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Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato-κ^3O,N,N']copper(II) tetrahydrate

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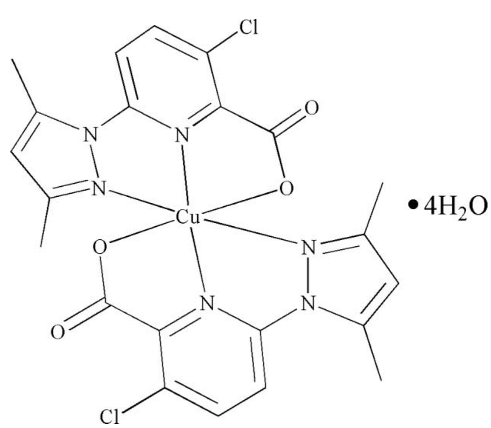
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 13.2.

In the title complex, $[Cu(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$, the Cu^{II} atom is in a distorted octahedral coordination environment, coordinated by four N atoms and two O atoms from two tridentate 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinate ligands. The molecules are linked *via* intermolecular O—H···O hydrogen bonds involving water molecules to form extended chains along [010], and there are short Cl···Cl contacts [3.153 (4) Å].

Related literature

For related literature, see: Aliev *et al.* (1988); Bhatia *et al.* (1981); Costamagna *et al.* (1992); Kai *et al.* (2007); Kuang *et al.* (1997); Ramazani *et al.* (2002); Xu *et al.* (2001); Yaghi & Li (1996); Yin *et al.* (2007); Zhao *et al.* (2007).



Experimental

Crystal data

$[Cu(C_{11}H_9ClN_3O_2)_2]\cdot 4H_2O$
M_r = 636.93
Triclinic, $P\overline{1}$
a = 9.6578 (9) Å
b = 11.2637 (14) Å
c = 14.3127 (18) Å
α = 92.349 (2)°
β = 106.090 (2)°
γ = 114.065 (3)°
V = 1344.7 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 298 (2) K
0.59 × 0.52 × 0.50 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.571, T_{max} = 0.617 (expected range = 0.543–0.586)
7014 measured reflections
4664 independent reflections
3789 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.03
4664 reflections
352 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.38 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
O5—H5A···O6	0.85	1.96	2.804 (4)	170
O5—H5B···O4^{i}	0.85	1.98	2.818 (4)	170
O6—H6A···O2	0.85	2.24	3.090 (5)	176
O6—H6B···O7^{ii}	0.85	1.85	2.697 (4)	176
O8—H8A···O5	0.85	2.10	2.947 (5)	178
O8—H8B···O5^{iii}	0.85	1.98	2.825 (5)	179

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: RN2033).

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supplementary materials

Acta Cryst. (2008). E**64**, m284-m285 [**doi:10.1107/S1600536807068110**]

Bis[3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato-κ^3*O*,*N*,*N*']copper(II) tetrahydrate

K. Zhao, X.-H. Yin, F.-L. Hu, C.-W. Lin, S.-S. Zhang and R.-W. Qing

Comment

Transition metal compounds containing pyrazolyl pyridine ligands have been of great interest for many years (Kuang *et al.*, 1997; Ramazani *et al.*, 2002). These compounds play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures (Costamagna *et al.*, 1992; Bhatia *et al.*, 1981). Inorganic supramolecular chemistry, and in particular the construction of polymeric coordination networks, is an extremely topical area of research (Xu *et al.*., 2001; Yaghi *et al.*., 1996) and the construction of a wide variety of network topologies has been achieved through ligand design and the use of different counter-anions. Our work is aimed at obtaining multidimensional metal complexes. On the basis of the above-mentioned considerations, we designed and synthesized the flexible tridentate ligand 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid (CDPA) (Kai *et al.*, 2007), which offers advantages over rigid ligands in that it can adopt a different coordination modes according to the geometric needs of the coordination environment of the transition metal. Recently we reported the crystal structures of bis(6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinato)zinc(II)trihydrate (Yin *et al.*, 2007). As a continuation of these investigations, we report in this paper the crystal structure of bis(6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol-1-yl))picolinato) copper(II)tetra-hydrate, (I), Fig. 1.

The title complex, (I), is an asymmetric electronically neutral mononuclear compound with four uncoordinated water molecules (Fig. 1). The Cu^{II} atom is coordinated by four N atoms and two O atoms from two tridentate, 6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol- 1-yl))picolinic acid (CDPA) ligands, respectively. that define a distorted octahedral environment for the copper atom. The Cu—O bond length is 2.073 (2)and 2.176 (2) Å, The Cu—N distances range from 1.969 (2) to 2.214 (2) Å, the C5—C6 and C9—C10 bond lengths are 1.388 (4) and 1.398 (5) Å; they are longer than the normal C=C bond length (1.38 Å) because they participate in the C—N conjugated system. There are many stacking interactions involving the CDPA ligand forming a supramolecular structure.

