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Bis(μ_2-hydroxydi-2-pyridylmethanolato-$\kappa^4N,O:O,N'$)bis[(pyridine-κN)copper(II)] bis(perchlorate)

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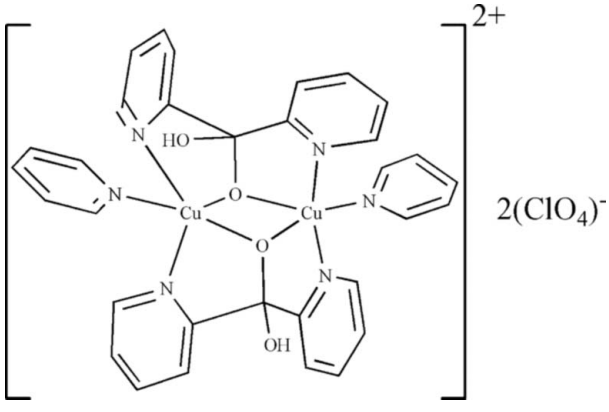
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.106; data-to-parameter ratio = 15.7.

The title dinuclear compound, $[Cu_2(C_{11}H_9N_2O_2)_2(C_5H_5N)_2](ClO_4)_2$, was obtained by the reaction of di-2-pyridyl ketone, copper(II) acetate, pyridine and sodium perchlorate. The two Cu^{II} atoms are coordinated by two hydroxydi-2-pyridylmethanolate ligands and two pyridine ligands, resulting in a distorted $[CuN_3O_2]$ square-pyramidal coordination geometry. The molecular structure is stabilized by intramolecular π–π (face-to-face distances of about 3.40 Å) and C—H$\cdots\pi$ (H$\cdots$centroid distances of about 2.80 Å) interactions of aromatic rings.

Related literature

Some complexes based on di-2-pyridyl ketone hydrolysed derivative have already been isolated and structurally characterized (Lalioti *et al.*, 2001; Papaefstathiou & Perlepes, 2002; Boudalis *et al.*, 2003, 2004; Steel & Sumby, 2003; Tong *et al.*, 2002; Serna *et al.*, 2000; Li *et al.*, 2006; Breeze *et al.*, 1996).



Experimental

Crystal data

$[Cu_2(C_{11}H_9N_2O_2)_2(C_5H_5N)_2](ClO_4)_2$
M_r = 886.58
Monoclinic, $P2_1/n$
a = 11.2269 (6) Å
b = 15.7136 (8) Å
c = 19.6142 (12) Å
β = 104.034 (3)°
V = 3357.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.50 mm^{-1}
T = 293 (2) K
0.40 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
T_{min} = 0.657, T_{max} = 0.798
25710 measured reflections
7663 independent reflections
6773 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.106
S = 1.08
7663 reflections
487 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: GK2068).

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supplementary materials

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Bis(μ_2-hydroxydi-2-pyridylmethanolato-$\kappa^4N,O:O,N'$)bis[(pyridine-κN)copper(II)] bis(perchlorate)

Y.-M. Li, J.-L. Zhang and X.-W. Zhao

Comment

Di-2-pyridylketone [$(C_5H_4N_2)CO$] and its hydrolyzed derivative, di-2-pyridylmethanediol [$(C_5H_4N)_2C(OH)_2$], are considered as excellent ligands because of their various coordination modes. Some complexes based on the monoanion and dianion of di-2-pyridylmethanediol have been reported (Lalioti *et al.*, 2001; Papaefstathiou & Perlepes, 2002; Boudalis *et al.*, 2004; Steel & Sumby, 2003; Tong *et al.*, 2002; Serna *et al.*, 2000; Li *et al.*, 2006). However, it is seldom reported that these ligands chelate the metal ion in *N*,*N*',*O*,*O*-tridentate mode (Breeze *et al.*, 1996; Boudalis *et al.*, 2003). Herein we present the crystal structure of the dinuclear compoud, (I), containing *N*,*N*',*O*,*O*-tridentate hydroxy-di-2-pyridylmethnolato ligand.

The structure of (I) consists of the cation, [bispyridyl-bis(hydroxy-di-2-pyridylmethanolato)]dicopper, and two percholrate anions (Fig. 1). In the cation, the two copper atoms, chelated by two *N*,*N*',*O*,*O*-tridentate hydroxy-di-2-pyridylmethanolato ligands, are not crystallographically equivalent. Each copper atom is also bound to one nitrogen atom from pyridine, resulting in a distorted square pyramidal coordination geometry. The Cu···Cu distance is 3.0375 (4) Å. The Cu—N and Cu—O bond lengths are 2.002 (2)—2.034 (2) Å and 1.9208 (17)—2.2837 (18) Å, respectively.

It is also noteworthy that the dinuclear structure is stabilized by intramolecular pyridine-pyridine π···π interation (the interplanar distance of 3.40 Å) and CH···π interaction (C14—H···the pyridine N5 centroid of 2.80 Å) (Fig. 2).

