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(2-Methacrylato)[tris(1-methyl-1*H*-benzimidazol-2-ylmethyl)amine]copper(II) perchlorate dimethylformamide disolvate hemihydrate at 153 (2) K

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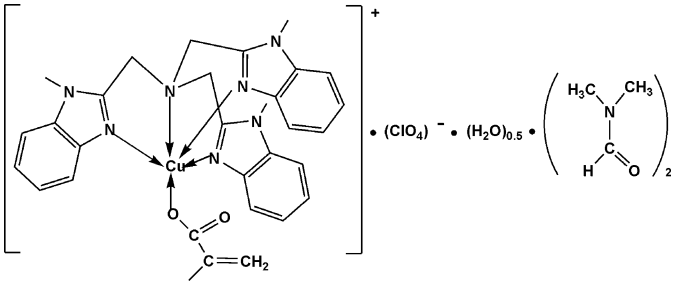
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.006 Å; disorder in main residue; R factor = 0.056; wR factor = 0.170; data-to-parameter ratio = 12.8.

In the title complex, $[Cu(C_4H_5O_2)(C_{27}H_{27}N_7)](ClO_4)\cdot 2C_3H_7NO\cdot 0.5H_2O$, the Cu^{II} ion is five-coordinated by four N atoms from a tris(*N*-methylbenzimidazol-2-ylmethyl)amine ligand and one O atom from a 2-methacrylate ligand in a distorted trigonal–bipyramidal geometry with approximate molecular C_3 symmetry. A half-occupancy solvent water molecule forms weak O—H···O hydrogen bonds and the atoms of the 2-methacrylate ligand are disordered over two sites with equal occupancy.

Related literature

For related literature, see: Allen *et al.* (1987); Youngme *et al.* (2007).



Experimental

Crystal data

$[Cu(C_4H_5O_2)(C_{27}H_{27}N_7)](ClO_4)\cdot 2C_3H_7NO\cdot 0.5H_2O$
M_r = 852.83
Triclinic, $P\overline{1}$
a = 12.2004 (5) Å
b = 12.6825 (6) Å
c = 13.6436 (6) Å
α = 88.703 (1)°
β = 74.892 (1)°
γ = 78.197 (1)°
V = 1993.98 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.68 mm^{-1}
T = 153 (2) K
0.29 × 0.23 × 0.21 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.828, T_{max} = 0.871
16373 measured reflections
7382 independent reflections
5587 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.170
S = 1.11
7382 reflections
578 parameters
46 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H1W···O4^{i}	0.84	2.71	3.55 (2)	180
O7—H2W···O2	0.84	2.21	3.05 (2)	179

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

Data collection: *RAPID-AUTO* (Rigaku/MSC, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); 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: LH2496).

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supplementary materials

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(2-Methacrylato)[tris(1-methyl-1*H*-benzimidazol-2-ylmethyl)amine]copper(II) perchlorate dimethylformamide disolvate hemihydrate at 153 (2) K

H. Wu, W. Ying, J. Ding and J. Yuan

Comment

The asymmetric unit of the title compound, (Fig. 1), consists of a discrete [Cu(Mentb)(2-Methacrylate)] cation [Mentb is tris(*N*-methylbenzimidazol-2-ylmethyl)amine], a perchlorate anion, 2 DMF molecules and a half occupancy water molecule. The 2-Methacrylate is disordered over two sites with equal occupanancies. The copper ion is five-coordinate with a N_4O ligand set. The Mentb ligand acts as a tetradentate N-donor, and an O atom of carboxylate group of the 2-methacrylate ligand completes the coordination. The coordination geometry of the Cu^{II} ion may best be described as distorted trigonal bipyramidal (tau = 0.46), with approximate site symmetry C_3. The parameter tau (Youngme *et al.*, 20070 is defined as (beta - alpha)/60 [where beta = O1—Cu—N7, alpha = N5—Cu—N3] and its value varies from 0 (in regular square-based pyramidal) to 1 (in regular trigonal bipyramidal). This geometry is assumed by the Cu^{II} ion to relieve the steric crowding. The equatorial plane is occupied by three N atoms of three benzimidazolyl groups, while the Cu^{II} atom protrudes towards O1 and is 0.343 (3)Å from the plane of atoms N1/N3/N5. The axial positions are occupyied by N7 and O1, with Cu—N7 = 2.177 (3) A, Cu—O1 = 1.925 (3)Å and O1—Cu—N7 = 176.25 (11)°. The three benzimidazole ring arms of the Mentb ligand form a cone-shaped cavity. The angles N3—Cu—N1, N5—Cu—N1 and N5—Cu—N3 are 89.51 (12), 110.77 (12) and 148.74 (13)° respectively. The angles N7—Cu—N1 = 78.62 (12), N7—Cu—N3 = 82.00 (11) and N7—Cu—N5 = 79.21 (11)°, are all *ca* 10 ° less than the ideal value of 90°, are imposed by the geometry of the Mentb ligand. The distance between the Cu^{II} ion and atom O2 is 2.886 (3) Å, and hence O2 does not form a coordination bond. The bond angles and distances in the Mentb and 2-Methacrylate ligands are within the normal ranges (Allen *et al.*, 1987). In the crystal structure, the solvent water molecule forms weak O—H···O hydrogen bonds.