In the crystal structure, all oxygen atoms, except O1 and O3, bound to the metal center, contribute to the formation of intermolecular hydrogen bonds involving the solvate water molecules (Zhao *et al.*, 2007), and there are short Cl···Cl contacts (Cl2—Cl2= 3.153 Å), their distances are much shorter than the van der Waal distance(Aliev *et al.*, 1988). (Fig.2. for symmetry codes see Table 2). A great number of H-bonds and short Cl···Cl contacts join the complex to form a three-dimensional supramolecular network structure along *b* axis.

Experimental

6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol-1-yl))picolinic acid, and $CuSO_4$. $6H_2O$ were available commercially and were used without further purification. Equimolar 6-(3-chloro-(3,5-dimethyl-1*H*-pyrazol-1-yl))picolinic acid (1 mmol, 217 mg) was dissolved in anhydrous alcohol (15 ml). The mixture was stirred to give a clear solution, To this solution was added $CuSO_4.6H_2O$ (0.5 mmol, 119 mg) in anhydrous alcohol (10 ml). After keeping the resulting solution in air to evaporate about half of the solvents, blue blocks of the title compound were formed. The crystals were isolated, washed with alcohol three times and dried in a vacuum desiccator using silica gel (Yield 72%). Elemental analysis: found: C, 53.708; H, 4.20; N, 17.04;; calc. for $C_{22}H_{2}0_{Cu}Cl_{N}6_{O}4$: C, 53.78; H, 4.10; N, 17.10.

Refinement

H atoms on C atoms were positoned geometrically and refined using a riding model with C—H =0.96Å and U_{iso}(H) = 1.2U_{eq}(C). The water H atoms were located in difference Fourier maps and the O—H distances were constrained 0.85 Å, with U_{iso}(H) = 1.2U_{eq}(O).

Figures

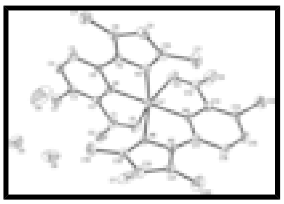

Fig. 1. The structure of the title compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme, H atoms have been omitted for clarity

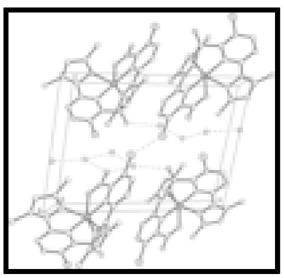

Fig. 2. Crystal packing of (I) showing the hydrogen bonded interactions as dashed lines, H atoms have been omitted for clarity.

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Crystal data

$[Cu(C_{11}H_9ClN_3O_2)_2]\cdot4H_2O$	$Z = 2$
$M_r = 636.93$	$F_{000} = 654$
Triclinic, $P\overline{1}$	$D_x = 1.573$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 9.6578$ (9) Å	Cell parameters from 3642 reflections
$b = 11.2637$ (14) Å	θ = 2.4–27.8°
$c = 14.3127$ (18) Å	μ = 1.07 mm^{-1}
α = 92.349 (2)°	$T = 298$ (2) K
β = 106.090 (2)°	Block, blue
γ = 114.065 (3)°	0.59 × 0.52 × 0.50 mm
$V = 1344.7$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	4664 independent reflections

Radiation source: fine-focus sealed tube	3789 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.016$
$T = 298(2)$ K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 1.5°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11\rightarrow11$
$T_{min} = 0.571$, $T_{max} = 0.617$	$k = -7\rightarrow13$
7014 measured reflections	$l = -16\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.138P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
4664 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
352 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	0.26465 (4)	0.01979 (4)	0.24804 (3)	0.03700 (13)
Cl1	0.05694 (11)	0.41095 (9)	0.17347 (7)	0.0574 (2)
Cl2	0.08351 (12)	−0.43064 (9)	0.42400 (7)	0.0646 (3)
N1	0.2134 (3)	0.1366 (2)	0.16023 (16)	0.0305 (5)
N2	0.2500 (3)	0.0211 (2)	0.04162 (17)	0.0352 (5)
N3	0.2667 (3)	−0.0574 (2)	0.11161 (18)	0.0395 (6)
N4	0.3193 (3)	−0.0982 (2)	0.33689 (16)	0.0324 (5)
N5	0.5845 (3)	0.0389 (2)	0.36071 (17)	0.0347 (5)
N6	0.5287 (3)	0.1231 (2)	0.31390 (18)	0.0376 (6)
O1	0.2253 (3)	0.1378 (2)	0.34278 (16)	0.0530 (6)

