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μ-Bromido-dibromido-μ-hydroxido-bis[(4*S*)-2-halo-6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine]dicopper(II) (halo: Cl/Br = 3:1)

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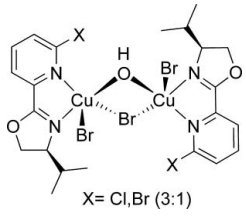
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.029; wR factor = 0.070; data-to-parameter ratio = 18.0.

The crystal structure of the title complex, $[Cu_2Br_3(OH)(C_{11}H_{13}Br_{0.5}Cl_{1.5}N_2O)_2]$, consists of two (2-halo-6-oxazolinyl)-pyridine·CuBr units bridged by a Br atom and a hydroxide group. The Cu^{II} atoms are five-coordinate with an (*N*,*N*)-BrCu(Br)(OH) distorted tetragonal–pyramidal core, and relatively short contacts to the bridging atoms (Cu—μ-OH and Cu—μ-Br). There are two symmetry-independent half-molecules in the asymmetric unit, which differ only in the arrangement of the isopropyl group. The molecules are located on a twofold rotation axes.

Related literature

For related literature, see: Chelucci & Thummel (2002); Fache *et al.* (2000); Karlin & Gultneh (1987); Kaim & Schwederski (1991); Lehn (1995); Mezei & Raptis (2004); Thompson *et al.* (1987); Walther *et al.* (1997).



X= Cl,Br (3:1)

Experimental

Crystal data

$[Cu_2Br_3(OH)(C_{11}H_{13}Br_{0.5}Cl_{1.5}N_2O)_2]$
M_r = 855.42
Monoclinic, *C*2
a = 23.2485 (5) Å
b = 7.98620 (10) Å
c = 17.9187 (4) Å
β = 119.9850 (9)°
V = 2881.63 (10) Å^3
Z = 4
Mo *K*α radiation
μ = 6.50 mm^{-1}
T = 100 (2) K
0.20 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
T_{min} = 0.313, T_{max} = 0.521
16751 measured reflections
6381 independent reflections
6086 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 1.06
6381 reflections
354 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Absolute structure: Flack (1983), 2880 Friedel pairs
Flack parameter: −0.002 (7)

Table 1
Selected geometric parameters (Å, °).

Br11—Cu11	2.4069 (5)	Br21—Cu21	2.4280 (5)
Br12—Cu11	2.5538 (5)	Br22—Cu21	2.5321 (6)
Cu11—O102	1.8706 (19)	Cu21—O202	1.8705 (19)
Cu11—N101	1.966 (3)	Cu21—N201	1.974 (3)
Cu11—N102	2.362 (3)	Cu21—N202	2.362 (3)
Cu11—Cu11^{i}	3.2480 (8)	Cu21—Cu21^{ii}	3.2415 (8)
Cu11—Br12—Cu11^{i}	78.98 (2)	Cu21—Br22—Cu21^{ii}	79.59 (2)
Cu11^{i}—O102—Cu11	120.5 (2)	Cu21^{ii}—O202—Cu21	120.1 (2)

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

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SK3162).

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supporting information

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μ-Bromido-dibromido-μ-hydroxido-bis[(4*S*)-2-halo-6-(4-isopropyl-4,5-dihydro-oxazol-2-yl)pyridine]dicopper(II) (halo: Cl/Br = 3:1)

Andy Ch. Laungani, Manfred Keller and Bernhard Breit

S1. Comment

Metal coordination and ligand geometry is essential in terms of activating and directing a metal-catalyzed process. Therefore, it is of interest to obtain a deeper insight into the structure of different coordination motifs and thus, this could help to enhance our understanding about the coordination behaviour and the scope and limitations of ligands applied in catalysis. Chiral oxazolines and pyridines are regarded as privileged ligands, which have found numerous applications in many asymmetric transformations (Fache *et al.*, 2000; Chelucci & Thummel, 2002). Moreover, *N*-donor ligands are also found as component parts of enzymatic processes such as the fixation, activation and transport of oxygen (Kaim & Schwederski, 1991; Karlin & Gultneh, 1987), or they are used for studies concerning self-organizing phenomena (Lehn, 1995).

During our work in the field of supramolecular ligands and catalysts, the novel title compound (I) was isolated from a mixture of Cl- and Br-substituted oxazolinyl-pyridine ligands. This mixture was obtained from the oxazoline ring closure reaction of 2-bromo-6-(4-isopropyl-4,5-dihydro-oxazol-2-yl)pyridine under acidic conditions (HCl), and subsequent partial aromatic substitution of the bromine. After complexation with $CuBr.SMe_2$, X-ray structure analysis reveales a 3:1 Cl/Br disorder ratio at the 2-halopyridine position, and the complex contains an unprecedented coordination motif of two [(2-halo-6-oxazolinyl)pyridine]$Cu^{II}Br$ units bridged by a Br atom and a hydroxide group. To the best of our knowledge there are various triple bridged dinuclear Cu^{II} complexes bearing different μ_3-bridging ligands (μ-OH, μ-Br and μ-pyridazine) (Thompson *et al.*, 1987), but only two double bridged dinuclear Cu^{II} complexes with Cl and OH as μ_2-bridging anions have been reported (Walther *et al.*, 1997; Mezei & Raptis, 2004).