Experimental

The title compound was synthesized by refluxing a 20 ml EtOH/H_2O solution (3:1, *v*/*v*) of $Cu(OAc)_2{\cdot}H_2O$ (0.257 g, 1.3 mmol), di-2-pyridylketone (0.185 g, 1 mmol) and pyridine (2.6 ml) for 1 h with stirring. After cooing, the solid $NaClO_4{\cdot}H_2O$ (0.210 g, 1.5 mmol) was added and the solution filtered. Blue prism crystals of (I) were obtained by slow evaporation of the blue filtrate for several days. Yield: 47.4% based on di-2-pyridylketone (0.210 g). (Anal. Calc. for $C_{32}H_{28}Cl_2Cu_2N_6O_{12}$: C, 43.35; H, 3.18; N 9.48. Found: C, 43.11; H, 2.97; N 9.49%).

Refinement

All H atoms were positioned geometrically and were treated as riding, with C—H distances of 0.93 Å and O—H distances of 0.82 Å, with U_{iso}(H) = 1.2 U_{eq}(C, N). The highest electron density peak in a difference Fourier map is located near the O11 atom from the perchlorate anion.

Figures

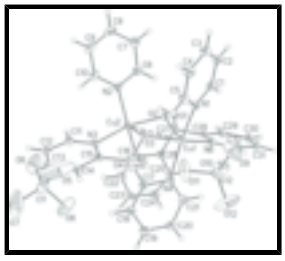


Fig. 1. The molecular structure of (I), with atomic labels and 50% probability displacement ellipsoids for non-H atoms.

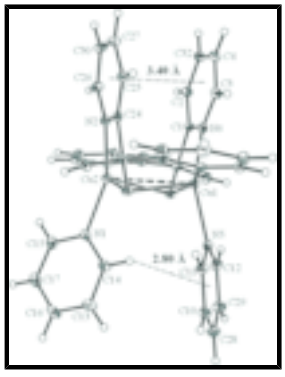


Fig. 2. The intramolecular π···π and CH···π interactions between pyridyl rings. The Cu—Cu contact is shown as a thick dashed line.

(I)

Crystal data

$[Cu_2(C_{11}H_9N_2O_2)_2(C_5H_5N)_2](ClO_4)_2$	F_{000} = 1800
M_r = 886.58	D_x = 1.754 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 11.2269 (6) Å	Cell parameters from 8489 reflections
b = 15.7136 (8) Å	θ = 3.2–27.5º
c = 19.6142 (12) Å	μ = 1.50 mm^{-1}
β = 104.034 (3)º	T = 293 (2) K
V = 3357.0 (3) Å^3	Prism, blue
Z = 4	0.40 × 0.20 × 0.15 mm

Data collection

Rigaku Mercury CCD diffractometer	7663 independent reflections
Radiation source: fine-focus sealed tube	6773 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.042
T = 293(2) K	θ_{max} = 27.5º
ω scans	θ_{min} = 3.2º
Absorption correction: multi-scan (CrystalClear; Rigaku, 2000)	h = −14→13
T_{min} = 0.657, T_{max} = 0.798	k = −20→20

25710 measured reflections	$l = -20 \rightarrow 25$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.106$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 2.8234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
7663 reflections	$\Delta\rho_{max} = 1.21$ e Å^{-3}
487 parameters	$\Delta\rho_{min} = -0.72$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. IR (KBr pellet, cm-1): v(OH) 3449, v(C–O) 1605, v(C?N, C?C) 1473, 1448, 1384, v(ClO4-)1089, 624.

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	0.64841 (3)	0.670160 (18)	0.367839 (15)	0.01667 (9)
Cu2	0.50841 (3)	0.561750 (18)	0.246451 (15)	0.01642 (9)
Cl1	1.17153 (6)	0.51344 (4)	0.15172 (4)	0.02879 (16)
Cl2	0.99762 (6)	0.75509 (4)	0.45799 (3)	0.02225 (14)
N1	0.7087 (2)	0.59111 (13)	0.45118 (11)	0.0176 (4)
N2	0.5160 (2)	0.43867 (13)	0.27837 (11)	0.0181 (4)
N3	0.6030 (2)	0.54674 (13)	0.17214 (11)	0.0182 (4)
N4	0.6705 (2)	0.75622 (13)	0.29634 (11)	0.0182 (4)
N5	0.42158 (19)	0.66984 (13)	0.20679 (11)	0.0168 (4)
N6	0.5364 (2)	0.73951 (13)	0.41114 (11)	0.0175 (4)
O1	0.26025 (16)	0.63617 (11)	0.32037 (9)	0.0192 (4)
H1A	0.2443	0.5952	0.2938	0.029*
O2	0.46562 (16)	0.60058 (10)	0.33105 (9)	0.0164 (3)
O3	0.70453 (16)	0.59285 (11)	0.30647 (9)	0.0177 (4)
O4	0.88631 (16)	0.62564 (12)	0.27555 (10)	0.0226 (4)
H3A	0.9115	0.6493	0.3136	0.034*