Experimental

To a stired solution of tris(*N*-methylbenzimidazol-2-ylmethyl)amine (0.0899 g, 0.2 mmol) in hot MeOH (10 ml) was added $Cu(ClO_4)_2(H_2O)_6$ (0.0741 g, 0.2 mmol), followed by a solution of Na(2-Methacrylate) (0.0216 g, 0.2 mmol) in MeOH (5 ml). A Blue-green crystalline product formed rapidly. The precipitate was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF to a blue-green solution that was allowed to evaporate at room temperature. Blue-green crystals suitable for X-ray diffraction studies were obtained after three weeks. Yield, 0.0904 g (53%). (found: C, 52.37; H, 5.32; N,14.74; Cu, 7.71. Calcd. for C37H47ClCuN9O8.50: C, 52.11; H, 5.55; N, 14.78; Cu, 7.45%)

Refinement

Very large displacement ellipsoids indicated that the 2-methacrylate ligand was disordered over two sites and the intemolecular contacts require the disorder components to be equal over two sites. All H atoms were found in difference electron maps and were subsequently refined in a riding-model approximation with C—H distances ranging from 0.95 to 0.99 Å, and

U_{iso}(H) = 1.2U_{eq}(C) of the carrier atom, The H atoms of the partial occupancy O atom [O7] were placed in positions which give suitable hydrogen bonding interactions and were refined as riding with U_{iso}(H) = 1.5U_{eq}(O).

Figures

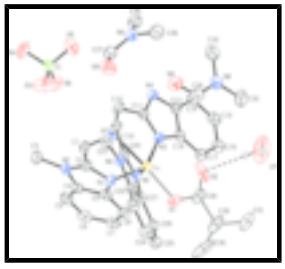


Fig. 1. The asymmetric unit of the title compound showing 30% probability ellipsoids. Only one component of the disordered atoms is shown and hydrogen bonds as shown as dashed lines. H atoms bonded to C atoms are not shown.

(2-Methacrylato)[tris(*N*-methylbenzimidazol-2-ylmethyl)amine]copper(II) perchlorate dimethylformamide disolvate hemihydrate

Crystal data

$[Cu(C_4H_5O_2)(C_{27}H_{27}N_7)](ClO_4)\cdot 2C_3H_7NO\cdot 0.5H_2O$	$Z = 2$
$M_r = 852.83$	$F_{000} = 892$
Triclinic, $P\overline{1}$	$D_x = 1.420$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.2004$ (5) Å	Cell parameters from 13990 reflections
$b = 12.6825$ (6) Å	$\theta = 3.1$–27.5º
$c = 13.6436$ (6) Å	$\mu = 0.68$ mm^{-1}
$\alpha = 88.703$ (1)º	$T = 153$ (2) K
$\beta = 74.892$ (1)º	Block, blue
$\gamma = 78.197$ (1)º	0.29 × 0.23 × 0.21 mm
$V = 1993.98$ (15) Å^3	

Data collection

Rigaku R-AXIS Spider diffractometer	7382 independent reflections
Radiation source: Rotating anode	5587 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.044$
$T = 153$(2) K	$\theta_{max} = 25.5$º
ω scans	$\theta_{min} = 3.1$º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -14\rightarrow14$
$T_{min} = 0.828$, $T_{max} = 0.871$	$k = -15\rightarrow15$
16373 measured reflections	$l = -16\rightarrow16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H-atom parameters constrained
$wR(F^2) = 0.170$	$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 0.7893P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
7382 reflections	$\Delta\rho_{max} = 0.70$ e Å^{-3}
578 parameters	$\Delta\rho_{min} = -0.76$ e Å^{-3}
46 restraints	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0075 (15)

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 $F^2 > 2$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}	Occ. (<1)
Cu	0.20984 (4)	0.67570 (3)	0.26999 (3)	0.03811 (17)	
Cl	0.46199 (10)	0.74020 (9)	0.62072 (8)	0.0567 (3)	
O1	0.0868 (13)	0.675 (2)	0.1931 (15)	0.044 (3)	0.50
O2	0.2054 (15)	0.7482 (17)	0.0845 (13)	0.084 (4)	0.50
O1'	0.1162 (12)	0.6748 (19)	0.1835 (13)	0.035 (2)	0.50
O2'	0.2176 (12)	0.7681 (14)	0.0628 (9)	0.054 (2)	0.50
O3	0.5018 (4)	0.6435 (3)	0.5636 (6)	0.150 (3)	
O4	0.5045 (5)	0.7340 (5)	0.7070 (4)	0.147 (3)	
O5	0.5028 (3)	0.8226 (3)	0.5606 (3)	0.0781 (10)	
O6	0.3378 (3)	0.7634 (3)	0.6486 (3)	0.0757 (10)	
O7	0.2715 (19)	0.8828 (10)	−0.1019 (12)	0.224 (10)	0.50
H1W	0.3265	0.8475	−0.1471	0.336*	0.50
H2W	0.2528	0.8460	−0.0505	0.336*	0.50
O8	0.4355 (3)	0.8897 (3)	0.1990 (3)	0.0680 (9)	
O9	0.7222 (3)	0.6694 (3)	0.2503 (4)	0.0880 (12)	
N1	0.1160 (3)	0.6297 (2)	0.4182 (2)	0.0444 (7)	
N2	0.1290 (3)	0.5942 (2)	0.5761 (2)	0.0451 (7)	
N3	0.1678 (3)	0.8287 (2)	0.3197 (2)	0.0395 (7)	
N4	0.1983 (3)	0.9579 (2)	0.4095 (2)	0.0396 (7)	
N5	0.3301 (3)	0.5530 (2)	0.1994 (2)	0.0356 (6)	