In analogy to a previous report, complex (I) was obtained by aerial oxidation of a $CDCl_3$ solution of a red oxazolinyl pyridine/CuBr complex (Walther *et al.*, 1997). The X-ray structure analysis confirms a distorted tetragonal-pyramidal coordination geometry at the Cu^{II} centers of the dimeric complex. Both chiral oxazolinyl pyridine ligands act as a bidentate *N,N*-ligand, forming a five-membered chelate ring. Although all nitrogen atoms are sp^2-hybridized, the bond lengths of the Cu — N(pyr) bonds [Cu11 — N102 = 2.362 (3) Å, Cu21 — N202 = 2.362 (3) Å] are significantly longer than the Cu — N(oxa) distance [Cu11 — N101 = 1.966 (3) Å, Cu21 — N201 = 1.97 (3) Å]. This presumably originates from dipole-dipole repulsion between the pyridinyl halides and the bridging ligands OH and Br.

Br(11) and Br(21) are bonded with somewhat shorter distances [Cu11 — Br11= 2.4069 (5) Å, Cu21 — Br21= 2.4280 (5) Å], and the bridging bromine Br12 and Br22 respectively are bonded by more distant contacts [Cu11 — Br12 = 2.5538 (5) Å, Cu21 — Br22 = 2.5321 (6) Å]. Although the atomic radii increase from Cl to Br, these Cu — Br bridging bonds and the Cu ··· Cu distances [Cu11 ··· Cu11*a* = 3.2480 (8) Å, Cu21 ··· Cu21*a* = 3.2415 (8) Å] in complex (I) are in the range of those observed in previous reported Cu ··· Cu contacts [3.1963 (7); Mezei & Raptis, 2004; 3.271 Å; Walther *et al.*, 1997] and Cu — μCl bonds [2.409 (1) and 2.450 (1); Mezei & Raptis, 2004; 2.648 (2) Å and 2.507 (2) Å; Walther

et al., 1997]. Moreover, the distance between the Cu atoms and the bridging hydroxo groups are slightly shorter [1.8716 (19) Å and 1.8705 (19) Å] when compared with both μ-Cl, μ-OH bridged Cu^{II} complexes [1.903 (3) and 1.905 (3); Mezei & Raptis, 2004; 1.914 (5) Å and 1.917 (5) Å; Walther *et al.*, 1997]. The hydroxide bridge angles [120.5 (2)° and 120.1 (2)°] are substantially larger [114.2 (2)°; Mezei & Raptis, 2004; 117.3 (2)°; Walther *et al.*, 1997], whereas the Cu — Br — Cu angle [78.98 (2)° and 79.59 (2)°] are in good agreement with one reported [78.7 (3)°; Walther *et al.*, 1997] and smaller than the other [82.27 (4)°; Mezei & Raptis, 2004]. The compound (I) obtained provides a new motif in Cu^{II} pyridine and oxazoline chemistry, and represents the first example of a Br and OH μ_2-bridged dinuclear (ligand)(halide)Cu^{II} complex.

Noteworthy is the absence of hydrogen bonds for the bridging OH-group. This OH-group is located in a "pocket" constituted by two Br and two Cl atoms of the same molecule. As a consequence no hydrogen-acceptor atom is accessible for hydrogen-bond formation. Although this hydrogen is on a restrained position, it is the only possible location.

S2. Experimental

A 3:1 mixture of (4*S*)-2-chloro-6-(4-isopropyl-4,5-dihydro-oxazol-2-yl)pyridine and (4*S*)-2-bromo-6-(4-isopropyl-4,5-dihydro-oxazol-2-yl)pyridine (15.1 mg, 56.1 μmol, 2.0 eq.) and $CuBr.SMe_2$ (5.70 mg, 27.7 μmol) were dissolved in $CDCl_3$ (0.7 ml) under argon atmosphere. The resulting deep red Cu^{I} complex could not be isolated and reacted with air to form a brown solution and a black precipitate after five days. The reaction mixture was allowed to evaporate in air at room temperature. Black crystals of (I) were separated from the filtrate after two weeks.

S3. Refinement

The two positions of the disordered Cl- *versus* Br-atoms were determined from the difference map and refined anisotropically with occupancies of 0.75 (Cl) and 0.25 (Br). All H atom bound to C atoms were placed in calculated positions (C — H = 0.95 or 0.98 or 0.99 or 1.00 Å) and refined as riding on their parent atoms with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C). The H atoms bound to the bridging OH groups were found in Fourier difference map, restrained with O—H = 0.85 (2) Å and refined with U_{iso} = 1.2U_{eq}(O)