O2	0.1882 (3)	0.3198 (3)	0.35335 (17)	0.0664 (7)
O3	0.0307 (3)	−0.1408 (3)	0.22898 (19)	0.0631 (7)
O4	−0.0869 (3)	−0.2981 (3)	0.3052 (2)	0.0967 (12)
O5	0.6077 (3)	0.6078 (3)	0.1622 (2)	0.0812 (9)
H5A	0.5484	0.5881	0.1987	0.097*
H5B	0.7046	0.6379	0.1991	0.097*
O6	0.4476 (4)	0.5544 (4)	0.3027 (2)	0.1041 (11)
H6A	0.3801	0.4903	0.3196	0.125*
H6B	0.5371	0.5849	0.3487	0.125*
O7	0.2625 (4)	0.3401 (4)	0.5565 (2)	0.1128 (14)
H7D	0.2174	0.3287	0.4946	0.135*
H7E	0.1920	0.3234	0.5851	0.135*
O8	0.5577 (6)	0.3762 (5)	0.0299 (3)	0.151 (2)
H8A	0.5727	0.4423	0.0690	0.182*
H8B	0.5076	0.3798	−0.0282	0.182*
C1	0.1974 (4)	0.2295 (3)	0.3083 (2)	0.0409 (7)
C2	0.1742 (3)	0.2257 (3)	0.1976 (2)	0.0324 (6)
C3	0.1224 (3)	0.3012 (3)	0.1356 (2)	0.0381 (7)
C4	0.1170 (4)	0.2856 (3)	0.0382 (2)	0.0479 (8)
H4	0.0841	0.3371	−0.0034	0.057*
C5	0.1595 (4)	0.1955 (3)	0.0018 (2)	0.0453 (8)
H5	0.1559	0.1847	−0.0637	0.054*
C6	0.2079 (3)	0.1210 (3)	0.0667 (2)	0.0331 (6)
C7	0.2632 (5)	0.0403 (4)	−0.1324 (3)	0.0605 (10)
H7A	0.1546	0.0238	−0.1664	0.091*
H7B	0.3021	0.0037	−0.1754	0.091*
H7C	0.3289	0.1338	−0.1134	0.091*
C8	0.2695 (4)	−0.0226 (3)	−0.0424 (2)	0.0421 (7)
C9	0.2988 (4)	−0.1298 (3)	−0.0245 (3)	0.0484 (8)
H9	0.3181	−0.1806	−0.0676	0.058*
C10	0.2944 (4)	−0.1488 (3)	0.0707 (3)	0.0444 (8)
C11	0.3113 (5)	−0.2561 (4)	0.1247 (3)	0.0666 (11)
H11A	0.4186	−0.2238	0.1694	0.100*
H11B	0.2892	−0.3304	0.0780	0.100*
H11C	0.2370	−0.2828	0.1611	0.100*
C12	0.0307 (4)	−0.2160 (3)	0.2893 (2)	0.0481 (8)
C13	0.1965 (3)	−0.2044 (3)	0.3486 (2)	0.0359 (7)
C14	0.2302 (4)	−0.2895 (3)	0.4077 (2)	0.0405 (7)
C15	0.3880 (4)	−0.2626 (3)	0.4558 (2)	0.0466 (8)
H15	0.4108	−0.3189	0.4966	0.056*
C16	0.5106 (4)	−0.1545 (3)	0.4443 (2)	0.0446 (8)
H16	0.6169	−0.1354	0.4771	0.054*
C17	0.4708 (3)	−0.0740 (3)	0.3816 (2)	0.0331 (6)
C18	0.6426 (4)	0.3362 (3)	0.2609 (3)	0.0595 (10)
H18A	0.5317	0.3178	0.2349	0.089*
H18B	0.6886	0.3486	0.2085	0.089*
H18C	0.6986	0.4149	0.3101	0.089*
C19	0.6568 (4)	0.2227 (3)	0.3066 (2)	0.0407 (7)
C20	0.7943 (4)	0.2036 (3)	0.3471 (2)	0.0456 (8)