N6	0.5161 (3)	0.4712 (2)	0.1562 (2)	0.0404 (7)
N7	0.3382 (3)	0.6680 (2)	0.3563 (2)	0.0430 (7)
N8	0.3167 (3)	1.0308 (3)	0.1525 (3)	0.0570 (9)
N9	0.6795 (3)	0.8511 (3)	0.2718 (3)	0.0559 (9)
C1	0.3140 (4)	0.5884 (3)	0.4367 (3)	0.0461 (9)
H1A	0.3468	0.5143	0.4078	0.055*
H1B	0.3506	0.5994	0.4914	0.055*
C2	0.1869 (4)	0.6031 (3)	0.4783 (3)	0.0434 (9)
C3	0.1783 (5)	0.5612 (3)	0.6612 (3)	0.0607 (12)
H3A	0.1782	0.4848	0.6734	0.073*
H3B	0.1318	0.6044	0.7222	0.073*
H3C	0.2582	0.5724	0.6454	0.073*
C4	0.0109 (4)	0.6158 (3)	0.5806 (3)	0.0469 (9)
C5	−0.0857 (4)	0.6188 (3)	0.6600 (3)	0.0571 (11)
H5	−0.0802	0.6018	0.7269	0.069*
C6	−0.1919 (4)	0.6478 (4)	0.6371 (4)	0.0626 (12)
H6	−0.2613	0.6516	0.6898	0.075*
C7	−0.1990 (4)	0.6717 (3)	0.5378 (4)	0.0573 (11)
H7	−0.2734	0.6916	0.5252	0.069*
C8	−0.1028 (4)	0.6673 (3)	0.4589 (3)	0.0498 (9)
H8	−0.1088	0.6833	0.3919	0.060*
C9	0.0053 (3)	0.6382 (3)	0.4806 (3)	0.0422 (8)
C10	0.3291 (4)	0.7765 (3)	0.4005 (3)	0.0510 (10)
H10A	0.4025	0.8014	0.3726	0.061*
H10B	0.3159	0.7726	0.4751	0.061*
C11	0.2313 (3)	0.8543 (3)	0.3760 (3)	0.0401 (8)
C12	0.2511 (4)	1.0132 (3)	0.4723 (3)	0.0524 (10)
H12A	0.3112	0.9611	0.4934	0.063*
H12B	0.1915	1.0463	0.5325	0.063*
H12C	0.2860	1.0692	0.4330	0.063*
C13	0.1032 (3)	1.0033 (3)	0.3734 (3)	0.0396 (8)
C14	0.0337 (4)	1.1051 (3)	0.3859 (3)	0.0491 (9)
H14	0.0469	1.1603	0.4247	0.059*
C15	−0.0559 (4)	1.1230 (3)	0.3393 (4)	0.0552 (10)
H15	−0.1056	1.1922	0.3459	0.066*
C16	−0.0751 (4)	1.0409 (3)	0.2822 (4)	0.0531 (10)
H16	−0.1376	1.0559	0.2513	0.064*
C17	−0.0056 (3)	0.9397 (3)	0.2700 (3)	0.0445 (8)
H17	−0.0192	0.8846	0.2314	0.053*
C18	0.0855 (3)	0.9205 (3)	0.3164 (3)	0.0380 (7)
C19	0.4525 (3)	0.6286 (3)	0.2836 (3)	0.0449 (9)
H19A	0.5100	0.5939	0.3201	0.054*
H19B	0.4809	0.6891	0.2451	0.054*
C20	0.4347 (3)	0.5485 (3)	0.2132 (3)	0.0384 (8)
C21	0.6394 (3)	0.4414 (3)	0.1553 (3)	0.0474 (9)
H21A	0.6627	0.5025	0.1811	0.057*
H21B	0.6864	0.4223	0.0856	0.057*
H21C	0.6514	0.3796	0.1984	0.057*
C22	0.4609 (3)	0.4195 (3)	0.1005 (3)	0.0387 (8)