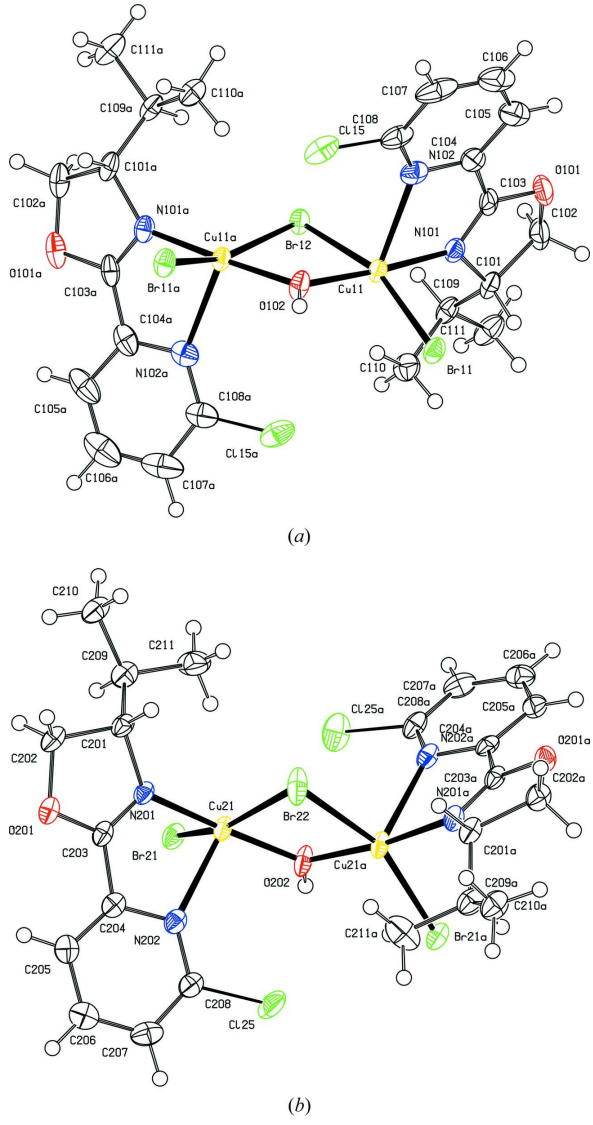

Figure 1

The independent components of (I), showing the atom-labelling scheme. The structure contains a 3:1 Cl/Br disorder at the 2-halopyridine position. The figure displays the Cl-part of this disorder (Cl15). Displacement ellipsoids are drawn at the 50% probability level.

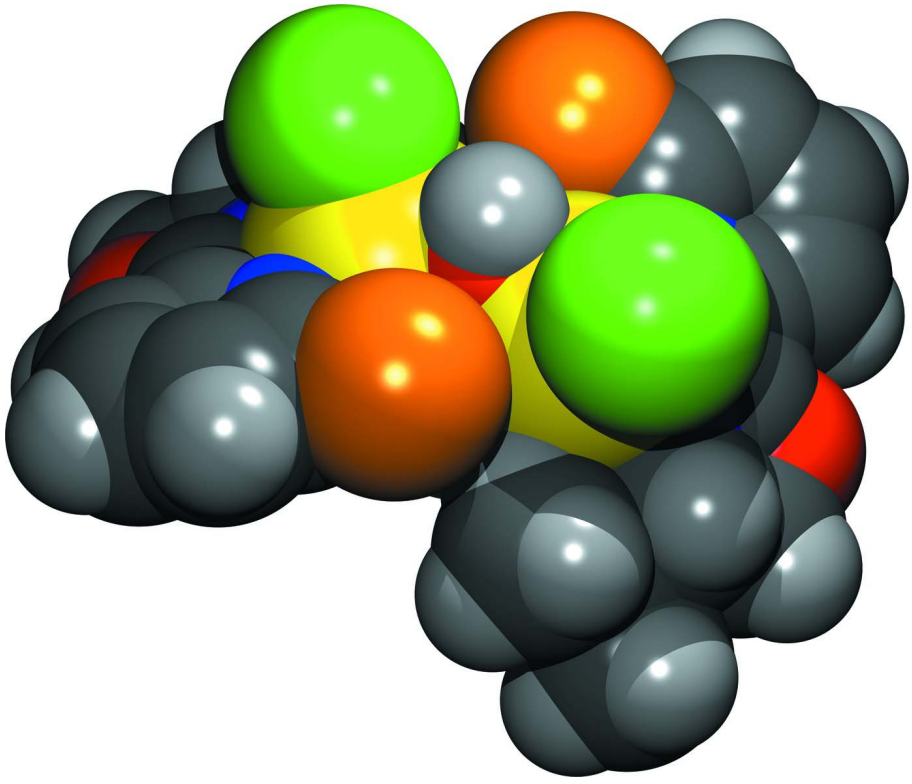

Figure 2

CPK-plot of the bridging OH-group located in a pocket constituted by two Br (green) and two Cl (orange) atoms, illustrating no possibility for hydrogen bonding.

μ-Bromido-dibromido-bis[(4*S*)-2-(bromo/chloro)- 6-(4-isopropyl-4,5-dihydrooxazol-2-yl)pyridine]-μ-hydroxido-dicopper(II)

Crystal data

$[Cu_2Br_3(OH)(C_{11}H_{13}Br_{0.5}Cl_{1.5}N_2O)_2]$
M_r = 855.42
Monoclinic, *C*2
Hall symbol: C 2y
a = 23.2485 (5) Å
b = 7.9862 (1) Å
c = 17.9187 (4) Å
β = 119.9850 (9)°
V = 2881.63 (10) Å^3
Z = 4
F(000) = 1668
D_x = 1.972 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9966 reflections
θ = 1.0–27.5°
μ = 6.50 mm^{-1}
T = 100 K
Irregular, green
0.20 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: long-fine-focus sealed tube
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD scans
Absorption correction: multi-scan (*SORTAV*; Blessing 1995)
T_{min} = 0.313, T_{max} = 0.521
16751 measured reflections
6381 independent reflections
6086 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 27.5°, θ_{min} = 2.4°
h = −29→26
k = −10→10
l = −19→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.070$
$S = 1.06$
6381 reflections
354 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 2.2361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}
Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00132 (10)
Absolute structure: Flack (1983), 2880 Friedel pairs
Absolute structure parameter: −0.002 (7)

