogen bonding network between adjacent dinuclear molecules in the title compound which serve to connect the chains into a three-dimensional architecture.

Bis[*μ*-methoxy(pyridin-2-yl)methanolato-*κ³N,O:O*]bis[chloridocopper(II)]

Crystal data

$[Cu_2(C_7H_8NO_2)_2Cl_2]$
$M_r = 474.29$
Monoclinic, $P2_1/n$
$a = 10.5568\ (14)$ Å
$b = 4.0728\ (6)$ Å
$c = 19.257\ (3)$ Å
$β = 95.280\ (3)°$
$V = 824.5\ (2)$ Å³
$Z = 2$

$F(000) = 476$
$D_x = 1.910$ Mg m⁻³
Mo *Kα* radiation, $λ = 0.71073$ Å
Cell parameters from 546 reflections
$θ = 3.6–25.4°$
$μ = 2.92$ mm⁻¹
$T = 298$ K
Plate, pale-green
$0.16 × 0.10 × 0.06$ mm

Data collection

Bruker D8 QUEST CMOS
   diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm⁻¹
φ and *ω* scans
Absorption correction: multi-scan
   (*SADABS*; Bruker, 2014)
$T_{min} = 0.645$, $T_{max} = 0.745$

7703 measured reflections
1485 independent reflections
1030 reflections with $I > 2σ(I)$
$R_{int} = 0.091$
$θ_{max} = 25.4°$, $θ_{min} = 3.6°$
$h = −12→12$
$k = −4→4$
$l = −23→23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2σ(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.04$
1485 reflections
110 parameters
0 restraints
0 constraints
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
$w = 1/[σ^2(F_o^2) + (0.0544P)^2 + 0.5475P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(Δ/σ)_{max} = 0.001$
$Δρ_{max} = 0.52$ e Å⁻³
$Δρ_{min} = −0.42$ e Å⁻³

Special details

Experimental. SADABS-2014/4 (Bruker,2014/4) was used for absorption correction. wR2(int) was 0.0681 before and 0.0535 after correction. The Ratio of minimum to maximum transmission is 0.8650. The $\lambda/2$ correction factor is 0.00150.

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	0.36725 (5)	0.3633 (2)	0.49239 (3)	0.0376 (3)
Cl1	0.25368 (12)	−0.0100 (4)	0.42980 (7)	0.0431 (4)
O1	0.4853 (3)	0.5904 (12)	0.55882 (18)	0.0542 (13)
O2	0.4934 (3)	0.5112 (11)	0.6792 (2)	0.0491 (11)
N1	0.2501 (3)	0.4522 (11)	0.5649 (2)	0.0301 (11)
C1	0.1248 (4)	0.3804 (15)	0.5620 (3)	0.0371 (14)
H1	0.0886	0.2558	0.5248	0.044*
C2	0.0492 (5)	0.4839 (17)	0.6114 (3)	0.0486 (17)
H2	−0.0368	0.4299	0.6080	0.058*
C3	0.1015 (5)	0.6680 (17)	0.6662 (3)	0.0470 (16)
H3	0.0515	0.7428	0.7003	0.056*
C4	0.2300 (5)	0.7412 (15)	0.6700 (3)	0.0399 (14)
H4	0.2677	0.8658	0.7067	0.048*
C5	0.3014 (4)	0.6271 (14)	0.6186 (2)	0.0304 (12)
C6	0.4438 (4)	0.6921 (15)	0.6201 (3)	0.0336 (13)
H6	0.4613	0.9267	0.6272	0.040*
C7	0.6176 (5)	0.6071 (19)	0.7070 (3)	0.0587 (19)
H7A	0.6792	0.5237	0.6779	0.088*
H7B	0.6344	0.5200	0.7532	0.088*
H7C	0.6227	0.8424	0.7086	0.088*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0240 (3)	0.0552 (5)	0.0340 (4)	−0.0123 (3)	0.0041 (2)	−0.0096 (4)
Cl1	0.0392 (7)	0.0395 (9)	0.0504 (9)	−0.0114 (7)	0.0034 (6)	−0.0065 (7)
O1	0.0265 (18)	0.099 (4)	0.038 (2)	−0.020 (2)	0.0092 (16)	−0.025 (2)
O2	0.037 (2)	0.051 (3)	0.057 (3)	−0.0029 (19)	−0.0100 (18)	0.010 (2)
N1	0.026 (2)	0.032 (3)	0.032 (2)	−0.0024 (19)	0.0013 (18)	0.006 (2)
C1	0.025 (2)	0.044 (4)	0.041 (3)	−0.002 (3)	0.000 (2)	0.007 (3)
C2	0.024 (3)	0.060 (4)	0.063 (4)	−0.003 (3)	0.013 (3)	0.014 (4)
C3	0.042 (3)	0.050 (4)	0.052 (4)	0.013 (3)	0.020 (3)	0.008 (4)
C4	0.045 (3)	0.033 (4)	0.043 (3)	0.003 (3)	0.010 (3)	−0.001 (3)
C5	0.030 (2)	0.028 (3)	0.033 (3)	0.000 (2)	0.001 (2)	0.011 (3)

| C6 | 0.028 (2) | 0.038 (4) | 0.034 (3) | −0.002 (2) | 0.000 (2) | 0.002 (3) |
| C7 | 0.042 (3) | 0.073 (5) | 0.058 (4) | −0.011 (3) | −0.009 (3) | 0.013 (4) |

