

The copper(II) complexes di- μ -bromo-bis[[2,6-bis(pyrazol-1-yl)pyridine]perchloratocopper(II)] and [2,6-bis(pyrazol-1-yl)pyridine]dibromocopper(II)

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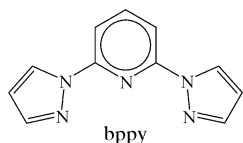
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The two title compounds, di- μ -bromo-bis[[2,6-bis(pyrazol-1-yl)- κ N²]pyridine- κ N](perchlorato- κ O)copper(II)], [Cu₂Br₂(ClO₄)₂(C₁₁H₉N₅)₂], (I), and [2,6-bis(pyrazol-1-yl)pyridine]dibromocopper(II), [CuBr₂(C₁₁H₉N₅)], (II), were synthesized by only slight modifications of the same reaction; compound (II) was formed by adding one molar equivalent of pyrazole (C₃N₂H₄) to the reaction mixture of (I). Compound (I) is a bromo-bridged dinuclear copper(II) compound stabilized by weak interactions with the perchlorate anions (ClO₄⁻), while (II) is a related mononuclear species, which has a distorted square-pyramidal geometry.

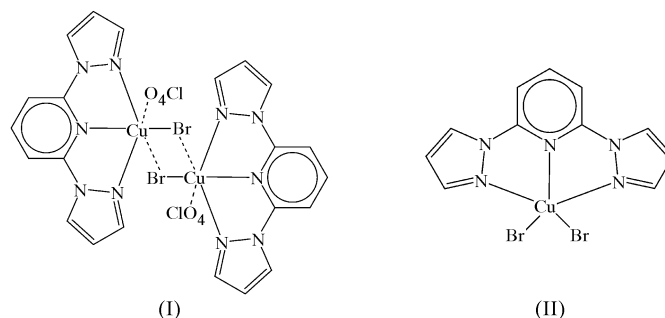
Comment

After the discovery of planar tridentate N-atom donor ligands by Jameson & Goldsby (1990), much work has been carried out in the past decade with various transition metals and the 2,6-bis(pyrazolyl)pyridine ligand (bppy; see first scheme below), because of its potential in bonding to metal atoms (Jameson *et al.*, 1989; Downard *et al.*, 1991; Abel *et al.*, 1994; Solanki *et al.*, 1998). Examples include iron(II) complexes of bppy derivatives, which have been shown to exhibit thermal



and light-induced spin-crossover transitions (Holland *et al.*, 2002; Money *et al.*, 2004). Previous work carried out on related copper(II) complexes has shown that they exhibit an axially compressed octahedral geometry (Solanki *et al.*, 1998). In this context, we have synthesized two new copper(II) complexes and have carried out a structural study.

The bromine-bridged dicopper complex [Cu₂Br₂(ClO₄)₂(bppy)₂] (I), and the monocopper complex [CuBr₂(bppy)] (II), were prepared *via* essentially the same route, except that pyrazole was added to the reaction mixture that yielded (II).



Compound (I) contains two Cu atoms, each ligated in a square-planar geometry by a tridentate bppy ligand and one Br atom. Pairs of these square-planar copper complexes form dimers bridged by the two bromine ions. In addition, these dinuclear species are stabilized by two ligating ClO₄⁻ anions, with the result that both copper centres exhibit a pseudo-octahedral geometry (Carranza *et al.*, 2003). Thus, each distorted octahedron contains a bppy ligand together with one of the bridging Br atoms in the equatorial plane, and is capped by a ClO₄⁻ anion and the remaining bridging Br atom. The two halves of the molecule are related by a non-crystallographic inversion centre situated between the copper centres (Fig. 1).

The equatorial CuN₃Br planes each contain three Cu–N bonds of approximately 2.0 Å and one longer Cu–Br bond [2.3436 (10) and 2.3578 (10) Å; Table 1]. Bridging halides are quite common and bridging pairs of Br atoms have been reported many times in the literature, with various bond lengths (Marsh *et al.*, 1983; Hoffmann *et al.*, 1984; Xu *et al.*, 2000). In the case of (I) however, the axial and equatorial Cu–Br bonds are highly asymmetric, the axial bonds being longer at approximately 3.0 Å.