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}	Occ. (<1)
C101	1.19690 (17)	0.7710 (4)	1.0541 (3)	0.0261 (8)	
H101	1.2314	0.8603	1.0820	0.031*	
C102	1.2139 (2)	0.6644 (6)	0.9968 (3)	0.0353 (9)	
H10A	1.2622	0.6676	1.0178	0.042*	
H10B	1.2003	0.5465	0.9957	0.042*	
C103	1.12960 (19)	0.8306 (4)	0.9153 (3)	0.0268 (8)	
C104	1.0775 (2)	0.9089 (5)	0.8353 (3)	0.0308 (9)	
C105	1.0784 (3)	0.9087 (6)	0.7593 (3)	0.0432 (12)	
H105	1.1125	0.8517	0.7549	0.052*	
C106	1.0294 (3)	0.9923 (7)	0.6900 (3)	0.0498 (13)	
H106	1.0298	0.9969	0.6373	0.060*	
C107	0.9790 (3)	1.0704 (6)	0.6970 (3)	0.0490 (14)	
H107	0.9444	1.1295	0.6500	0.059*	
C108	0.9812 (2)	1.0585 (5)	0.7764 (3)	0.0342 (9)	
C109	1.19183 (17)	0.6747 (4)	1.1239 (3)	0.0259 (8)	
H109	1.1518	0.6008	1.0957	0.031*	
C110	1.1840 (2)	0.7949 (5)	1.1846 (3)	0.0324 (8)	
H11A	1.2213	0.8739	1.2093	0.049*	
H11B	1.1836	0.7311	1.2311	0.049*	
H11C	1.1422	0.8566	1.1525	0.049*	
C111	1.25314 (19)	0.5648 (5)	1.1744 (3)	0.0378 (10)	
H11D	1.2568	0.4860	1.1351	0.057*	