C23	0.5040 (4)	0.3346 (3)	0.0286 (3)	0.0466 (9)	
H23	0.5835	0.2998	0.0104	0.056*	
C24	0.4247 (4)	0.3044 (3)	−0.0144 (3)	0.0509 (10)	
H24	0.4503	0.2474	−0.0644	0.061*	
C25	0.3077 (4)	0.3548 (3)	0.0131 (3)	0.0496 (9)	
H25	0.2557	0.3304	−0.0178	0.060*	
C26	0.2651 (3)	0.4393 (3)	0.0841 (3)	0.0420 (8)	
H26	0.1854	0.4734	0.1024	0.050*	
C27	0.3448 (3)	0.4720 (3)	0.1274 (2)	0.0356 (7)	
C28	0.119 (2)	0.708 (3)	0.1037 (14)	0.056 (3)	0.50
C29	0.0410 (16)	0.6789 (14)	0.0425 (11)	0.076 (5)	0.50
C30	−0.0334 (19)	0.614 (2)	0.0828 (12)	0.119 (7)	0.50
H30A	−0.0864	0.5997	0.0472	0.142*	0.50
H30B	−0.0329	0.5832	0.1468	0.142*	0.50
C31	0.0497 (12)	0.7321 (13)	−0.0553 (9)	0.090 (4)	0.50
H31A	−0.0097	0.7163	−0.0859	0.108*	0.50
H31B	0.1268	0.7053	−0.1009	0.108*	0.50
H31C	0.0379	0.8101	−0.0443	0.108*	0.50
C28'	0.138 (2)	0.722 (3)	0.0995 (14)	0.050 (3)	0.50
C29'	0.0666 (15)	0.7212 (13)	0.0231 (11)	0.071 (4)	0.50
C30'	−0.0053 (19)	0.6513 (18)	0.0330 (12)	0.108 (7)	0.50
H30C	−0.0431	0.6447	−0.0186	0.130*	0.50
H30D	−0.0180	0.6088	0.0915	0.130*	0.50
C31'	0.0906 (13)	0.7897 (13)	−0.0651 (10)	0.090 (4)	0.50
H31D	0.0353	0.7878	−0.1054	0.108*	0.50
H31E	0.1697	0.7630	−0.1070	0.108*	0.50
H31F	0.0830	0.8640	−0.0416	0.108*	0.50
C32	0.3548 (6)	1.1102 (4)	0.2017 (4)	0.0846 (17)	
H32A	0.2912	1.1452	0.2584	0.101*	
H32B	0.3786	1.1644	0.1529	0.101*	
H32C	0.4207	1.0752	0.2274	0.101*	
C33	0.2233 (5)	1.0689 (5)	0.1047 (4)	0.0861 (17)	
H33A	0.1995	1.0072	0.0807	0.103*	
H33B	0.2502	1.1131	0.0470	0.103*	
H33C	0.1572	1.1124	0.1541	0.103*	
C34	0.3610 (4)	0.9272 (4)	0.1563 (3)	0.0585 (11)	
H34	0.3324	0.8780	0.1230	0.070*	
C35	0.6143 (5)	0.9441 (4)	0.3354 (4)	0.0667 (12)	
H35A	0.5501	0.9800	0.3080	0.080*	
H35B	0.6652	0.9943	0.3371	0.080*	
H35C	0.5833	0.9213	0.4044	0.080*	
C36	0.7279 (5)	0.8712 (4)	0.1659 (4)	0.0739 (14)	
H36A	0.7808	0.8057	0.1324	0.089*	
H36B	0.7706	0.9295	0.1612	0.089*	
H36C	0.6651	0.8920	0.1324	0.089*	
C37	0.6793 (4)	0.7516 (4)	0.3030 (4)	0.0670 (13)	
H37	0.6426	0.7434	0.3725	0.080*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0399 (3)	0.0342 (3)	0.0402 (3)	0.00393 (18)	−0.0184 (2)	−0.00935 (17)
Cl	0.0595 (6)	0.0589 (6)	0.0660 (6)	−0.0203 (5)	−0.0367 (6)	0.0220 (5)
O1	0.020 (8)	0.056 (3)	0.049 (4)	−0.003 (6)	0.001 (5)	−0.019 (3)
O2	0.081 (6)	0.061 (7)	0.076 (8)	0.004 (5)	0.020 (6)	0.037 (5)
O1'	0.008 (6)	0.053 (3)	0.043 (4)	0.001 (5)	−0.009 (4)	−0.012 (3)
O2'	0.052 (4)	0.062 (7)	0.032 (4)	0.000 (3)	0.004 (4)	0.024 (4)
O3	0.084 (3)	0.060 (2)	0.324 (8)	0.022 (2)	−0.106 (5)	−0.055 (4)
O4	0.133 (4)	0.269 (7)	0.113 (3)	−0.134 (5)	−0.098 (3)	0.117 (4)
O5	0.081 (3)	0.064 (2)	0.078 (2)	−0.0133 (19)	−0.0029 (19)	0.0221 (17)
O6	0.054 (2)	0.113 (3)	0.067 (2)	−0.0225 (19)	−0.0244 (17)	0.0101 (19)
O7	0.41 (3)	0.117 (10)	0.181 (13)	0.012 (13)	−0.185 (17)	0.011 (9)
O8	0.059 (2)	0.0605 (19)	0.079 (2)	0.0048 (15)	−0.0206 (18)	−0.0114 (16)
O9	0.075 (3)	0.056 (2)	0.132 (3)	−0.0031 (19)	−0.033 (3)	0.007 (2)
N1	0.060 (2)	0.0300 (14)	0.0455 (16)	0.0030 (14)	−0.0265 (16)	−0.0063 (12)
N2	0.063 (2)	0.0310 (15)	0.0420 (16)	−0.0020 (14)	−0.0215 (16)	−0.0013 (12)
N3	0.0447 (18)	0.0306 (14)	0.0432 (15)	0.0029 (13)	−0.0194 (15)	−0.0036 (12)
N4	0.0499 (18)	0.0293 (14)	0.0389 (15)	−0.0014 (13)	−0.0154 (14)	−0.0036 (12)
N5	0.0377 (16)	0.0324 (14)	0.0347 (14)	0.0005 (12)	−0.0112 (13)	−0.0054 (11)
N6	0.0379 (17)	0.0361 (15)	0.0461 (16)	0.0010 (13)	−0.0156 (14)	−0.0009 (13)
N7	0.056 (2)	0.0316 (15)	0.0422 (15)	0.0027 (13)	−0.0222 (15)	−0.0090 (12)
N8	0.057 (2)	0.061 (2)	0.0507 (19)	−0.0092 (18)	−0.0131 (18)	0.0036 (16)
N9	0.059 (2)	0.057 (2)	0.0562 (19)	−0.0142 (17)	−0.0213 (18)	0.0011 (16)
C1	0.059 (2)	0.0362 (18)	0.0427 (18)	0.0070 (17)	−0.0256 (19)	−0.0020 (15)
C2	0.058 (2)	0.0255 (16)	0.0468 (19)	0.0040 (15)	−0.0234 (19)	−0.0065 (14)
C3	0.087 (3)	0.050 (2)	0.051 (2)	−0.010 (2)	−0.033 (2)	0.0086 (19)
C4	0.066 (3)	0.0262 (17)	0.052 (2)	−0.0114 (17)	−0.020 (2)	−0.0015 (15)
C5	0.073 (3)	0.043 (2)	0.055 (2)	−0.018 (2)	−0.012 (2)	0.0018 (18)
C6	0.067 (3)	0.051 (2)	0.069 (3)	−0.023 (2)	−0.006 (2)	−0.001 (2)
C7	0.054 (3)	0.043 (2)	0.078 (3)	−0.017 (2)	−0.016 (2)	−0.004 (2)
C8	0.058 (3)	0.0332 (19)	0.062 (2)	−0.0065 (17)	−0.024 (2)	−0.0026 (17)
C9	0.047 (2)	0.0291 (17)	0.0484 (19)	−0.0048 (15)	−0.0105 (18)	−0.0060 (15)
C10	0.066 (3)	0.0355 (19)	0.058 (2)	0.0057 (18)	−0.039 (2)	−0.0097 (16)
C11	0.051 (2)	0.0316 (17)	0.0377 (17)	−0.0019 (16)	−0.0171 (17)	−0.0009 (14)
C12	0.074 (3)	0.0347 (19)	0.053 (2)	−0.0065 (19)	−0.028 (2)	−0.0059 (16)
C13	0.044 (2)	0.0294 (17)	0.0423 (17)	−0.0017 (15)	−0.0102 (16)	0.0009 (14)
C14	0.054 (2)	0.0290 (18)	0.058 (2)	−0.0017 (17)	−0.009 (2)	−0.0018 (16)
C15	0.045 (2)	0.0326 (19)	0.081 (3)	0.0042 (17)	−0.013 (2)	−0.0013 (19)
C16	0.042 (2)	0.040 (2)	0.075 (3)	0.0023 (17)	−0.019 (2)	0.0021 (19)
C17	0.041 (2)	0.0354 (18)	0.055 (2)	0.0004 (15)	−0.0145 (18)	0.0005 (16)
C18	0.041 (2)	0.0304 (17)	0.0384 (17)	0.0002 (15)	−0.0078 (16)	−0.0014 (14)
C19	0.041 (2)	0.0410 (19)	0.054 (2)	0.0015 (16)	−0.0230 (19)	−0.0036 (16)
C20	0.039 (2)	0.0345 (18)	0.0414 (18)	−0.0005 (15)	−0.0160 (16)	0.0002 (14)
C21	0.036 (2)	0.050 (2)	0.053 (2)	−0.0022 (17)	−0.0106 (18)	0.0054 (18)
C22	0.042 (2)	0.0339 (17)	0.0359 (16)	−0.0021 (15)	−0.0064 (16)	0.0016 (14)