H20	0.8981	0.2598	0.3502	0.055*
C21	0.7478 (3)	0.0879 (3)	0.3812 (2)	0.0398 (7)
C22	0.8476 (4)	0.0199 (4)	0.4272 (3)	0.0674 (11)
H22A	0.9540	0.0668	0.4241	0.101*
H22B	0.8008	−0.0689	0.3919	0.101*
H22C	0.8519	0.0181	0.4949	0.101*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0349 (2)	0.0417 (2)	0.0385 (2)	0.01931 (17)	0.01275 (16)	0.01578 (16)
Cl1	0.0640 (5)	0.0492 (5)	0.0682 (6)	0.0368 (4)	0.0159 (5)	0.0117 (4)
Cl2	0.0792 (7)	0.0425 (5)	0.0685 (6)	0.0132 (4)	0.0369 (5)	0.0254 (4)
N1	0.0250 (11)	0.0347 (13)	0.0303 (12)	0.0120 (10)	0.0074 (10)	0.0088 (10)
N2	0.0373 (13)	0.0372 (14)	0.0299 (13)	0.0158 (11)	0.0096 (11)	0.0087 (10)
N3	0.0433 (14)	0.0409 (14)	0.0388 (14)	0.0223 (12)	0.0131 (12)	0.0136 (11)
N4	0.0308 (12)	0.0356 (13)	0.0313 (12)	0.0144 (11)	0.0101 (10)	0.0109 (10)
N5	0.0297 (12)	0.0386 (14)	0.0354 (13)	0.0172 (11)	0.0058 (10)	0.0105 (11)
N6	0.0317 (13)	0.0386 (14)	0.0432 (14)	0.0171 (11)	0.0093 (11)	0.0151 (11)
O1	0.0644 (15)	0.0755 (17)	0.0426 (13)	0.0471 (14)	0.0236 (11)	0.0286 (12)
O2	0.094 (2)	0.087 (2)	0.0413 (14)	0.0615 (17)	0.0213 (14)	0.0092 (13)
O3	0.0385 (12)	0.0869 (19)	0.0636 (16)	0.0240 (13)	0.0163 (11)	0.0444 (15)
O4	0.0394 (15)	0.117 (3)	0.111 (3)	0.0099 (16)	0.0215 (15)	0.069 (2)
O5	0.0692 (18)	0.104 (2)	0.0615 (17)	0.0372 (17)	0.0076 (15)	0.0196 (16)
O6	0.0652 (19)	0.133 (3)	0.080 (2)	0.019 (2)	0.0139 (17)	−0.007 (2)
O7	0.072 (2)	0.211 (4)	0.0474 (17)	0.059 (2)	0.0128 (15)	0.008 (2)
O8	0.246 (6)	0.188 (5)	0.074 (2)	0.163 (4)	0.027 (3)	0.014 (3)
C1	0.0380 (16)	0.054 (2)	0.0366 (16)	0.0244 (15)	0.0141 (14)	0.0125 (15)
C2	0.0257 (14)	0.0333 (15)	0.0353 (15)	0.0110 (12)	0.0085 (12)	0.0059 (12)
C3	0.0320 (15)	0.0339 (16)	0.0462 (18)	0.0147 (13)	0.0083 (13)	0.0091 (13)
C4	0.053 (2)	0.049 (2)	0.0448 (19)	0.0280 (17)	0.0092 (16)	0.0218 (16)
C5	0.0541 (19)	0.052 (2)	0.0303 (16)	0.0250 (16)	0.0103 (14)	0.0120 (14)
C6	0.0276 (14)	0.0341 (15)	0.0316 (15)	0.0103 (12)	0.0052 (12)	0.0074 (12)
C7	0.077 (3)	0.069 (3)	0.043 (2)	0.034 (2)	0.0275 (19)	0.0136 (18)
C8	0.0354 (16)	0.0464 (19)	0.0366 (17)	0.0109 (14)	0.0112 (13)	0.0033 (14)
C9	0.0469 (19)	0.0461 (19)	0.053 (2)	0.0185 (16)	0.0208 (16)	−0.0001 (16)
C10	0.0394 (17)	0.0386 (18)	0.057 (2)	0.0178 (14)	0.0177 (15)	0.0094 (15)
C11	0.084 (3)	0.053 (2)	0.086 (3)	0.043 (2)	0.041 (2)	0.025 (2)
C12	0.0336 (17)	0.055 (2)	0.0461 (19)	0.0095 (16)	0.0134 (14)	0.0179 (16)
C13	0.0392 (16)	0.0363 (16)	0.0313 (15)	0.0129 (13)	0.0152 (13)	0.0094 (12)
C14	0.0547 (19)	0.0350 (16)	0.0340 (16)	0.0164 (15)	0.0216 (15)	0.0121 (13)
C15	0.066 (2)	0.0470 (19)	0.0388 (17)	0.0337 (17)	0.0184 (16)	0.0209 (15)
C16	0.0451 (18)	0.054 (2)	0.0394 (17)	0.0282 (16)	0.0082 (14)	0.0178 (15)
C17	0.0323 (15)	0.0373 (16)	0.0302 (14)	0.0164 (13)	0.0087 (12)	0.0078 (12)
C18	0.057 (2)	0.047 (2)	0.076 (3)	0.0202 (17)	0.025 (2)	0.0254 (19)
C19	0.0402 (17)	0.0364 (17)	0.0423 (17)	0.0142 (14)	0.0122 (14)	0.0088 (14)
C20	0.0285 (15)	0.0469 (19)	0.054 (2)	0.0098 (14)	0.0124 (14)	0.0057 (15)
C21	0.0283 (15)	0.0466 (18)	0.0399 (17)	0.0165 (14)	0.0047 (13)	0.0035 (14)