O5	1.2489 (3)	0.48847 (19)	0.2173 (2)	0.1021 (16)
O6	1.0668 (2)	0.45880 (17)	0.13553 (15)	0.0496 (7)
O7	1.2369 (4)	0.5094 (3)	0.1002 (2)	0.125 (2)
O8	1.1369 (2)	0.59838 (14)	0.16146 (16)	0.0527 (7)
O9	1.0527 (3)	0.7139 (2)	0.52231 (13)	0.0615 (8)
O10	0.8692 (2)	0.77013 (15)	0.45334 (13)	0.0391 (5)
O11	1.0113 (2)	0.6996 (2)	0.40201 (13)	0.0566 (8)
O12	1.0597 (2)	0.83263 (15)	0.4540 (2)	0.0697 (10)
C1	0.6436 (2)	0.57286 (16)	0.49830 (13)	0.0203 (5)
H11A	0.5737	0.6048	0.4979	0.024*
C2	0.6760 (3)	0.50846 (17)	0.54751 (13)	0.0226 (5)
H10A	0.6289	0.4975	0.5795	0.027*
C3	0.7797 (3)	0.46070 (17)	0.54814 (14)	0.0256 (6)
H28A	0.8035	0.4169	0.5805	0.031*
C4	0.8474 (3)	0.47919 (18)	0.49981 (15)	0.0264 (6)
H29A	0.9172	0.4477	0.4989	0.032*
C5	0.8100 (2)	0.54520 (17)	0.45283 (14)	0.0220 (5)
H12A	0.8570	0.5582	0.4212	0.026*
C6	0.5483 (3)	0.42389 (16)	0.34787 (14)	0.0220 (5)
H14A	0.5774	0.4690	0.3780	0.026*
C7	0.5400 (3)	0.34432 (17)	0.37629 (16)	0.0272 (6)
H13A	0.5639	0.3360	0.4246	0.033*
C8	0.4958 (3)	0.27754 (17)	0.33183 (17)	0.0293 (6)
H16A	0.4868	0.2238	0.3497	0.035*
C9	0.4653 (3)	0.29174 (17)	0.26040 (16)	0.0276 (6)
H17A	0.4377	0.2472	0.2294	0.033*
C10	0.4761 (3)	0.37286 (17)	0.23539 (15)	0.0240 (6)
H15A	0.4550	0.3821	0.1871	0.029*
C11	0.5641 (3)	0.50168 (16)	0.11228 (13)	0.0219 (5)
H9A	0.4838	0.4816	0.1005	0.026*
C12	0.6394 (3)	0.48436 (16)	0.06794 (14)	0.0231 (6)
H31A	0.6104	0.4526	0.0273	0.028*
C13	0.7584 (3)	0.51476 (16)	0.08466 (14)	0.0240 (6)
H8A	0.8108	0.5035	0.0556	0.029*
C14	0.7984 (3)	0.56241 (16)	0.14549 (14)	0.0221 (5)
H7A	0.8778	0.5843	0.1574	0.026*
C15	0.7190 (2)	0.57706 (15)	0.18827 (13)	0.0179 (5)
C16	0.7557 (2)	0.62835 (16)	0.25636 (13)	0.0185 (5)
C17	0.7140 (2)	0.72213 (15)	0.24421 (13)	0.0167 (5)
C18	0.7191 (2)	0.76819 (16)	0.18493 (13)	0.0209 (5)
H2A	0.7470	0.7431	0.1488	0.025*
C19	0.6816 (3)	0.85284 (17)	0.18036 (14)	0.0237 (6)
H32A	0.6843	0.8851	0.1410	0.028*
C20	0.6404 (3)	0.88850 (17)	0.23488 (15)	0.0249 (6)
H4A	0.6159	0.9452	0.2330	0.030*
C21	0.6363 (3)	0.83846 (16)	0.29222 (14)	0.0229 (5)
H3B	0.6091	0.8624	0.3291	0.027*
C22	0.4119 (3)	0.70408 (17)	0.14300 (13)	0.0213 (5)
H26A	0.4423	0.6738	0.1101	0.026*