C23	0.051 (2)	0.0360 (19)	0.0447 (19)	−0.0005 (17)	−0.0048 (18)	0.0005 (16)
C24	0.065 (3)	0.040 (2)	0.0404 (19)	−0.0011 (19)	−0.008 (2)	−0.0085 (16)
C25	0.065 (3)	0.046 (2)	0.0410 (19)	−0.014 (2)	−0.016 (2)	−0.0027 (16)
C26	0.046 (2)	0.0396 (19)	0.0406 (18)	−0.0059 (16)	−0.0143 (17)	0.0005 (15)
C27	0.0388 (19)	0.0333 (17)	0.0301 (15)	−0.0029 (14)	−0.0045 (15)	−0.0009 (13)
C28	0.047 (7)	0.067 (9)	0.046 (4)	0.017 (5)	−0.020 (4)	−0.016 (4)
C29	0.060 (9)	0.097 (13)	0.063 (6)	0.028 (7)	−0.033 (7)	−0.030 (6)
C30	0.057 (10)	0.189 (18)	0.114 (14)	0.011 (8)	−0.051 (12)	−0.072 (13)
C31	0.070 (8)	0.144 (13)	0.057 (5)	−0.004 (6)	−0.033 (6)	0.001 (7)
C28'	0.040 (7)	0.065 (9)	0.044 (4)	0.015 (5)	−0.027 (4)	−0.015 (4)
C29'	0.058 (8)	0.091 (13)	0.061 (6)	0.028 (6)	−0.039 (6)	−0.030 (6)
C30'	0.061 (11)	0.180 (17)	0.090 (13)	0.006 (8)	−0.048 (11)	−0.056 (12)
C31'	0.078 (9)	0.123 (12)	0.066 (5)	0.004 (6)	−0.035 (6)	0.014 (7)
C32	0.121 (5)	0.059 (3)	0.080 (3)	−0.021 (3)	−0.037 (4)	0.012 (3)
C33	0.076 (4)	0.106 (5)	0.080 (3)	−0.014 (3)	−0.034 (3)	0.034 (3)
C34	0.056 (3)	0.062 (3)	0.055 (2)	−0.008 (2)	−0.011 (2)	−0.010 (2)
C35	0.075 (3)	0.068 (3)	0.062 (3)	−0.016 (3)	−0.024 (3)	−0.008 (2)
C36	0.089 (4)	0.076 (3)	0.057 (3)	−0.022 (3)	−0.016 (3)	−0.002 (2)
C37	0.061 (3)	0.062 (3)	0.086 (3)	−0.014 (2)	−0.032 (3)	0.013 (3)