Each Cu atom also forms a bond to the nearest perchlorate O atom [Cu1–O5 = 2.466 (6) Å and Cu2–O4 = 2.564 (6) Å],

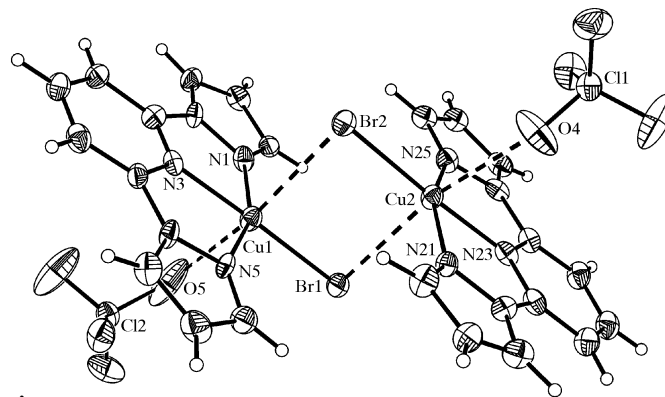
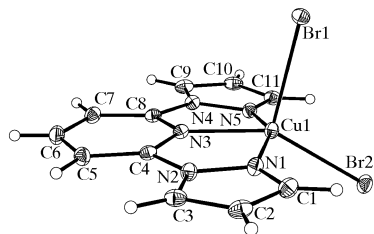


Figure 1
A view of (I), showing the long Cu–Br and Cu–O bonds as broken lines. The square-planar geometry of the CuBr(bppy) moiety can clearly be seen, as can the pseudo-octahedral geometry around the Cu centre in the dimer. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.


Figure 2

A view of (II), showing the square-pyramidal geometry around the Cu centre. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

resulting in a distorted elongated octahedral geometry around each metal atom. As in many perchlorate compounds, the ClO_4^- ions have larger displacement parameters than the rest of the molecule, indicating a tendency to disorder (Ragunathan & Bharadwaj, 1992). However, the coordination to the copper centres has reduced this motion, making it possible to refine anisotropic displacement parameters.

In contrast to (I), the mononuclear compound (II) consists of a single Cu atom ligated by the bppy ligand and two Br atoms (Fig. 2). The five-coordinate geometry is best described with respect to (I) as pseudo-square-pyramidal, with the 'equatorial' Br2 atom 1.04 Å (29.7°) out of the plane of the bppy ligand. This configuration also leads to a difference in the positions of the axial Br atoms, which in (I) made angles of 87.83 (16) and 89.69 (16)° with the bppy ligand planes, and in (II) makes an angle of 104.03 (4)°. There is also an increase in the Br—Cu—Br angle [93.39 (4) and 93.88 (3)° in (I), and 107.203 (10)° in (II)], due to the reduction in coordination number, and a reduction in the asymmetry that is seen in the Cu—Br distances for (I) (Table 2).

Another consequence of the lower coordination number is that the central Cu atom lies slightly out of the plane of the bppy ligand. Thus, while the internal parameters of the bppy ligand ring system are in accordance with anticipated values (Bessel *et al.*, 1992), the separate aromatic rings of the bppy ligand are not coplanar and the angles between the planes of the pyridine ring and the pyrazole rings are 2.8 (2)° (for N1/C1—C3/N2) and 4.3 (2)° (for N4/C9—C11/N5).

Experimental

Compound (I) was prepared by stirring a mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.370 g, 1 mmol), bppy (0.211 g, 1 mmol) and potassium bromide (0.0297 g, 0.25 mmol) in acetonitrile (25 ml) for 4 h at room temperature. During this time, the colour of the solution changed from blue to blue–green. After evaporation of the solvent, blue–green crystals were obtained (yield 0.390 g, 63.85%). Compound (II) was prepared using a mixture of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, bppy and potassium bromide in acetonitrile (as above), which was stirred for 2 h. Pyrazole (0.068 g, 1 mmol) was added to the reaction mixture and the mixture was stirred for a further 2 h. During this time, the colour of the solution changed from blue–green to deep green. On evaporation of the solvent, the solution yielded the green compound (II) together with a pale-blue compound thought to be unreacted starting material (yield 0.280 g, 41.19%). Caution: perchlorate salts of metal complexes are potentially explosive. Suitable care should be taken when handling such hazardous compounds. Compounds (I) and (II) were both purified by passing them through a silica-gel column using methanol–

acetonitrile–dichloromethane (1:1:2) as eluant. X-ray quality crystals of both (I) and (II) were grown by keeping a saturated solution of the purified compound in acetonitrile for several days at room temperature.