H11E	1.2490	0.5023	1.2187	0.057*	
H11F	1.2929	0.6355	1.2020	0.057*	
Br11	1.140591 (18)	1.23282 (4)	1.04093 (2)	0.02632 (9)	
Br12	1.0000	0.74718 (6)	1.0000	0.02323 (11)	
Br15	0.9118 (6)	1.1501 (12)	0.7897 (7)	0.0444 (19)	0.25
Cl15	0.9179 (4)	1.1483 (8)	0.7855 (5)	0.0382 (12)	0.75
Cu11	1.06770 (2)	0.99397 (5)	0.99464 (3)	0.02011 (10)	
N101	1.13358 (15)	0.8501 (4)	0.9880 (2)	0.0242 (6)	
N102	1.02942 (16)	0.9853 (4)	0.8453 (2)	0.0279 (7)	
O101	1.17680 (15)	0.7393 (4)	0.9118 (2)	0.0357 (7)	
O102	1.0000	1.1102 (5)	1.0000	0.0269 (8)	
H102	1.0000	1.215 (3)	1.0000	0.05 (2)*	
C201	0.83962 (18)	0.8232 (4)	0.5075 (2)	0.0233 (7)	
H201	0.8631	0.9209	0.4998	0.028*	
C202	0.81820 (18)	0.8714 (5)	0.5736 (3)	0.0283 (8)	
H20A	0.8190	0.9944	0.5807	0.034*	
H20B	0.7728	0.8303	0.5547	0.034*	
C203	0.90193 (17)	0.6897 (4)	0.6330 (2)	0.0211 (7)	
C204	0.95679 (17)	0.5943 (4)	0.7024 (2)	0.0216 (7)	
C205	0.96634 (19)	0.5830 (5)	0.7843 (3)	0.0268 (8)	
H205	0.9363	0.6337	0.7990	0.032*	
C206	1.0221 (2)	0.4941 (5)	0.8456 (3)	0.0308 (8)	
H206	1.0296	0.4793	0.9024	0.037*	
C207	1.0657 (2)	0.4288 (5)	0.8229 (3)	0.0314 (9)	
H207	1.1043	0.3701	0.8637	0.038*	
C208	1.05201 (18)	0.4507 (4)	0.7385 (3)	0.0258 (8)	
C209	0.78238 (19)	0.7738 (5)	0.4198 (3)	0.0289 (8)	
H209	0.7591	0.6755	0.4272	0.035*	
C210	0.7332 (2)	0.9214 (5)	0.3837 (3)	0.0340 (9)	
H21A	0.7564	1.0215	0.3808	0.051*	
H21B	0.7149	0.9432	0.4215	0.051*	
H21C	0.6971	0.8935	0.3258	0.051*	
C211	0.8058 (2)	0.7261 (6)	0.3569 (3)	0.0438 (11)	
H21D	0.8316	0.8186	0.3524	0.066*	
H21E	0.7672	0.7034	0.3002	0.066*	
H21F	0.8337	0.6257	0.3779	0.066*	
Br21	0.868653 (17)	0.29997 (4)	0.49113 (3)	0.02563 (9)	
Br22	1.0000	0.78245 (7)	0.5000	0.03828 (16)	
Br25	1.1113 (5)	0.3707 (13)	0.7061 (8)	0.0325 (13)	0.25
Cl25	1.1087 (5)	0.3860 (12)	0.7098 (7)	0.0410 (15)	0.75
Cu21	0.94230 (2)	0.53885 (5)	0.52565 (3)	0.02187 (10)	
N201	0.88948 (14)	0.6897 (4)	0.5554 (2)	0.0211 (6)	
N202	0.99806 (15)	0.5291 (4)	0.6777 (2)	0.0234 (6)	
O201	0.86664 (13)	0.7907 (3)	0.65432 (17)	0.0262 (5)	
O202	1.0000	0.4219 (5)	0.5000	0.0282 (8)	
H202	1.0000	0.317 (3)	0.5000	0.05 (2)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C101	0.0164 (17)	0.0216 (18)	0.041 (2)	−0.0028 (13)	0.0149 (16)	−0.0031 (15)
C102	0.032 (2)	0.033 (2)	0.054 (3)	0.0000 (17)	0.031 (2)	−0.0058 (19)
C103	0.0271 (19)	0.0214 (18)	0.043 (2)	−0.0101 (14)	0.0258 (18)	−0.0072 (15)
C104	0.035 (2)	0.0281 (19)	0.036 (2)	−0.0183 (17)	0.0226 (19)	−0.0106 (16)
C105	0.058 (3)	0.044 (2)	0.037 (2)	−0.032 (2)	0.031 (2)	−0.0140 (19)
C106	0.067 (4)	0.048 (3)	0.035 (2)	−0.036 (3)	0.026 (2)	−0.012 (2)
C107	0.056 (3)	0.040 (3)	0.028 (2)	−0.029 (2)	0.003 (2)	0.0048 (18)
C108	0.036 (2)	0.029 (2)	0.028 (2)	−0.0167 (17)	0.0080 (18)	0.0003 (15)
C109	0.0162 (16)	0.0192 (16)	0.037 (2)	0.0020 (13)	0.0098 (16)	0.0008 (14)
C110	0.0254 (19)	0.0320 (19)	0.036 (2)	0.0065 (16)	0.0121 (17)	−0.0001 (17)
C111	0.022 (2)	0.0246 (19)	0.053 (3)	0.0011 (16)	0.0090 (19)	−0.0005 (18)
Br11	0.02191 (18)	0.02086 (17)	0.0380 (2)	−0.00514 (13)	0.01633 (16)	−0.00369 (14)
Br12	0.0214 (2)	0.0200 (2)	0.0320 (3)	0.000	0.0161 (2)	0.000
Br15	0.033 (3)	0.043 (3)	0.044 (3)	−0.0047 (19)	0.0094 (19)	0.020 (2)
Cl15	0.0285 (17)	0.0254 (17)	0.042 (2)	−0.0022 (11)	0.0032 (15)	0.0027 (15)
Cu11	0.0165 (2)	0.0181 (2)	0.0272 (2)	−0.00104 (16)	0.01203 (18)	−0.00062 (16)
N101	0.0200 (15)	0.0221 (15)	0.0324 (17)	−0.0041 (11)	0.0145 (14)	−0.0039 (12)
N102	0.0321 (18)	0.0205 (15)	0.0292 (17)	−0.0113 (13)	0.0139 (14)	−0.0019 (13)
O101	0.0381 (16)	0.0355 (15)	0.0512 (18)	−0.0059 (13)	0.0356 (15)	−0.0109 (14)
O102	0.0208 (19)	0.0166 (18)	0.047 (2)	0.000	0.0195 (17)	0.000
C201	0.0204 (17)	0.0166 (16)	0.035 (2)	0.0031 (13)	0.0151 (16)	0.0042 (14)
C202	0.0216 (18)	0.0266 (18)	0.037 (2)	0.0065 (15)	0.0146 (17)	0.0001 (16)
C203	0.0189 (17)	0.0148 (16)	0.033 (2)	−0.0023 (12)	0.0154 (16)	−0.0016 (13)
C204	0.0185 (17)	0.0151 (15)	0.0294 (19)	−0.0060 (12)	0.0108 (15)	−0.0032 (13)
C205	0.028 (2)	0.0230 (18)	0.032 (2)	−0.0069 (15)	0.0170 (17)	−0.0047 (14)
C206	0.034 (2)	0.0247 (18)	0.030 (2)	−0.0062 (16)	0.0130 (17)	−0.0029 (15)
C207	0.027 (2)	0.0198 (17)	0.036 (2)	−0.0021 (14)	0.0076 (18)	0.0034 (15)
C208	0.0213 (18)	0.0187 (17)	0.038 (2)	−0.0016 (13)	0.0155 (17)	0.0046 (14)
C209	0.0258 (19)	0.0223 (19)	0.038 (2)	−0.0007 (14)	0.0152 (17)	0.0013 (15)
C210	0.0221 (19)	0.035 (2)	0.041 (2)	0.0059 (15)	0.0133 (18)	0.0032 (17)
C211	0.051 (3)	0.044 (2)	0.032 (2)	0.024 (2)	0.018 (2)	0.0063 (19)
Br21	0.01980 (17)	0.02221 (17)	0.0378 (2)	−0.00142 (13)	0.01654 (15)	0.00206 (14)
Br22	0.0538 (4)	0.0178 (3)	0.0731 (4)	0.000	0.0542 (4)	0.000
Br25	0.025 (2)	0.0273 (19)	0.052 (3)	0.0113 (16)	0.0246 (19)	0.0141 (16)
Cl25	0.032 (2)	0.038 (2)	0.059 (3)	0.0180 (14)	0.0271 (17)	0.0128 (16)
Cu21	0.0209 (2)	0.0171 (2)	0.0357 (2)	0.00226 (16)	0.0202 (2)	0.00261 (17)
N201	0.0202 (15)	0.0163 (14)	0.0312 (17)	0.0039 (11)	0.0160 (13)	0.0028 (11)
N202	0.0200 (15)	0.0189 (15)	0.0334 (17)	−0.0015 (11)	0.0148 (13)	0.0023 (12)
O201	0.0233 (13)	0.0276 (13)	0.0330 (14)	0.0021 (10)	0.0180 (11)	−0.0025 (11)
O202	0.029 (2)	0.0177 (18)	0.054 (2)	0.000	0.033 (2)	0.000