Geometric parameters (Å, °)

Cu—O1'	1.845 (17)	C10—H10B	0.9900
Cu—N5	1.975 (3)	C12—H12A	0.9800
Cu—N3	1.989 (3)	C12—H12B	0.9800
Cu—O1	2.045 (18)	C12—H12C	0.9800
Cu—N7	2.178 (3)	C13—C14	1.379 (5)
Cu—N1	2.180 (3)	C13—C18	1.404 (5)
Cl—O3	1.396 (5)	C14—C15	1.380 (6)
Cl—O4	1.399 (4)	C14—H14	0.9500
Cl—O5	1.404 (3)	C15—C16	1.406 (6)
Cl—O6	1.431 (4)	C15—H15	0.9500
O1—C28	1.2701 (10)	C16—C17	1.373 (5)
O2—C28	1.2302 (10)	C16—H16	0.9500
O1'—C28'	1.2701 (10)	C17—C18	1.395 (5)
O2'—C28'	1.2301 (10)	C17—H17	0.9500
O7—H1W	0.8400	C19—C20	1.498 (5)
O7—H2W	0.8400	C19—H19A	0.9900
O8—C34	1.216 (5)	C19—H19B	0.9900
O9—C37	1.222 (6)	C21—H21A	0.9800
N1—C2	1.331 (4)	C21—H21B	0.9800
N1—C9	1.380 (5)	C21—H21C	0.9800
N2—C2	1.351 (5)	C22—C27	1.393 (5)
N2—C4	1.396 (5)	C22—C23	1.394 (5)
N2—C3	1.458 (5)	C23—C24	1.373 (6)
N3—C11	1.312 (4)	C23—H23	0.9500
N3—C18	1.382 (4)	C24—C25	1.395 (6)
N4—C11	1.346 (4)	C24—H24	0.9500
N4—C13	1.391 (5)	C25—C26	1.383 (5)

N4—C12	1.463 (4)	C25—H25	0.9500
N5—C20	1.328 (4)	C26—C27	1.394 (5)
N5—C27	1.389 (4)	C26—H26	0.9500
N6—C20	1.336 (5)	C28—C29	1.5201 (10)
N6—C22	1.390 (4)	C29—C30	1.3501 (10)
N6—C21	1.471 (5)	C29—C31	1.4700 (10)
N7—C19	1.481 (5)	C30—H30A	0.9500
N7—C10	1.487 (4)	C30—H30B	0.9500
N7—C1	1.487 (5)	C31—H31A	0.9800
N8—C34	1.320 (6)	C31—H31B	0.9800
N8—C32	1.438 (6)	C31—H31C	0.9800
N8—C33	1.450 (6)	C28'—C29'	1.5202 (10)
N9—C37	1.323 (6)	C29'—C30'	1.3501 (10)
N9—C35	1.442 (6)	C29'—C31'	1.4700 (10)
N9—C36	1.450 (6)	C30'—H30C	0.9500
C1—C2	1.480 (6)	C30'—H30D	0.9500
C1—H1A	0.9900	C31'—H31D	0.9800
C1—H1B	0.9900	C31'—H31E	0.9800
C3—H3A	0.9800	C31'—H31F	0.9800
C3—H3B	0.9800	C32—H32A	0.9800
C3—H3C	0.9800	C32—H32B	0.9800
C4—C5	1.371 (6)	C32—H32C	0.9800
C4—C9	1.403 (5)	C33—H33A	0.9800
C5—C6	1.386 (7)	C33—H33B	0.9800
C5—H5	0.9500	C33—H33C	0.9800
C6—C7	1.402 (6)	C34—H34	0.9500
C6—H6	0.9500	C35—H35A	0.9800
C7—C8	1.363 (6)	C35—H35B	0.9800
C7—H7	0.9500	C35—H35C	0.9800
C8—C9	1.402 (5)	C36—H36A	0.9800
C8—H8	0.9500	C36—H36B	0.9800
C10—C11	1.490 (5)	C36—H36C	0.9800
C10—H10A	0.9900	C37—H37	0.9500
O1'—Cu—N5	94.5 (7)	N4—C13—C18	105.3 (3)
O1'—Cu—N3	102.3 (8)	C13—C14—C15	116.8 (3)
N5—Cu—N3	148.71 (13)	C13—C14—H14	121.6
O1'—Cu—O1	8.5 (9)	C15—C14—H14	121.6
N5—Cu—O1	99.7 (7)	C14—C15—C16	121.3 (4)
N3—Cu—O1	100.4 (7)	C14—C15—H15	119.4
O1'—Cu—N7	172.9 (6)	C16—C15—H15	119.4
N5—Cu—N7	79.21 (11)	C17—C16—C15	121.7 (4)
N3—Cu—N7	81.95 (11)	C17—C16—H16	119.1
O1—Cu—N7	176.5 (6)	C15—C16—H16	119.1
O1'—Cu—N1	106.9 (4)	C16—C17—C18	117.6 (3)
N5—Cu—N1	110.80 (11)	C16—C17—H17	121.2
N3—Cu—N1	89.47 (12)	C18—C17—H17	121.2
O1—Cu—N1	98.7 (4)	N3—C18—C17	131.4 (3)
N7—Cu—N1	78.63 (12)	N3—C18—C13	108.7 (3)
O3—Cl—O4	110.8 (4)	C17—C18—C13	119.9 (3)