Compound (I)

Crystal data

$[\text{Cu}_2\text{Br}_2(\text{ClO}_4)_2(\text{C}_{11}\text{H}_9\text{N}_5)_2]$
 $M_r = 908.26$
 Monoclinic, $P2_1$
 $a = 7.8033$ (2) Å
 $b = 15.1425$ (5) Å
 $c = 12.7301$ (3) Å
 $\beta = 106.305$ (2)°
 $V = 1443.71$ (7) Å³
 $Z = 2$

$D_x = 2.089$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 10 240 reflections
 $\theta = 1.8$ – 32.9°
 $\mu = 4.49$ mm⁻¹
 $T = 120$ (2) K
 Tube, blue–green
 0.13 × 0.12 × 0.10 mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer
 ω and φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.604$, $T_{\max} = 0.662$
 56 664 measured reflections

9732 independent reflections
 6041 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.092$
 $\theta_{\text{max}} = 32.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -22 \rightarrow 22$
 $l = -19 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.128$
 $S = 1.03$
 9732 reflections
 416 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.2337P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.66$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.13$ e Å⁻³
 Absolute structure: Flack (1983), 4335 Friedel pairs
 Flack parameter = 0.000 (12)

Table 1

Selected geometric parameters (Å, °) for (I).

Br1—Cu1	2.3436 (10)	Cu1—N5	2.016 (6)
Br1—Cu2	2.9945 (11)	Cu1—O5	2.466 (6)
Br2—Cu2	2.3578 (10)	Cu2—N21	2.016 (6)
Br2—Cu1	3.0249 (11)	Cu2—N23	1.962 (6)
Cu1—N3	1.977 (5)	Cu2—N25	2.013 (5)
Cu1—N1	1.998 (6)	Cu2—O4	2.564 (6)
Cu1—Br1—Cu2	86.84 (3)	Br1—Cu1—Br2	93.39 (4)
Cu2—Br2—Cu1	85.88 (3)	N21—Cu2—Br2	100.95 (15)
N1—Cu1—Br1	102.00 (17)	N23—Cu2—Br2	176.42 (17)
N3—Cu1—Br1	178.59 (16)	N25—Cu2—Br2	101.72 (18)
N5—Cu1—Br1	100.43 (15)	N21—Cu2—Br1	94.87 (16)
N1—Cu1—Br2	94.25 (17)	N23—Cu2—Br1	89.69 (16)
N3—Cu1—Br2	87.83 (16)	N25—Cu2—Br1	85.04 (16)
N5—Cu1—Br2	86.26 (16)	Br2—Cu2—Br1	93.88 (3)

Compound (II)

Crystal data

$[\text{CuBr}_2(\text{C}_{11}\text{H}_9\text{N}_5)]$
 $M_r = 434.58$
 Monoclinic, $P2_1/c$
 $a = 11.0056$ (2) Å
 $b = 7.8940$ (1) Å
 $c = 15.2370$ (2) Å
 $\beta = 93.856$ (1)°
 $V = 1320.77$ (3) Å³
 $Z = 4$