Geometric parameters (Å, º)

Cu1—Cu1i	3.0051 (12)	C1—C2	1.365 (7)
Cu1—Cl1	2.2215 (15)	C2—H2	0.9300
Cu1—O1i	1.927 (3)	C2—C3	1.368 (8)
Cu1—O1	1.937 (4)	C3—H3	0.9300
Cu1—N1	1.982 (4)	C3—C4	1.385 (7)
O1—Cu1i	1.927 (3)	C4—H4	0.9300
O1—C6	1.361 (6)	C4—C5	1.378 (7)
O2—C6	1.415 (6)	C5—C6	1.524 (6)
O2—C7	1.424 (6)	C6—H6	0.9800
N1—C1	1.351 (6)	C7—H7A	0.9600
N1—C5	1.330 (6)	C7—H7B	0.9600
C1—H1	0.9300	C7—H7C	0.9600
Cl1—Cu1—Cu1i	139.33 (5)	C3—C2—H2	120.4
O1—Cu1—Cu1i	38.82 (10)	C2—C3—H3	120.6
O1i—Cu1—Cu1i	39.07 (11)	C2—C3—C4	118.8 (5)
O1i—Cu1—Cl1	102.14 (12)	C4—C3—H3	120.6
O1—Cu1—Cl1	165.33 (16)	C3—C4—H4	120.4
O1i—Cu1—O1	77.89 (16)	C5—C4—C3	119.2 (5)
O1—Cu1—N1	81.54 (15)	C5—C4—H4	120.4
O1i—Cu1—N1	158.20 (18)	N1—C5—C4	121.9 (5)
N1—Cu1—Cu1i	120.03 (12)	N1—C5—C6	116.0 (4)
N1—Cu1—Cl1	99.59 (13)	C4—C5—C6	122.1 (5)
Cu1i—O1—Cu1	102.11 (16)	O1—C6—O2	114.5 (5)
C6—O1—Cu1	118.6 (3)	O1—C6—C5	109.0 (4)
C6—O1—Cu1i	138.9 (3)	O1—C6—H6	110.2
C6—O2—C7	114.8 (4)	O2—C6—C5	102.5 (4)
C1—N1—Cu1	127.1 (4)	O2—C6—H6	110.2
C5—N1—Cu1	114.2 (3)	C5—C6—H6	110.2
C5—N1—C1	118.4 (4)	O2—C7—H7A	109.5
N1—C1—H1	118.7	O2—C7—H7B	109.5
N1—C1—C2	122.5 (5)	O2—C7—H7C	109.5
C2—C1—H1	118.7	H7A—C7—H7B	109.5
C1—C2—H2	120.4	H7A—C7—H7C	109.5
C1—C2—C3	119.1 (5)	H7B—C7—H7C	109.5
Cu1—O1—C6—O2	108.4 (4)	C1—N1—C5—C6	178.4 (5)
Cu1i—O1—C6—O2	−79.8 (7)	C1—C2—C3—C4	−0.6 (9)
Cu1—O1—C6—C5	−5.7 (6)	C2—C3—C4—C5	0.0 (9)
Cu1i—O1—C6—C5	166.1 (4)	C3—C4—C5—N1	1.0 (8)
Cu1—N1—C1—C2	−172.6 (4)	C3—C4—C5—C6	−178.8 (5)
Cu1—N1—C5—C4	172.9 (4)	C4—C5—C6—O1	−171.8 (5)
Cu1—N1—C5—C6	−7.4 (6)	C4—C5—C6—O2	66.5 (7)

N1—C1—C2—C3	0.2 (9)	C5—N1—C1—C2	0.8 (8)
N1—C5—C6—O1	8.4 (7)	C7—O2—C6—O1	81.5 (6)
N1—C5—C6—O2	−113.2 (5)	C7—O2—C6—C5	−160.6 (5)
C1—N1—C5—C4	−1.4 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Cl1[ii]	0.93	2.90	3.756 (6)	154
C3—H3···O2[iii]	0.93	2.65	3.517 (7)	156
C6—H6···O2[iv]	0.98	2.59	3.548 (8)	165

Symmetry codes: (ii) −*x*, −*y*, −*z*+1; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iv) *x*, *y*+1, *z*.