C23	0.3584 (3)	0.78284 (18)	0.12438 (14)	0.0237 (6)
H30A	0.3511	0.8045	0.0794	0.028*
C24	0.3160 (3)	0.82844 (17)	0.17371 (14)	0.0245 (6)
H27A	0.2822	0.8823	0.1630	0.029*
C25	0.3242 (2)	0.79327 (16)	0.23946 (13)	0.0196 (5)
H25A	0.2955	0.8229	0.2733	0.024*
C26	0.3760 (2)	0.71316 (15)	0.25385 (12)	0.0159 (5)
C27	0.3808 (2)	0.66539 (15)	0.32260 (13)	0.0159 (5)
C28	0.4148 (2)	0.72546 (15)	0.38598 (12)	0.0175 (5)
C29	0.3283 (3)	0.76266 (16)	0.41599 (13)	0.0211 (5)
H20A	0.2452	0.7516	0.3983	0.025*
C30	0.3675 (3)	0.81696 (17)	0.47304 (14)	0.0244 (6)
H22A	0.3109	0.8424	0.4942	0.029*
C31	0.4911 (3)	0.83256 (16)	0.49771 (14)	0.0240 (6)
H21A	0.5188	0.8694	0.5353	0.029*
C32	0.5734 (3)	0.79289 (16)	0.46606 (13)	0.0220 (5)
H18A	0.6569	0.8033	0.4831	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02118 (17)	0.01560 (15)	0.01365 (15)	0.00121 (11)	0.00500 (12)	0.00078 (11)
Cu2	0.02116 (17)	0.01498 (15)	0.01423 (15)	0.00170 (11)	0.00645 (12)	−0.00007 (11)
Cl1	0.0244 (3)	0.0229 (3)	0.0364 (4)	0.0040 (3)	0.0022 (3)	−0.0075 (3)
Cl2	0.0254 (3)	0.0222 (3)	0.0198 (3)	0.0008 (2)	0.0069 (2)	0.0008 (2)
N1	0.0193 (11)	0.0180 (10)	0.0153 (10)	−0.0013 (8)	0.0035 (8)	−0.0002 (8)
N2	0.0185 (11)	0.0162 (10)	0.0210 (11)	−0.0015 (8)	0.0075 (9)	−0.0014 (8)
N3	0.0220 (11)	0.0172 (10)	0.0157 (10)	0.0010 (8)	0.0052 (8)	0.0016 (8)
N4	0.0207 (11)	0.0170 (10)	0.0163 (10)	−0.0020 (8)	0.0035 (8)	−0.0003 (8)
N5	0.0182 (10)	0.0181 (10)	0.0144 (10)	−0.0006 (8)	0.0047 (8)	−0.0001 (8)
N6	0.0234 (11)	0.0146 (9)	0.0143 (9)	0.0022 (8)	0.0045 (8)	0.0009 (8)
O1	0.0206 (9)	0.0190 (8)	0.0198 (9)	−0.0028 (7)	0.0084 (7)	−0.0012 (7)
O2	0.0223 (9)	0.0136 (8)	0.0136 (8)	0.0031 (7)	0.0050 (7)	0.0008 (6)
O3	0.0237 (9)	0.0165 (8)	0.0135 (8)	0.0008 (7)	0.0059 (7)	0.0016 (6)
O4	0.0174 (9)	0.0272 (9)	0.0225 (9)	−0.0001 (7)	0.0038 (7)	−0.0011 (8)
O5	0.078 (2)	0.0474 (17)	0.133 (3)	−0.0171 (16)	−0.067 (2)	0.0420 (19)
O6	0.0327 (13)	0.0512 (14)	0.0619 (17)	−0.0109 (11)	0.0056 (12)	−0.0258 (13)
O7	0.138 (4)	0.130 (4)	0.151 (4)	−0.078 (3)	0.119 (3)	−0.098 (3)
O8	0.0483 (15)	0.0254 (11)	0.0778 (19)	0.0152 (11)	0.0027 (14)	−0.0088 (12)
O9	0.072 (2)	0.081 (2)	0.0336 (13)	0.0340 (16)	0.0159 (13)	0.0261 (14)
O10	0.0263 (11)	0.0409 (12)	0.0534 (14)	0.0024 (10)	0.0162 (10)	0.0030 (11)
O11	0.0406 (14)	0.093 (2)	0.0338 (13)	0.0099 (14)	0.0051 (11)	−0.0287 (14)
O12	0.0335 (14)	0.0254 (12)	0.149 (3)	−0.0024 (10)	0.0194 (17)	0.0098 (15)
C1	0.0226 (13)	0.0207 (12)	0.0185 (12)	0.0016 (10)	0.0065 (10)	0.0002 (10)
C2	0.0274 (14)	0.0229 (12)	0.0194 (12)	−0.0041 (11)	0.0093 (11)	0.0012 (10)
C3	0.0320 (16)	0.0234 (13)	0.0209 (13)	0.0018 (11)	0.0058 (11)	0.0078 (10)
C4	0.0230 (14)	0.0280 (14)	0.0292 (14)	0.0067 (11)	0.0081 (11)	0.0067 (11)
C5	0.0188 (13)	0.0276 (13)	0.0202 (13)	0.0005 (10)	0.0057 (10)	0.0044 (10)