$D_x = 2.186$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 10 000 reflections
 $\theta = 1.8$ – 32.9°
 $\mu = 7.70$ mm⁻¹
 $T = 120$ (2) K
 Tube, green
 0.30 × 0.27 × 0.25 mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer	4675 independent reflections
ω and φ scans	3978 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.206$, $T_{\text{max}} = 0.249$	$\theta_{\text{max}} = 32.5^\circ$
24 033 measured reflections	$h = -16 \rightarrow 16$
	$k = -11 \rightarrow 11$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 0.8921P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
4675 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e } \text{\AA}^{-3}$
172 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Cu1—Br1	2.5740 (3)	N2—C4	1.406 (2)
Cu1—Br2	2.3946 (3)	N3—C4	1.329 (2)
Cu1—N1	2.0218 (15)	N3—C8	1.331 (2)
Cu1—N3	1.9854 (14)	N4—C9	1.363 (2)
Cu1—N5	2.0264 (15)	N4—N5	1.376 (2)
N1—C1	1.329 (2)	N4—C8	1.402 (2)
N1—N2	1.371 (2)	N5—C11	1.327 (2)
N2—C3	1.360 (2)		
N3—Cu1—N1	77.86 (6)	N5—Cu1—Br2	100.07 (4)
N3—Cu1—N5	77.87 (6)	N3—Cu1—Br1	104.03 (4)
N1—Cu1—N5	154.50 (6)	N1—Cu1—Br1	100.58 (4)
N3—Cu1—Br2	148.76 (4)	N5—Cu1—Br1	92.76 (4)
N1—Cu1—Br2	96.62 (4)	Br2—Cu1—Br1	107.203 (10)

H atoms were treated using a riding model ($\text{C—H} = 0.93 \text{ \AA}$), with isotropic displacement parameters fixed at 120% of the U_{eq} values of the parent C atoms.

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker,

1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1771). Services for accessing these data are described at the back of the journal.

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supporting information

Acta Cryst. (2004). C60, m628–m630 [doi:10.1107/S0108270104026459]

The copper(II) complexes di- μ -bromo-bis{[2,6-bis(pyrazol-1-yl)pyridine]-perchloratocopper(II)} and [2,6-bis(pyrazol-1-yl)pyridine]dibromocopper(II)

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Computing details

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

(I) di- μ -bromo-bis{[2,6-bis(pyrazol-1-yl- κ N²)pyridine- κ N](perchlorato- κ O)copper(II)}

Crystal data

[Cu₂Br₂(ClO₄)₂(C₁₁H₉N₅)₂]

$M_r = 908.26$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 7.8033$ (2) Å

$b = 15.1425$ (5) Å

$c = 12.7301$ (3) Å

$\beta = 106.305$ (2)°

$V = 1443.71$ (7) Å³

$Z = 2$

$F(000) = 892$

10240 integrated reflections used for unit cell measurement.

$D_x = 2.089$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10240 reflections

$\theta = 1.8$ – 32.9 °

$\mu = 4.49$ mm⁻¹

$T = 120$ K

Tube, blue-green

$0.13 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1998)

$T_{\min} = 0.604$, $T_{\max} = 0.662$

56664 measured reflections

9732 independent reflections

6041 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.092$

$\theta_{\max} = 32.5$ °, $\theta_{\min} = 1.7$ °

$h = -11 \rightarrow 11$

$k = -22 \rightarrow 22$

$l = -19 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.128$

$S = 1.03$

9732 reflections

416 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.2337P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.66 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -1.13 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack H D (1983), Acta
 Cryst. A39, 876-881
 Absolute structure parameter: 0.000 (12)

Special details

Experimental. The absorption correction was done with *SADABS*, mu*r. The radius was calculated from the estimation of the crystal being a sphere ($r = 0.07 \text{ mm}$). The mu coefficient is calculated from the program FPrime (Program FPrime for Windows 1.0 for calculating real and anomalous X-ray dispersion coefficients, R·B. Von Dreele, 1994).

The data collection nominally covered over a full sphere of reciprocal space, by a combination of 6 sets of ω scans and a 2 of φ scan. Each scan was exposed for 3 s covering 0.3° in ω or φ . No sign of crystal decay was observed.