O3—Cl—O5	108.5 (3)	N7—C19—C20	106.5 (3)
O4—Cl—O5	108.3 (3)	N7—C19—H19A	110.4
O3—Cl—O6	108.8 (2)	C20—C19—H19A	110.4
O4—Cl—O6	110.8 (3)	N7—C19—H19B	110.4
O5—Cl—O6	109.6 (2)	C20—C19—H19B	110.4
C28—O1—Cu	110.6 (11)	H19A—C19—H19B	108.6
C28'—O1'—Cu	119.5 (12)	N5—C20—N6	113.1 (3)
H1W—O7—H2W	111.8	N5—C20—C19	120.1 (3)
C2—N1—C9	105.6 (3)	N6—C20—C19	126.8 (3)
C2—N1—Cu	110.7 (3)	N6—C21—H21A	109.5
C9—N1—Cu	141.9 (2)	N6—C21—H21B	109.5
C2—N2—C4	107.3 (3)	H21A—C21—H21B	109.5
C2—N2—C3	127.4 (4)	N6—C21—H21C	109.5
C4—N2—C3	125.2 (4)	H21A—C21—H21C	109.5
C11—N3—C18	106.2 (3)	H21B—C21—H21C	109.5
C11—N3—Cu	114.9 (2)	N6—C22—C27	106.0 (3)
C18—N3—Cu	138.8 (2)	N6—C22—C23	131.2 (4)
C11—N4—C13	107.0 (3)	C27—C22—C23	122.7 (3)
C11—N4—C12	127.1 (3)	C24—C23—C22	116.1 (4)
C13—N4—C12	125.9 (3)	C24—C23—H23	122.0
C20—N5—C27	105.4 (3)	C22—C23—H23	122.0
C20—N5—Cu	114.9 (2)	C23—C24—C25	121.9 (3)
C27—N5—Cu	139.3 (2)	C23—C24—H24	119.1
C20—N6—C22	106.8 (3)	C25—C24—H24	119.1
C20—N6—C21	127.4 (3)	C26—C25—C24	122.0 (4)
C22—N6—C21	125.7 (3)	C26—C25—H25	119.0
C19—N7—C10	112.1 (3)	C24—C25—H25	119.0
C19—N7—C1	110.4 (3)	C25—C26—C27	116.8 (4)
C10—N7—C1	111.6 (3)	C25—C26—H26	121.6
C19—N7—Cu	105.98 (19)	C27—C26—H26	121.6
C10—N7—Cu	109.7 (2)	N5—C27—C22	108.7 (3)
C1—N7—Cu	106.9 (2)	N5—C27—C26	130.8 (3)
C34—N8—C32	120.6 (4)	C22—C27—C26	120.5 (3)
C34—N8—C33	122.0 (4)	O2—C28—O1	116.8 (14)
C32—N8—C33	117.3 (4)	O2—C28—C29	135.0 (16)
C37—N9—C35	122.1 (4)	O1—C28—C29	108.0 (15)
C37—N9—C36	120.7 (4)	C30—C29—C31	125.9 (13)
C35—N9—C36	116.2 (4)	C30—C29—C28	119.3 (12)
C2—C1—N7	108.7 (3)	C31—C29—C28	114.7 (11)
C2—C1—H1A	110.0	C29—C30—H30A	120.0
N7—C1—H1A	110.0	C29—C30—H30B	120.0
C2—C1—H1B	110.0	H30A—C30—H30B	120.0
N7—C1—H1B	110.0	O2'—C28'—O1'	128.8 (13)
H1A—C1—H1B	108.3	O2'—C28'—C29'	108.7 (12)
N1—C2—N2	112.5 (4)	O1'—C28'—C29'	122.3 (13)
N1—C2—C1	120.6 (3)	C30'—C29'—C31'	123.2 (12)
N2—C2—C1	126.9 (3)	C30'—C29'—C28'	119.6 (13)
N2—C3—H3A	109.5	C31'—C29'—C28'	116.9 (11)
N2—C3—H3B	109.5	C29'—C30'—H30C	120.0