C22	0.0401 (19)	0.086 (3)	0.088 (3)	0.039 (2)	0.0181 (19)	0.035 (2)

Geometric parameters (Å, °)

Cu1—N1	1.969 (2)	C3—C4	1.382 (4)
Cu1—N4	2.000 (2)	C4—C5	1.373 (5)
Cu1—O1	2.073 (2)	C4—H4	0.9300
Cu1—N3	2.113 (3)	C5—C6	1.388 (4)
Cu1—O3	2.176 (2)	C5—H5	0.9300
Cu1—N6	2.214 (2)	C7—C8	1.495 (4)
Cl1—C3	1.730 (3)	C7—H7A	0.9600
Cl2—C14	1.722 (3)	C7—H7B	0.9600
N1—C6	1.327 (4)	C7—H7C	0.9600
N1—C2	1.347 (4)	C8—C9	1.366 (5)
N2—C8	1.370 (4)	C9—C10	1.398 (5)
N2—N3	1.382 (3)	C9—H9	0.9300
N2—C6	1.408 (4)	C10—C11	1.500 (4)
N3—C10	1.318 (4)	C11—H11A	0.9600
N4—C17	1.329 (3)	C11—H11B	0.9600
N4—C13	1.354 (3)	C11—H11C	0.9600
N5—C21	1.378 (4)	C12—C13	1.538 (4)
N5—N6	1.381 (3)	C13—C14	1.382 (4)
N5—C17	1.409 (4)	C14—C15	1.383 (4)
N6—C19	1.323 (4)	C15—C16	1.364 (4)
O1—C1	1.256 (4)	C15—H15	0.9300
O2—C1	1.229 (4)	C16—C17	1.392 (4)
O3—C12	1.235 (4)	C16—H16	0.9300
O4—C12	1.225 (4)	C18—C19	1.497 (4)
O5—H5A	0.8500	C18—H18A	0.9600
O5—H5B	0.8500	C18—H18B	0.9600
O6—H6A	0.8501	C18—H18C	0.9600
O6—H6B	0.8500	C19—C20	1.400 (4)
O7—H7D	0.8499	C20—C21	1.353 (4)
O7—H7E	0.8501	C20—H20	0.9300
O8—H8A	0.8501	C21—C22	1.497 (4)
O8—H8B	0.8500	C22—H22A	0.9600
C1—C2	1.534 (4)	C22—H22B	0.9600
C2—C3	1.386 (4)	C22—H22C	0.9600
N1—Cu1—N4	179.30 (9)	H7A—C7—H7B	109.5
N1—Cu1—O1	79.35 (9)	C8—C7—H7C	109.5
N4—Cu1—O1	101.05 (9)	H7A—C7—H7C	109.5
N1—Cu1—N3	77.32 (9)	H7B—C7—H7C	109.5
N4—Cu1—N3	102.32 (9)	C9—C8—N2	106.0 (3)
O1—Cu1—N3	156.38 (9)	C9—C8—C7	128.8 (3)
N1—Cu1—O3	103.12 (9)	N2—C8—C7	125.2 (3)
N4—Cu1—O3	77.47 (9)	C8—C9—C10	107.2 (3)
O1—Cu1—O3	90.45 (11)	C8—C9—H9	126.4
N3—Cu1—O3	91.28 (10)	C10—C9—H9	126.4
N1—Cu1—N6	103.57 (9)	N3—C10—C9	110.2 (3)