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. Absolute configuration was determined by inverting the structure and by checking Flack parameters.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.83413 (9)	0.76392 (4)	0.29061 (5)	0.02583 (15)
Br2	0.53815 (9)	0.55200 (4)	0.28052 (5)	0.02516 (15)
Cu1	0.80261 (11)	0.67318 (5)	0.43317 (7)	0.02240 (19)
Cu2	0.57084 (11)	0.64501 (5)	0.13886 (7)	0.02147 (18)
N1	1.0078 (7)	0.5900 (4)	0.4520 (5)	0.0230 (12)
N2	1.0240 (8)	0.5304 (4)	0.5356 (4)	0.0238 (12)
N3	0.7773 (7)	0.5992 (4)	0.5559 (4)	0.0187 (11)
N4	0.5439 (7)	0.6900 (4)	0.5486 (4)	0.0216 (12)
N5	0.5891 (7)	0.7298 (4)	0.4654 (4)	0.0206 (11)
N21	0.3616 (7)	0.7272 (4)	0.1224 (4)	0.0208 (11)
N22	0.3395 (7)	0.7828 (3)	0.0340 (4)	0.0205 (11)
N23	0.5880 (7)	0.7175 (4)	0.0144 (5)	0.0194 (11)
N24	0.8266 (7)	0.6331 (4)	0.0169 (5)	0.0194 (12)
N25	0.7861 (7)	0.5924 (4)	0.1050 (5)	0.0236 (12)
C1	1.1460 (9)	0.5702 (4)	0.4126 (6)	0.0237 (14)
H1	1.1719	0.5996	0.3547	0.028*
C2	1.2455 (9)	0.4997 (5)	0.4698 (6)	0.0251 (14)
H2	1.3456	0.4737	0.4568	0.030*
C3	1.1662 (10)	0.4772 (5)	0.5480 (6)	0.0270 (16)
H3	1.2033	0.4332	0.6005	0.032*
C4	0.8961 (9)	0.5372 (4)	0.5945 (6)	0.0218 (14)
C5	0.8874 (9)	0.4851 (4)	0.6834 (6)	0.0242 (14)
H5	0.9689	0.4399	0.7097	0.029*
C6	0.7511 (10)	0.5040 (5)	0.7306 (6)	0.0267 (16)
H6	0.7416	0.4715	0.7907	0.032*

C7	0.6277 (9)	0.5715 (5)	0.6887 (6)	0.0257 (15)
H7	0.5348	0.5840	0.7189	0.031*
C8	0.6499 (9)	0.6177 (4)	0.6026 (5)	0.0209 (13)
C9	0.4002 (9)	0.7303 (5)	0.5700 (6)	0.0275 (15)
H9	0.3447	0.7140	0.6229	0.033*
C10	0.3553 (9)	0.7983 (5)	0.4989 (6)	0.0306 (16)
H10	0.2641	0.8391	0.4939	0.037*
C11	0.4752 (9)	0.7950 (5)	0.4338 (6)	0.0260 (14)
H11	0.4737	0.8336	0.3767	0.031*
C21	0.2262 (9)	0.7442 (5)	0.1628 (6)	0.0263 (15)
H21	0.2086	0.7166	0.2243	0.032*
C22	0.1131 (9)	0.8086 (5)	0.1019 (6)	0.0265 (14)
H22	0.0085	0.8306	0.1133	0.032*
C23	0.1899 (9)	0.8325 (5)	0.0213 (6)	0.0276 (15)
H23	0.1473	0.8750	-0.0324	0.033*
C24	0.4643 (8)	0.7786 (5)	-0.0247 (5)	0.0211 (14)
C25	0.4717 (10)	0.8314 (5)	-0.1115 (6)	0.0269 (16)
H25	0.3888	0.8761	-0.1368	0.032*
C26	0.6075 (9)	0.8152 (5)	-0.1595 (6)	0.0274 (15)
H26	0.6135	0.8488	-0.2195	0.033*
C27	0.7334 (10)	0.7509 (5)	-0.1209 (6)	0.0282 (16)
H27	0.8258	0.7408	-0.1522	0.034*
C28	0.7156 (8)	0.7017 (4)	-0.0326 (5)	0.0208 (13)
C29	0.9765 (9)	0.5961 (4)	0.0024 (6)	0.0264 (15)
H29	1.0307	0.6115	-0.0514	0.032*
C30	1.0349 (9)	0.5321 (4)	0.0807 (6)	0.0271 (15)
H30	1.1352	0.4965	0.0911	0.032*
C31	0.9108 (9)	0.5321 (4)	0.1416 (6)	0.0251 (14)
H31	0.9157	0.4946	0.2002	0.030*
Cl1	0.3574 (2)	0.50429 (11)	-0.10475 (14)	0.0260 (3)
O1	0.5380 (7)	0.4775 (4)	-0.0894 (5)	0.0416 (14)
O2	0.2447 (8)	0.4311 (4)	-0.1002 (5)	0.0442 (14)
O3	0.2923 (8)	0.5485 (6)	-0.2068 (5)	0.067 (2)
O4	0.3512 (8)	0.5635 (5)	-0.0192 (5)	0.0557 (18)
Cl2	1.0087 (2)	0.80230 (11)	0.67630 (14)	0.0254 (3)
O5	1.0122 (8)	0.7597 (5)	0.5775 (5)	0.066 (2)
O6	1.1163 (8)	0.8794 (4)	0.6875 (5)	0.0468 (15)
O7	1.0796 (9)	0.7443 (6)	0.7655 (6)	0.077 (3)
O8	0.8273 (7)	0.8231 (4)	0.6724 (5)	0.0349 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0322 (4)	0.0253 (3)	0.0222 (3)	-0.0028 (3)	0.0111 (3)	0.0013 (3)
Br2	0.0282 (4)	0.0260 (3)	0.0228 (3)	-0.0011 (3)	0.0099 (3)	0.0022 (3)
Cu1	0.0232 (4)	0.0255 (4)	0.0210 (4)	0.0025 (3)	0.0104 (4)	0.0036 (3)
Cu2	0.0230 (4)	0.0244 (4)	0.0192 (4)	0.0027 (3)	0.0095 (3)	0.0026 (3)
N1	0.022 (3)	0.030 (3)	0.020 (3)	0.004 (2)	0.009 (2)	-0.002 (2)