C6	0.0261 (14)	0.0184 (12)	0.0237 (13)	0.0013 (10)	0.0101 (11)	−0.0005 (10)
C7	0.0342 (16)	0.0221 (13)	0.0288 (14)	0.0045 (12)	0.0146 (12)	0.0049 (11)
C8	0.0304 (15)	0.0159 (12)	0.0472 (18)	0.0000 (11)	0.0199 (14)	0.0022 (12)
C9	0.0245 (14)	0.0189 (12)	0.0413 (17)	−0.0015 (11)	0.0115 (12)	−0.0085 (12)
C10	0.0244 (14)	0.0220 (13)	0.0257 (13)	−0.0004 (11)	0.0064 (11)	−0.0062 (11)
C11	0.0289 (14)	0.0205 (12)	0.0160 (11)	−0.0015 (11)	0.0050 (10)	−0.0009 (10)
C12	0.0331 (15)	0.0200 (12)	0.0168 (12)	0.0013 (11)	0.0075 (11)	−0.0009 (10)
C13	0.0341 (15)	0.0210 (12)	0.0211 (13)	0.0035 (11)	0.0146 (11)	0.0023 (10)
C14	0.0274 (14)	0.0188 (12)	0.0237 (13)	−0.0010 (10)	0.0134 (11)	0.0027 (10)
C15	0.0245 (13)	0.0143 (11)	0.0161 (11)	0.0022 (10)	0.0072 (10)	0.0037 (9)
C16	0.0186 (12)	0.0195 (11)	0.0180 (12)	−0.0006 (10)	0.0056 (10)	0.0004 (9)
C17	0.0150 (12)	0.0170 (11)	0.0173 (11)	−0.0035 (9)	0.0027 (9)	0.0013 (9)
C18	0.0218 (13)	0.0222 (12)	0.0193 (12)	−0.0040 (10)	0.0063 (10)	0.0028 (10)
C19	0.0249 (14)	0.0219 (12)	0.0234 (13)	−0.0042 (11)	0.0043 (11)	0.0074 (10)
C20	0.0270 (14)	0.0165 (11)	0.0299 (14)	−0.0008 (10)	0.0044 (12)	0.0030 (10)
C21	0.0260 (14)	0.0182 (12)	0.0233 (13)	−0.0028 (10)	0.0038 (11)	−0.0016 (10)
C22	0.0249 (14)	0.0243 (13)	0.0160 (12)	0.0015 (11)	0.0074 (10)	0.0027 (10)
C23	0.0262 (14)	0.0285 (13)	0.0173 (12)	0.0036 (11)	0.0067 (11)	0.0086 (10)
C24	0.0277 (14)	0.0213 (12)	0.0239 (13)	0.0044 (11)	0.0053 (11)	0.0061 (10)
C25	0.0201 (13)	0.0207 (12)	0.0185 (12)	0.0007 (10)	0.0057 (10)	0.0002 (10)
C26	0.0148 (12)	0.0180 (11)	0.0151 (11)	−0.0016 (9)	0.0039 (9)	−0.0004 (9)
C27	0.0190 (12)	0.0144 (11)	0.0149 (11)	0.0011 (9)	0.0055 (9)	0.0007 (9)
C28	0.0243 (13)	0.0150 (11)	0.0135 (11)	0.0008 (10)	0.0052 (10)	0.0029 (9)
C29	0.0257 (14)	0.0210 (12)	0.0176 (12)	0.0031 (10)	0.0073 (10)	0.0011 (10)
C30	0.0347 (16)	0.0224 (12)	0.0189 (12)	0.0048 (11)	0.0118 (11)	−0.0015 (10)
C31	0.0350 (15)	0.0197 (12)	0.0169 (12)	0.0010 (11)	0.0056 (11)	−0.0053 (10)
C32	0.0260 (14)	0.0201 (12)	0.0177 (12)	−0.0004 (10)	0.0009 (10)	−0.0013 (10)

Geometric parameters (Å, °)

Cu1—O3	1.9208 (17)	C6—C7	1.381 (4)
Cu1—N6	2.002 (2)	C6—H14A	0.9300
Cu1—N4	2.007 (2)	C7—C8	1.378 (4)
Cu1—N1	2.034 (2)	C7—H13A	0.9300
Cu1—O2	2.2824 (18)	C8—C9	1.377 (4)
Cu1—Cu2	3.0375 (4)	C8—H16A	0.9300
Cu2—O2	1.9348 (17)	C9—C10	1.382 (4)
Cu2—N3	2.014 (2)	C9—H17A	0.9300
Cu2—N5	2.018 (2)	C10—H15A	0.9300
Cu2—N2	2.028 (2)	C11—C12	1.379 (4)
Cu2—O3	2.2837 (18)	C11—H9A	0.9300
Cl1—O7	1.386 (3)	C12—C13	1.381 (4)
Cl1—O8	1.416 (2)	C12—H31A	0.9300
Cl1—O5	1.421 (3)	C13—C14	1.388 (4)
Cl1—O6	1.428 (2)	C13—H8A	0.9300
Cl2—O12	1.415 (2)	C14—C15	1.384 (4)
Cl2—O9	1.419 (2)	C14—H7A	0.9300
Cl2—O11	1.439 (2)	C15—C16	1.528 (3)
Cl2—O10	1.442 (2)	C16—C17	1.547 (3)