Geometric parameters (Å, º)

C101—N101	1.492 (5)	C201—N201	1.491 (4)
C101—C109	1.522 (5)	C201—C209	1.518 (5)

C101—C102	1.530 (5)	C201—C202	1.546 (5)
C101—H101	1.0000	C201—H201	1.0000
C102—O101	1.451 (6)	C202—O201	1.466 (5)
C102—H10A	0.9900	C202—H20A	0.9900
C102—H10B	0.9900	C202—H20B	0.9900
C103—N101	1.268 (5)	C203—N201	1.271 (5)
C103—O101	1.345 (5)	C203—O201	1.334 (4)
C103—C104	1.476 (6)	C203—C204	1.472 (5)
C104—N102	1.361 (5)	C204—N202	1.346 (5)
C104—C105	1.372 (6)	C204—C205	1.375 (5)
C105—C106	1.369 (8)	C205—C206	1.403 (6)
C105—H105	0.9500	C205—H205	0.9500
C106—C107	1.388 (8)	C206—C207	1.371 (6)
C106—H106	0.9500	C206—H206	0.9500
C107—C108	1.401 (7)	C207—C208	1.393 (6)
C107—H107	0.9500	C207—H207	0.9500
C108—N102	1.319 (5)	C208—N202	1.336 (5)
C108—Cl15	1.715 (11)	C208—Cl25	1.715 (10)
C108—Br15	1.891 (14)	C208—Br25	1.855 (12)
C109—C111	1.527 (5)	C209—C211	1.524 (6)
C109—C110	1.529 (5)	C209—C210	1.541 (5)
C109—H109	1.0000	C209—H209	1.0000
C110—H11A	0.9800	C210—H21A	0.9800
C110—H11B	0.9800	C210—H21B	0.9800
C110—H11C	0.9800	C210—H21C	0.9800
C111—H11D	0.9800	C211—H21D	0.9800
C111—H11E	0.9800	C211—H21E	0.9800
C111—H11F	0.9800	C211—H21F	0.9800
Br11—Cu11	2.4069 (5)	Br21—Cu21	2.4280 (5)
Br12—Cu11	2.5538 (5)	Br22—Cu21	2.5321 (6)
Br12—Cu11^{i}	2.5538 (5)	Br22—Cu21^{ii}	2.5321 (6)
Cu11—O102	1.8706 (19)	Cu21—O202	1.8705 (19)
Cu11—N101	1.966 (3)	Cu21—N201	1.974 (3)
Cu11—N102	2.362 (3)	Cu21—N202	2.362 (3)
O102—Cu11^{i}	1.8706 (19)	O202—Cu21^{ii}	1.8705 (19)
O102—H102	0.83 (2)	O202—H202	0.84 (2)
Cu11—Cu11^{i}	3.2480 (8)	Cu21—Cu21^{ii}	3.2415 (8)

N101—C101—C109	114.6 (3)	N201—C201—C209	115.9 (3)
N101—C101—C102	100.7 (3)	N201—C201—C202	101.1 (3)
C109—C101—C102	115.0 (3)	C209—C201—C202	114.0 (3)
N101—C101—H101	108.7	N201—C201—H201	108.5
C109—C101—H101	108.7	C209—C201—H201	108.5
C102—C101—H101	108.7	C202—C201—H201	108.5
O101—C102—C101	104.9 (3)	O201—C202—C201	105.3 (3)
O101—C102—H10A	110.8	O201—C202—H20A	110.7
C101—C102—H10A	110.8	C201—C202—H20A	110.7
O101—C102—H10B	110.8	O201—C202—H20B	110.7