N4—Cu1—N6	75.84 (9)	N3—C10—C11	120.7 (3)
O1—Cu1—N6	94.00 (10)	C9—C10—C11	129.0 (3)
N3—Cu1—N6	94.97 (10)	C10—C11—H11A	109.5
O3—Cu1—N6	153.30 (9)	C10—C11—H11B	109.5
C6—N1—C2	122.1 (2)	H11A—C11—H11B	109.5
C6—N1—Cu1	120.64 (19)	C10—C11—H11C	109.5
C2—N1—Cu1	117.06 (18)	H11A—C11—H11C	109.5
C8—N2—N3	110.4 (2)	H11B—C11—H11C	109.5
C8—N2—C6	133.3 (2)	O4—C12—O3	126.5 (3)
N3—N2—C6	116.2 (2)	O4—C12—C13	118.1 (3)
C10—N3—N2	106.1 (2)	O3—C12—C13	115.4 (3)
C10—N3—Cu1	141.9 (2)	N4—C13—C14	119.0 (3)
N2—N3—Cu1	111.56 (18)	N4—C13—C12	113.3 (2)
C17—N4—C13	121.4 (2)	C14—C13—C12	127.6 (3)
C17—N4—Cu1	120.97 (18)	C13—C14—C15	119.5 (3)
C13—N4—Cu1	117.61 (18)	C13—C14—Cl2	122.9 (2)
C21—N5—N6	110.6 (2)	C15—C14—Cl2	117.6 (2)
C21—N5—C17	132.6 (2)	C16—C15—C14	120.9 (3)
N6—N5—C17	116.7 (2)	C16—C15—H15	119.6
C19—N6—N5	105.3 (2)	C14—C15—H15	119.6
C19—N6—Cu1	142.4 (2)	C15—C16—C17	117.6 (3)
N5—N6—Cu1	109.55 (16)	C15—C16—H16	121.2
C1—O1—Cu1	115.75 (19)	C17—C16—H16	121.2
C12—O3—Cu1	114.4 (2)	N4—C17—C16	121.6 (3)
H5A—O5—H5B	108.1	N4—C17—N5	114.6 (2)
H6A—O6—H6B	108.5	C16—C17—N5	123.8 (3)
H7D—O7—H7E	108.8	C19—C18—H18A	109.5
H8A—O8—H8B	108.4	C19—C18—H18B	109.5
O2—C1—O1	127.3 (3)	H18A—C18—H18B	109.5
O2—C1—C2	118.0 (3)	C19—C18—H18C	109.5
O1—C1—C2	114.7 (3)	H18A—C18—H18C	109.5
N1—C2—C3	118.9 (3)	H18B—C18—H18C	109.5
N1—C2—C1	112.4 (2)	N6—C19—C20	110.7 (3)
C3—C2—C1	128.7 (3)	N6—C19—C18	120.5 (3)
C4—C3—C2	119.1 (3)	C20—C19—C18	128.8 (3)
C4—C3—Cl1	117.9 (2)	C21—C20—C19	107.2 (3)
C2—C3—Cl1	122.9 (2)	C21—C20—H20	126.4
C5—C4—C3	121.1 (3)	C19—C20—H20	126.4
C5—C4—H4	119.4	C20—C21—N5	106.1 (3)
C3—C4—H4	119.4	C20—C21—C22	128.5 (3)
C4—C5—C6	117.3 (3)	N5—C21—C22	125.4 (3)
C4—C5—H5	121.3	C21—C22—H22A	109.5
C6—C5—H5	121.3	C21—C22—H22B	109.5
N1—C6—C5	121.3 (3)	H22A—C22—H22B	109.5
N1—C6—N2	113.4 (2)	C21—C22—H22C	109.5
C5—C6—N2	125.2 (3)	H22A—C22—H22C	109.5
C8—C7—H7A	109.5	H22B—C22—H22C	109.5
C8—C7—H7B	109.5		

O1—Cu1—N1—C6	−178.1 (2)	N1—C2—C3—Cl1	175.8 (2)