N1—C1	1.341 (3)	C17—C18	1.383 (3)
N1—C5	1.341 (3)	C18—C19	1.391 (4)
N2—C10	1.341 (3)	C18—H2A	0.9300
N2—C6	1.343 (3)	C19—C20	1.383 (4)
N3—C11	1.350 (3)	C19—H32A	0.9300
N3—C15	1.351 (3)	C20—C21	1.382 (4)
N4—C21	1.345 (3)	C20—H4A	0.9300
N4—C17	1.346 (3)	C21—H3B	0.9300
N5—C22	1.342 (3)	C22—C23	1.386 (4)
N5—C26	1.344 (3)	C22—H26A	0.9300
N6—C32	1.349 (3)	C23—C24	1.378 (4)
N6—C28	1.353 (3)	C23—H30A	0.9300
O1—C27	1.420 (3)	C24—C25	1.385 (4)
O1—H1A	0.8200	C24—H27A	0.9300
O2—C27	1.377 (3)	C25—C26	1.387 (3)
O3—C16	1.372 (3)	C25—H25A	0.9300
O4—C16	1.423 (3)	C26—C27	1.533 (3)
O4—H3A	0.8200	C27—C28	1.534 (3)
C1—C2	1.385 (4)	C28—C29	1.382 (4)
C1—H11A	0.9300	C29—C30	1.391 (4)
C2—C3	1.383 (4)	C29—H20A	0.9300
C2—H10A	0.9300	C30—C31	1.376 (4)
C3—C4	1.382 (4)	C30—H22A	0.9300
C3—H28A	0.9300	C31—C32	1.381 (4)
C4—C5	1.383 (4)	C31—H21A	0.9300
C4—H29A	0.9300	C32—H18A	0.9300
C5—H12A	0.9300		
O3—Cu1—N6	160.98 (8)	C7—C6—H14A	118.7
O3—Cu1—N4	82.71 (8)	C8—C7—C6	118.9 (3)
N6—Cu1—N4	97.27 (9)	C8—C7—H13A	120.5
O3—Cu1—N1	91.24 (8)	C6—C7—H13A	120.5
N6—Cu1—N1	96.45 (8)	C9—C8—C7	118.9 (3)
N4—Cu1—N1	154.14 (9)	C9—C8—H16A	120.6
O3—Cu1—O2	84.57 (7)	C7—C8—H16A	120.6
N6—Cu1—O2	77.64 (8)	C8—C9—C10	119.3 (3)
N4—Cu1—O2	110.87 (7)	C8—C9—H17A	120.4
N1—Cu1—O2	93.44 (7)	C10—C9—H17A	120.4
O3—Cu1—Cu2	48.71 (5)	N2—C10—C9	122.2 (3)
N6—Cu1—Cu2	112.28 (6)	N2—C10—H15A	118.9
N4—Cu1—Cu2	87.62 (6)	C9—C10—H15A	118.9
N1—Cu1—Cu2	107.19 (6)	N3—C11—C12	122.3 (3)
O2—Cu1—Cu2	39.54 (4)	N3—C11—H9A	118.9
O2—Cu2—N3	160.32 (8)	C12—C11—H9A	118.9
O2—Cu2—N5	82.41 (8)	C11—C12—C13	119.2 (2)
N3—Cu2—N5	96.30 (8)	C11—C12—H31A	120.4
O2—Cu2—N2	92.09 (8)	C13—C12—H31A	120.4
N3—Cu2—N2	96.99 (8)	C12—C13—C14	118.9 (3)
N5—Cu2—N2	154.38 (9)	C12—C13—H8A	120.5
O2—Cu2—O3	84.22 (7)	C14—C13—H8A	120.5

N3—Cu2—O3	77.68 (8)	C15—C14—C13	119.3 (3)
N5—Cu2—O3	109.50 (7)	C15—C14—H7A	120.4
N2—Cu2—O3	94.70 (7)	C13—C14—H7A	120.4
O2—Cu2—Cu1	48.68 (5)	N3—C15—C14	121.7 (2)
N3—Cu2—Cu1	111.69 (6)	N3—C15—C16	115.5 (2)
N5—Cu2—Cu1	86.55 (6)	C14—C15—C16	122.7 (2)
N2—Cu2—Cu1	108.53 (6)	O3—C16—O4	112.5 (2)
O3—Cu2—Cu1	39.19 (4)	O3—C16—C15	109.9 (2)
O7—Cl1—O8	110.6 (2)	O4—C16—C15	104.9 (2)
O7—Cl1—O5	109.3 (3)	O3—C16—C17	109.5 (2)
O8—Cl1—O5	105.4 (2)	O4—C16—C17	108.9 (2)
O7—Cl1—O6	111.3 (2)	C15—C16—C17	111.1 (2)
O8—Cl1—O6	111.02 (16)	N4—C17—C18	121.8 (2)
O5—Cl1—O6	108.96 (18)	N4—C17—C16	114.5 (2)
O12—Cl2—O9	109.1 (2)	C18—C17—C16	123.7 (2)
O12—Cl2—O11	109.6 (2)	C17—C18—C19	118.8 (2)
O9—Cl2—O11	107.33 (18)	C17—C18—H2A	120.6
O12—Cl2—O10	110.69 (15)	C19—C18—H2A	120.6
O9—Cl2—O10	110.15 (16)	C20—C19—C18	119.4 (2)
O11—Cl2—O10	109.94 (15)	C20—C19—H32A	120.3
C1—N1—C5	118.0 (2)	C18—C19—H32A	120.3
C1—N1—Cu1	123.64 (18)	C21—C20—C19	118.8 (2)
C5—N1—Cu1	117.58 (17)	C21—C20—H4A	120.6
C10—N2—C6	118.1 (2)	C19—C20—H4A	120.6
C10—N2—Cu2	123.97 (19)	N4—C21—C20	122.0 (3)
C6—N2—Cu2	117.32 (17)	N4—C21—H3B	119.0
C11—N3—C15	118.6 (2)	C20—C21—H3B	119.0
C11—N3—Cu2	125.09 (19)	N5—C22—C23	122.4 (2)
C15—N3—Cu2	115.90 (16)	N5—C22—H26A	118.8
C21—N4—C17	119.2 (2)	C23—C22—H26A	118.8
C21—N4—Cu1	127.41 (19)	C24—C23—C22	118.7 (2)
C17—N4—Cu1	113.06 (16)	C24—C23—H30A	120.6
C22—N5—C26	118.6 (2)	C22—C23—H30A	120.6
C22—N5—Cu2	128.24 (18)	C23—C24—C25	119.3 (2)
C26—N5—Cu2	112.97 (16)	C23—C24—H27A	120.3
C32—N6—C28	118.7 (2)	C25—C24—H27A	120.3
C32—N6—Cu1	125.03 (18)	C24—C25—C26	118.8 (2)
C28—N6—Cu1	116.01 (16)	C24—C25—H25A	120.6
C27—O1—H1A	109.5	C26—C25—H25A	120.6
C27—O2—Cu2	116.00 (14)	N5—C26—C25	122.0 (2)
C27—O2—Cu1	103.08 (13)	N5—C26—C27	114.7 (2)
Cu2—O2—Cu1	91.77 (7)	C25—C26—C27	123.2 (2)
C16—O3—Cu1	116.75 (15)	O2—C27—O1	113.01 (19)
C16—O3—Cu2	103.70 (14)	O2—C27—C26	110.1 (2)
Cu1—O3—Cu2	92.10 (7)	O1—C27—C26	107.54 (19)
C16—O4—H3A	109.5	O2—C27—C28	109.19 (19)
N1—C1—C2	122.8 (2)	O1—C27—C28	105.80 (19)
N1—C1—H11A	118.6	C26—C27—C28	111.12 (19)
C2—C1—H11A	118.6	N6—C28—C29	121.8 (2)