C101—C102—H10B	110.8	C201—C202—H20B	110.7
H10A—C102—H10B	108.8	H20A—C202—H20B	108.8
N101—C103—O101	118.1 (4)	N201—C203—O201	118.5 (3)
N101—C103—C104	123.3 (3)	N201—C203—C204	123.4 (3)
O101—C103—C104	118.5 (3)	O201—C203—C204	118.0 (3)
N102—C104—C105	123.5 (4)	N202—C204—C205	124.4 (3)
N102—C104—C103	113.0 (3)	N202—C204—C203	112.5 (3)
C105—C104—C103	123.4 (4)	C205—C204—C203	123.0 (3)
C106—C105—C104	118.7 (5)	C204—C205—C206	117.5 (4)
C106—C105—H105	120.6	C204—C205—H205	121.2
C104—C105—H105	120.6	C206—C205—H205	121.2
C105—C106—C107	119.7 (4)	C207—C206—C205	119.4 (4)
C105—C106—H106	120.2	C207—C206—H206	120.3
C107—C106—H106	120.2	C205—C206—H206	120.3
C106—C107—C108	117.3 (4)	C206—C207—C208	118.3 (4)
C106—C107—H107	121.4	C206—C207—H207	120.9
C108—C107—H107	121.4	C208—C207—H207	120.9
N102—C108—C107	124.2 (5)	N202—C208—C207	123.8 (4)
N102—C108—Cl15	117.8 (4)	N202—C208—Cl25	116.5 (5)
C107—C108—Cl15	118.0 (5)	C207—C208—Cl25	119.7 (5)
N102—C108—Br15	115.7 (5)	N202—C208—Br25	116.6 (5)
C107—C108—Br15	120.1 (5)	C207—C208—Br25	119.6 (5)
C101—C109—C111	110.2 (3)	C201—C209—C211	112.2 (3)
C101—C109—C110	110.7 (3)	C201—C209—C210	108.6 (3)
C111—C109—C110	110.2 (3)	C211—C209—C210	110.2 (3)
C101—C109—H109	108.6	C201—C209—H209	108.6
C111—C109—H109	108.6	C211—C209—H209	108.6
C110—C109—H109	108.6	C210—C209—H209	108.6
C109—C110—H11A	109.5	C209—C210—H21A	109.5
C109—C110—H11B	109.5	C209—C210—H21B	109.5
H11A—C110—H11B	109.5	H21A—C210—H21B	109.5
C109—C110—H11C	109.5	C209—C210—H21C	109.5
H11A—C110—H11C	109.5	H21A—C210—H21C	109.5
H11B—C110—H11C	109.5	H21B—C210—H21C	109.5
C109—C111—H11D	109.5	C209—C211—H21D	109.5
C109—C111—H11E	109.5	C209—C211—H21E	109.5
H11D—C111—H11E	109.5	H21D—C211—H21E	109.5
C109—C111—H11F	109.5	C209—C211—H21F	109.5
H11D—C111—H11F	109.5	H21D—C211—H21F	109.5
H11E—C111—H11F	109.5	H21E—C211—H21F	109.5
Cu11—Br12—Cu11^{i}	78.98 (2)	Cu21—Br22—Cu21^{ii}	79.59 (2)
O102—Cu11—N101	173.95 (13)	O202—Cu21—N201	171.98 (13)
O102—Cu11—N102	102.86 (9)	O202—Cu21—N202	102.67 (8)
N101—Cu11—N102	77.15 (13)	N201—Cu21—N202	76.43 (11)
O102—Cu11—Br11	93.13 (10)	O202—Cu21—Br21	92.64 (10)
N101—Cu11—Br11	92.77 (9)	N201—Cu21—Br21	95.36 (9)
N102—Cu11—Br11	102.44 (8)	N202—Cu21—Br21	100.29 (7)
O102—Cu11—Br12	80.27 (10)	O202—Cu21—Br22	80.15 (10)

N101—Cu11—Br12	93.71 (9)	N201—Cu21—Br22	92.17 (9)
N102—Cu11—Br12	97.44 (8)	N202—Cu21—Br22	101.51 (7)
Br11—Cu11—Br12	160.00 (2)	Br21—Cu21—Br22	158.06 (2)
C103—N101—C101	107.5 (3)	C203—N201—C201	108.4 (3)
C103—N101—Cu11	118.4 (3)	C203—N201—Cu21	117.6 (2)
C101—N101—Cu11	133.5 (2)	C201—N201—Cu21	133.6 (2)
C108—N102—C104	116.5 (4)	C208—N202—C204	116.5 (3)
C108—N102—Cu11	135.2 (3)	C208—N202—Cu21	134.9 (3)
C104—N102—Cu11	107.1 (3)	C204—N202—Cu21	107.2 (2)
C103—O101—C102	104.3 (3)	C203—O201—C202	105.2 (3)
Cu11^{i}—O102—Cu11	120.5 (2)	Cu21^{ii}—O202—Cu21	120.1 (2)
Cu11^{i}—O102—H102	119.76 (10)	Cu21^{ii}—O202—H202	119.95 (10)
Cu11—O102—H102	119.76 (9)	Cu21—O202—H202	119.95 (10)