N3—Cu1—N1—C6	−1.8 (2)	C1—C2—C3—Cl1	−5.3 (4)
O3—Cu1—N1—C6	−90.2 (2)	C2—C3—C4—C5	1.1 (5)
N6—Cu1—N1—C6	90.3 (2)	Cl1—C3—C4—C5	−176.7 (3)
O1—Cu1—N1—C2	−2.46 (19)	C3—C4—C5—C6	0.0 (5)
N3—Cu1—N1—C2	173.8 (2)	C2—N1—C6—C5	−0.7 (4)
O3—Cu1—N1—C2	85.5 (2)	Cu1—N1—C6—C5	174.8 (2)
N6—Cu1—N1—C2	−94.04 (19)	C2—N1—C6—N2	−178.7 (2)
C8—N2—N3—C10	−0.6 (3)	Cu1—N1—C6—N2	−3.3 (3)
C6—N2—N3—C10	175.6 (2)	C4—C5—C6—N1	−0.2 (4)
C8—N2—N3—Cu1	173.32 (18)	C4—C5—C6—N2	177.6 (3)
C6—N2—N3—Cu1	−10.5 (3)	C8—N2—C6—N1	−175.6 (3)
N1—Cu1—N3—C10	177.1 (4)	N3—N2—C6—N1	9.3 (3)
N4—Cu1—N3—C10	−2.3 (4)	C8—N2—C6—C5	6.4 (5)
O1—Cu1—N3—C10	−173.8 (3)	N3—N2—C6—C5	−168.7 (3)
O3—Cu1—N3—C10	−79.8 (3)	N3—N2—C8—C9	−0.1 (3)
N6—Cu1—N3—C10	74.3 (3)	C6—N2—C8—C9	−175.3 (3)
N1—Cu1—N3—N2	6.59 (17)	N3—N2—C8—C7	−178.5 (3)
N4—Cu1—N3—N2	−172.80 (17)	C6—N2—C8—C7	6.2 (5)
O1—Cu1—N3—N2	15.7 (4)	N2—C8—C9—C10	0.6 (3)
O3—Cu1—N3—N2	109.75 (18)	C7—C8—C9—C10	179.0 (3)
N6—Cu1—N3—N2	−96.23 (18)	N2—N3—C10—C9	1.0 (3)
O1—Cu1—N4—C17	−98.3 (2)	Cu1—N3—C10—C9	−169.8 (3)
N3—Cu1—N4—C17	85.1 (2)	N2—N3—C10—C11	−177.1 (3)
O3—Cu1—N4—C17	173.7 (2)	Cu1—N3—C10—C11	12.1 (5)
N6—Cu1—N4—C17	−7.0 (2)	C8—C9—C10—N3	−1.1 (4)
O1—Cu1—N4—C13	82.6 (2)	C8—C9—C10—C11	176.9 (3)
N3—Cu1—N4—C13	−94.0 (2)	Cu1—O3—C12—O4	166.2 (4)
O3—Cu1—N4—C13	−5.4 (2)	Cu1—O3—C12—C13	−14.6 (4)
N6—Cu1—N4—C13	173.9 (2)	C17—N4—C13—C14	−0.6 (4)
C21—N5—N6—C19	−0.4 (3)	Cu1—N4—C13—C14	178.5 (2)
C17—N5—N6—C19	177.3 (3)	C17—N4—C13—C12	−179.0 (3)
C21—N5—N6—Cu1	165.40 (19)	Cu1—N4—C13—C12	0.1 (3)
C17—N5—N6—Cu1	−16.9 (3)	O4—C12—C13—N4	−170.4 (3)
N1—Cu1—N6—C19	−10.0 (4)	O3—C12—C13—N4	10.2 (4)
N4—Cu1—N6—C19	169.6 (4)	O4—C12—C13—C14	11.3 (6)
O1—Cu1—N6—C19	−90.0 (4)	O3—C12—C13—C14	−168.1 (3)
N3—Cu1—N6—C19	68.2 (4)	N4—C13—C14—C15	2.0 (4)
O3—Cu1—N6—C19	171.0 (3)	C12—C13—C14—C15	−179.9 (3)
N1—Cu1—N6—N5	−167.16 (17)	N4—C13—C14—Cl2	−177.5 (2)
N4—Cu1—N6—N5	12.44 (17)	C12—C13—C14—Cl2	0.7 (5)
O1—Cu1—N6—N5	112.84 (18)	C13—C14—C15—C16	−1.2 (5)
N3—Cu1—N6—N5	−89.03 (18)	Cl2—C14—C15—C16	178.2 (3)
O3—Cu1—N6—N5	13.8 (3)	C14—C15—C16—C17	−0.8 (5)
N1—Cu1—O1—C1	−3.6 (2)	C13—N4—C17—C16	−1.5 (4)
N4—Cu1—O1—C1	175.8 (2)	Cu1—N4—C17—C16	179.4 (2)
N3—Cu1—O1—C1	−12.7 (4)	C13—N4—C17—N5	179.0 (2)
O3—Cu1—O1—C1	−106.9 (2)	Cu1—N4—C17—N5	−0.1 (3)
N6—Cu1—O1—C1	99.4 (2)	C15—C16—C17—N4	2.2 (5)
N1—Cu1—O3—C12	−168.9 (3)	C15—C16—C17—N5	−178.4 (3)