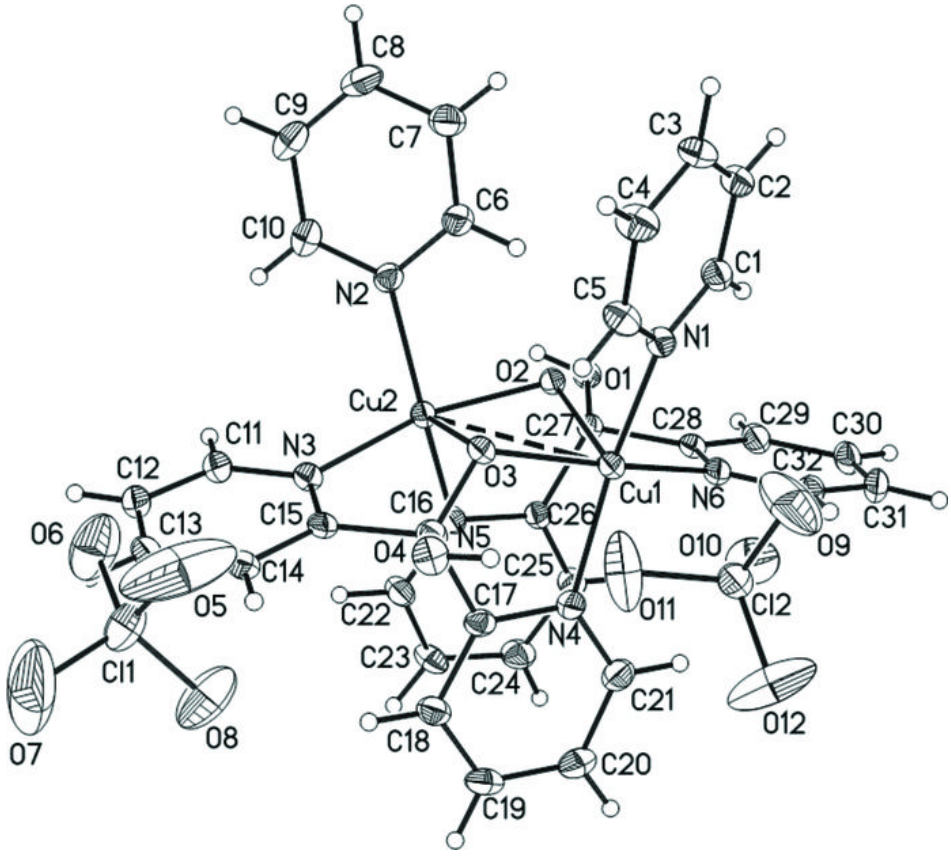
C3—C2—C1	118.8 (3)	N6—C28—C27	115.3 (2)
C3—C2—H10A	120.6	C29—C28—C27	122.9 (2)
C1—C2—H10A	120.6	C28—C29—C30	119.0 (3)
C4—C3—C2	118.8 (2)	C28—C29—H20A	120.5
C4—C3—H28A	120.6	C30—C29—H20A	120.5
C2—C3—H28A	120.6	C31—C30—C29	119.2 (3)
C3—C4—C5	119.1 (3)	C31—C30—H22A	120.4
C3—C4—H29A	120.5	C29—C30—H22A	120.4
C5—C4—H29A	120.5	C30—C31—C32	119.3 (2)
N1—C5—C4	122.6 (3)	C30—C31—H21A	120.4
N1—C5—H12A	118.7	C32—C31—H21A	120.4
C4—C5—H12A	118.7	N6—C32—C31	122.0 (3)
N2—C6—C7	122.5 (3)	N6—C32—H18A	119.0
N2—C6—H14A	118.7	C31—C32—H18A	119.0

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···O5^{i}	0.82	2.26	3.060 (5)	165
O4—H3A···O11	0.82	1.99	2.790 (3)	166

Symmetry codes: (i) *x*−1, *y*, *z*.