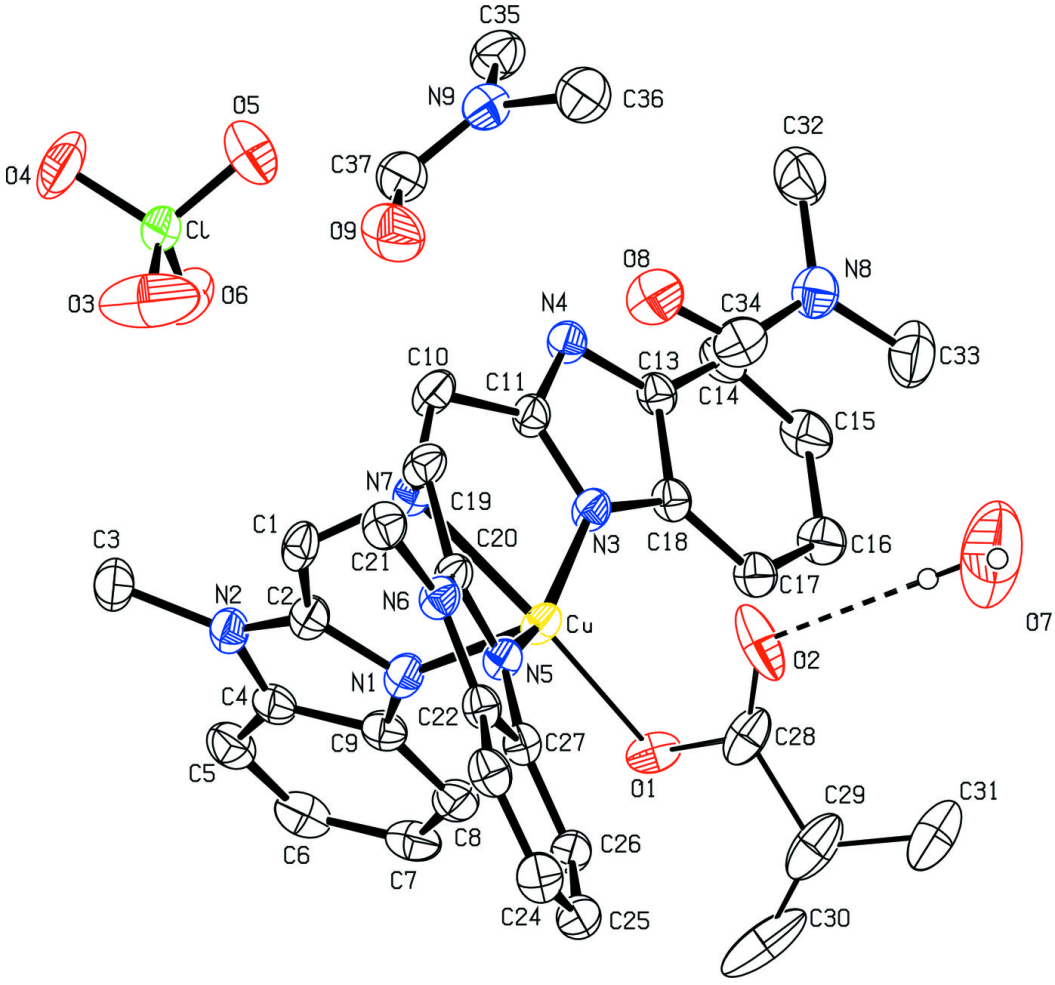
H3A—C3—H3B	109.5	C29'—C30'—H30D	120.0
N2—C3—H3C	109.5	H30C—C30'—H30D	120.0
H3A—C3—H3C	109.5	C29'—C31'—H31D	109.5
H3B—C3—H3C	109.5	C29'—C31'—H31E	109.5
C5—C4—N2	132.0 (4)	H31D—C31'—H31E	109.5
C5—C4—C9	123.0 (4)	C29'—C31'—H31F	109.5
N2—C4—C9	105.0 (4)	H31D—C31'—H31F	109.5
C4—C5—C6	116.3 (4)	H31E—C31'—H31F	109.5
C4—C5—H5	121.8	N8—C32—H32A	109.5
C6—C5—H5	121.8	N8—C32—H32B	109.5
C5—C6—C7	121.3 (5)	H32A—C32—H32B	109.5
C5—C6—H6	119.3	N8—C32—H32C	109.5
C7—C6—H6	119.3	H32A—C32—H32C	109.5
C8—C7—C6	122.2 (4)	H32B—C32—H32C	109.5
C8—C7—H7	118.9	N8—C33—H33A	109.5
C6—C7—H7	118.9	N8—C33—H33B	109.5
C7—C8—C9	117.2 (4)	H33A—C33—H33B	109.5
C7—C8—H8	121.4	N8—C33—H33C	109.5
C9—C8—H8	121.4	H33A—C33—H33C	109.5
N1—C9—C8	130.5 (4)	H33B—C33—H33C	109.5
N1—C9—C4	109.7 (3)	O8—C34—N8	125.3 (4)
C8—C9—C4	119.8 (4)	O8—C34—H34	117.4
N7—C10—C11	110.0 (3)	N8—C34—H34	117.4
N7—C10—H10A	109.7	N9—C35—H35A	109.5
C11—C10—H10A	109.7	N9—C35—H35B	109.5
N7—C10—H10B	109.7	H35A—C35—H35B	109.5
C11—C10—H10B	109.7	N9—C35—H35C	109.5
H10A—C10—H10B	108.2	H35A—C35—H35C	109.5
N3—C11—N4	112.8 (3)	H35B—C35—H35C	109.5
N3—C11—C10	123.4 (3)	N9—C36—H36A	109.5
N4—C11—C10	123.8 (3)	N9—C36—H36B	109.5
N4—C12—H12A	109.5	H36A—C36—H36B	109.5
N4—C12—H12B	109.5	N9—C36—H36C	109.5
H12A—C12—H12B	109.5	H36A—C36—H36C	109.5
N4—C12—H12C	109.5	H36B—C36—H36C	109.5
H12A—C12—H12C	109.5	O9—C37—N9	125.7 (5)
H12B—C12—H12C	109.5	O9—C37—H37	117.2
C14—C13—N4	132.0 (3)	N9—C37—H37	117.2
C14—C13—C18	122.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H1W···O4^{i}	0.84	2.71	3.55 (2)	180
O7—H2W···O2	0.84	2.21	3.05 (2)	179

Symmetry codes: (i) *x*, *y*, *z*−1.

Fig. 1


C35
N9
C36
O5
O4
Cl
C37
O9
C32
O8
N8
O3
O6
N4
C34
C33
C10
C11
C13
C14
C15
N7
C19
C1
C20
N3
C18
C16
C3
C21
C17
O7
N2
C2
N6
Cu
O2
N1
N5
C4
C22
C28
C9
C27
O1
C5
C29
C31
C8
C26
C6
C7
C24
C25
C30