N4—Cu1—O3—C12	11.5 (3)	C21—N5—C17—N4	−170.6 (3)
O1—Cu1—O3—C12	−89.7 (3)	N6—N5—C17—N4	12.3 (4)
N3—Cu1—O3—C12	113.9 (3)	C21—N5—C17—C16	9.9 (5)
N6—Cu1—O3—C12	10.1 (4)	N6—N5—C17—C16	−167.1 (3)
Cu1—O1—C1—O2	−171.3 (3)	N5—N6—C19—C20	0.5 (3)
Cu1—O1—C1—C2	8.2 (3)	Cu1—N6—C19—C20	−157.2 (3)
C6—N1—C2—C3	1.7 (4)	N5—N6—C19—C18	−178.7 (3)
Cu1—N1—C2—C3	−173.9 (2)	Cu1—N6—C19—C18	23.6 (5)
C6—N1—C2—C1	−177.4 (2)	N6—C19—C20—C21	−0.4 (4)
Cu1—N1—C2—C1	7.0 (3)	C18—C19—C20—C21	178.7 (3)
O2—C1—C2—N1	169.5 (3)	C19—C20—C21—N5	0.2 (4)
O1—C1—C2—N1	−10.0 (4)	C19—C20—C21—C22	177.2 (4)
O2—C1—C2—C3	−9.5 (5)	N6—N5—C21—C20	0.1 (3)
O1—C1—C2—C3	171.0 (3)	C17—N5—C21—C20	−177.1 (3)
N1—C2—C3—C4	−1.9 (4)	N6—N5—C21—C22	−177.0 (3)
C1—C2—C3—C4	177.0 (3)	C17—N5—C21—C22	5.8 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5A···O6	0.85	1.96	2.804 (4)	170
O5—H5B···O4^{i}	0.85	1.98	2.818 (4)	170
O6—H6A···O2	0.85	2.24	3.090 (5)	176
O6—H6B···O7^{ii}	0.85	1.85	2.697 (4)	176
O8—H8A···O5	0.85	2.10	2.947 (5)	178
O8—H8B···O5^{iii}	0.85	1.98	2.825 (5)	179

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

Fig. 1

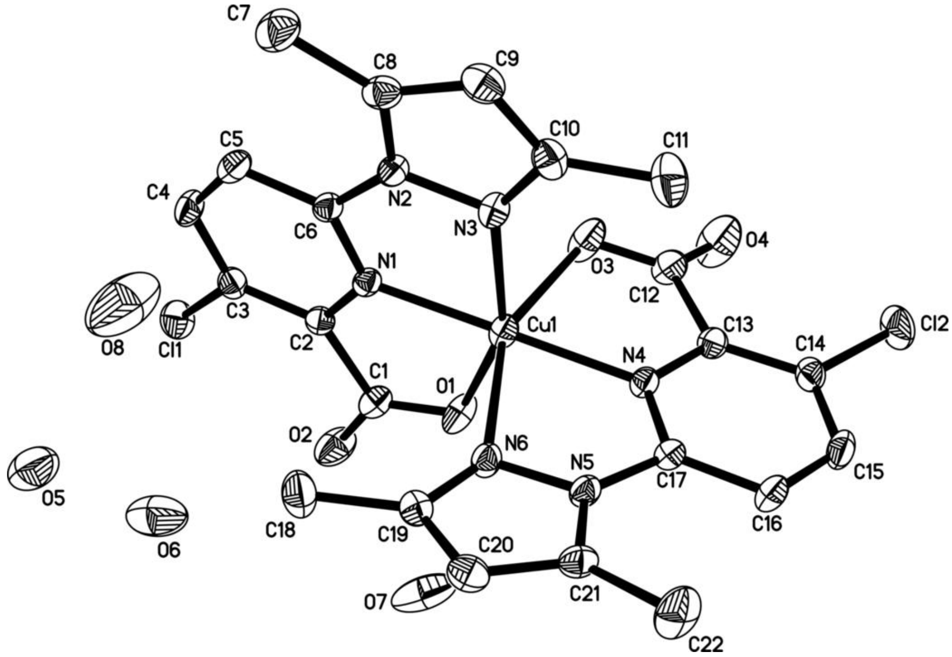
C7
C8
C9
C10
C11
C5
C4
N2
C6
N3
O3
O4
N1
C12
C3
Cu1
C13
C14
Cl2
O8
Cl1
C2
N4
C1
O1
O2
N6
N5
C17
C15
O5
C16
C18
C19
C20
O6
C21
O7
C22

Fig. 2