Fig. 1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C9
C7
C6
C10
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C3
C4
C2
C1
C5
N1
O2
O1
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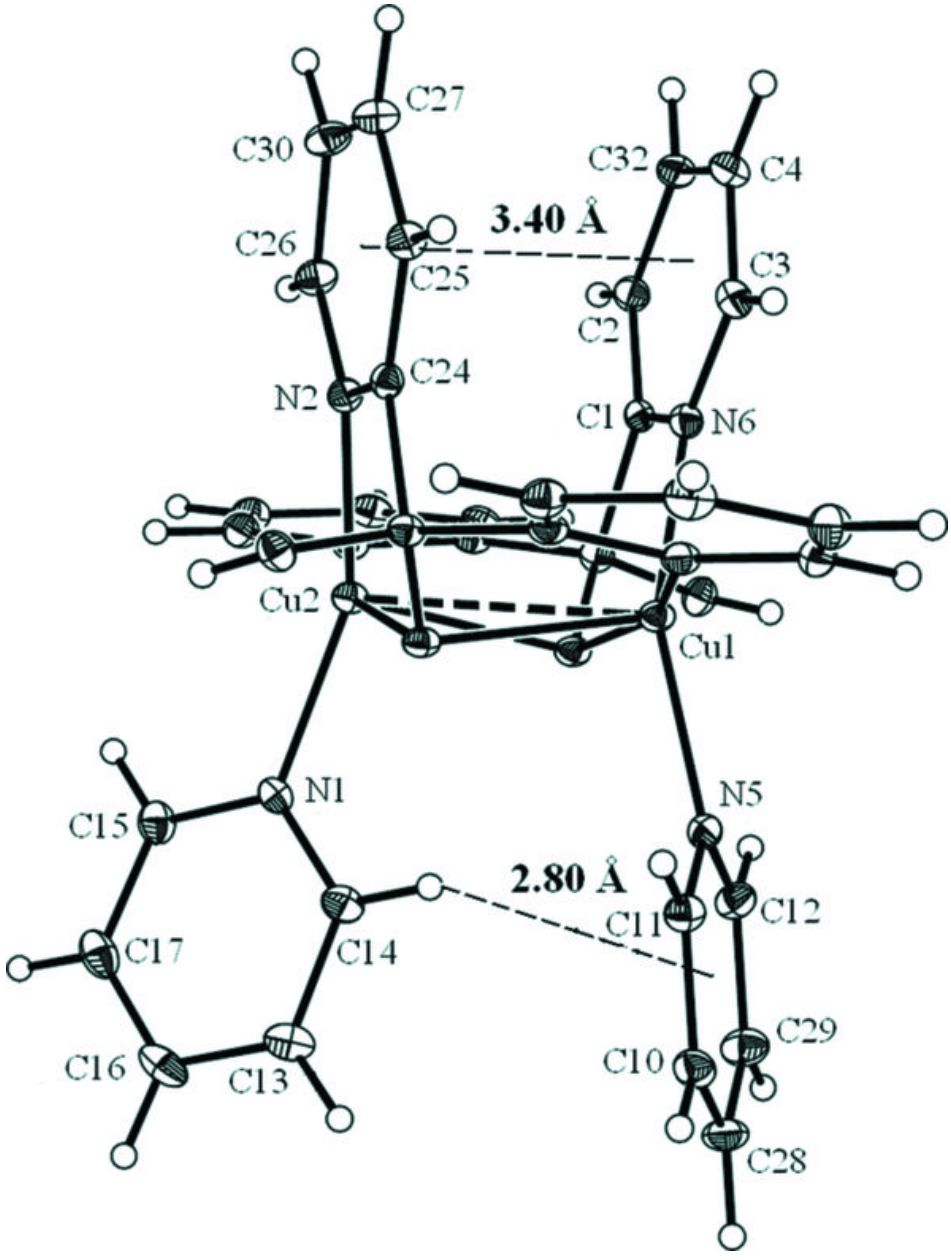
C28
C29
C30
C11
N3
C12
O3
Cu1
N6
C32
C31
C15
C16
C26
C13
O6
N5
O4
C25
O10
O9
C14
O5
C17
C22
O11
Cl2
N4
C23
C24
C21
Cl1
O7
O8
C18
O12
C20
C19

Fig. 2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C4
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C26
C25
C3
C2
C24
N2
C1
N6
Cu2
Cu1
N1
N5
C15
2.80 Å
C11
C12
C17
C14
C29
C16
C13
C10
C28