N101—C101—C102—O101	20.7 (3)	N201—C201—C202—O201	11.8 (3)
C109—C101—C102—O101	144.4 (3)	C209—C201—C202—O201	136.9 (3)
N101—C103—C104—N102	−8.1 (5)	N201—C203—C204—N202	9.8 (5)
O101—C103—C104—N102	174.5 (3)	O201—C203—C204—N202	−165.2 (3)
N101—C103—C104—C105	170.1 (4)	N201—C203—C204—C205	−174.0 (3)
O101—C103—C104—C105	−7.3 (5)	O201—C203—C204—C205	11.0 (5)
N102—C104—C105—C106	1.4 (6)	N202—C204—C205—C206	−1.6 (5)
C103—C104—C105—C106	−176.7 (4)	C203—C204—C205—C206	−177.4 (3)
C104—C105—C106—C107	−2.0 (6)	C204—C205—C206—C207	2.7 (5)
C105—C106—C107—C108	−0.1 (6)	C205—C206—C207—C208	−1.3 (6)
C106—C107—C108—N102	3.4 (6)	C206—C207—C208—N202	−1.3 (6)
C106—C107—C108—Cl15	−178.0 (4)	C206—C207—C208—Cl25	174.7 (5)
C106—C107—C108—Br15	−176.4 (5)	C206—C207—C208—Br25	177.9 (5)
N101—C101—C109—C111	166.2 (3)	N201—C201—C209—C211	−62.8 (4)
C102—C101—C109—C111	50.2 (4)	C202—C201—C209—C211	−179.6 (3)
N101—C101—C109—C110	−71.6 (4)	N201—C201—C209—C210	175.1 (3)
C102—C101—C109—C110	172.4 (3)	C202—C201—C209—C210	58.4 (4)
Cu11^{i}—Br12—Cu11—O102	0.0	Cu21^{ii}—Br22—Cu21—O202	0.0
Cu11^{i}—Br12—Cu11—N101	−179.35 (10)	Cu21^{ii}—Br22—Cu21—N201	177.65 (9)
Cu11^{i}—Br12—Cu11—N102	−101.85 (9)	Cu21^{ii}—Br22—Cu21—N202	101.06 (7)
Cu11^{i}—Br12—Cu11—Br11	71.98 (6)	Cu21^{ii}—Br22—Cu21—Br21	−72.21 (5)
O101—C103—N101—C101	4.5 (4)	O201—C203—N201—C201	5.6 (4)
C104—C103—N101—C101	−172.8 (3)	C204—C203—N201—C201	−169.4 (3)
O101—C103—N101—Cu11	176.6 (2)	O201—C203—N201—Cu21	−179.9 (2)
C104—C103—N101—Cu11	−0.8 (5)	C204—C203—N201—Cu21	5.1 (4)
C109—C101—N101—C103	−139.6 (3)	C209—C201—N201—C203	−134.4 (3)
C102—C101—N101—C103	−15.7 (4)	C202—C201—N201—C203	−10.6 (4)
C109—C101—N101—Cu11	50.1 (4)	C209—C201—N201—Cu21	52.3 (4)
C102—C101—N101—Cu11	174.0 (3)	C202—C201—N201—Cu21	176.1 (3)
N102—Cu11—N101—C103	5.2 (3)	N202—Cu21—N201—C203	−10.5 (3)
Br11—Cu11—N101—C103	−96.9 (3)	Br21—Cu21—N201—C203	88.8 (3)
Br12—Cu11—N101—C103	102.0 (3)	Br22—Cu21—N201—C203	−111.8 (3)
N102—Cu11—N101—C101	174.7 (3)	N202—Cu21—N201—C201	162.3 (3)
Br11—Cu11—N101—C101	72.6 (3)	Br21—Cu21—N201—C201	−98.3 (3)

Br12—Cu11—N101—C101	−88.5 (3)	Br22—Cu21—N201—C201	61.0 (3)
C107—C108—N102—C104	−4.0 (6)	C207—C208—N202—C204	2.4 (5)
Cl15—C108—N102—C104	177.3 (4)	Cl25—C208—N202—C204	−173.7 (5)
Br15—C108—N102—C104	175.7 (4)	Br25—C208—N202—C204	−176.8 (4)
C107—C108—N102—Cu11	161.2 (3)	C207—C208—N202—Cu21	−162.2 (3)
Cl15—C108—N102—Cu11	−17.5 (5)	Cl25—C208—N202—Cu21	21.7 (6)
Br15—C108—N102—Cu11	−19.1 (6)	Br25—C208—N202—Cu21	18.6 (6)
C105—C104—N102—C108	1.6 (5)	C205—C204—N202—C208	−0.9 (5)
C103—C104—N102—C108	179.8 (3)	C203—C204—N202—C208	175.3 (3)
C105—C104—N102—Cu11	−167.5 (3)	C205—C204—N202—Cu21	167.7 (3)
C103—C104—N102—Cu11	10.7 (3)	C203—C204—N202—Cu21	−16.1 (3)
O102—Cu11—N102—C108	11.1 (4)	O202—Cu21—N202—C208	−7.7 (3)
N101—Cu11—N102—C108	−175.1 (4)	N201—Cu21—N202—C208	−179.5 (3)
Br11—Cu11—N102—C108	−85.1 (4)	Br21—Cu21—N202—C208	87.4 (3)
Br12—Cu11—N102—C108	92.7 (4)	Br22—Cu21—N202—C208	−90.0 (3)
O102—Cu11—N102—C104	177.2 (2)	O202—Cu21—N202—C204	−173.2 (2)
N101—Cu11—N102—C104	−9.0 (2)	N201—Cu21—N202—C204	14.9 (2)
Br11—Cu11—N102—C104	81.0 (2)	Br21—Cu21—N202—C204	−78.1 (2)
Br12—Cu11—N102—C104	−101.1 (2)	Br22—Cu21—N202—C204	104.4 (2)
N101—C103—O101—C102	9.7 (4)	N201—C203—O201—C202	2.8 (4)
C104—C103—O101—C102	−172.8 (3)	C204—C203—O201—C202	178.0 (3)
C101—C102—O101—C103	−18.8 (4)	C201—C202—O201—C203	−9.4 (4)
N102—Cu11—O102—Cu11^{i}	95.49 (8)	N202—Cu21—O202—Cu21^{ii}	−99.70 (8)
Br11—Cu11—O102—Cu11^{i}	−160.99 (2)	Br21—Cu21—O202—Cu21^{ii}	159.13 (2)
Br12—Cu11—O102—Cu11^{i}	0.0	Br22—Cu21—O202—Cu21^{ii}	0.0

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