N2	0.029 (3)	0.028 (3)	0.016 (3)	0.000 (2)	0.009 (2)	0.002 (2)
N3	0.017 (3)	0.024 (3)	0.016 (3)	-0.005 (2)	0.006 (2)	-0.005 (2)
N4	0.024 (3)	0.029 (3)	0.015 (3)	0.002 (2)	0.009 (2)	0.006 (2)
N5	0.027 (3)	0.022 (3)	0.014 (3)	-0.001 (2)	0.008 (2)	0.007 (2)
N21	0.024 (3)	0.024 (3)	0.018 (3)	-0.003 (2)	0.011 (2)	0.000 (2)
N22	0.019 (3)	0.021 (3)	0.023 (3)	0.000 (2)	0.006 (2)	0.002 (2)
N23	0.013 (2)	0.024 (3)	0.021 (3)	0.001 (2)	0.005 (2)	-0.007 (2)
N24	0.011 (3)	0.021 (3)	0.025 (3)	-0.003 (2)	0.003 (2)	-0.007 (2)
N25	0.020 (3)	0.029 (3)	0.020 (3)	0.002 (2)	0.004 (2)	-0.005 (2)
C1	0.031 (4)	0.023 (3)	0.019 (3)	-0.010 (3)	0.009 (3)	-0.002 (3)
C2	0.018 (3)	0.027 (3)	0.030 (4)	0.006 (3)	0.007 (3)	-0.004 (3)
C3	0.030 (4)	0.024 (4)	0.024 (4)	0.005 (3)	0.003 (3)	0.006 (3)
C4	0.019 (3)	0.023 (3)	0.022 (3)	-0.002 (3)	0.004 (3)	0.000 (3)
C5	0.027 (3)	0.023 (3)	0.021 (3)	0.004 (3)	0.004 (3)	0.003 (3)
C6	0.032 (4)	0.028 (4)	0.025 (4)	-0.002 (3)	0.016 (3)	0.002 (3)
C7	0.024 (4)	0.034 (4)	0.022 (3)	-0.007 (3)	0.010 (3)	-0.004 (3)
C8	0.021 (3)	0.025 (3)	0.016 (3)	-0.005 (3)	0.004 (3)	-0.003 (2)
C9	0.020 (3)	0.037 (4)	0.029 (4)	0.000 (3)	0.011 (3)	0.000 (3)
C10	0.023 (3)	0.037 (4)	0.032 (4)	0.009 (3)	0.009 (3)	-0.004 (3)
C11	0.027 (4)	0.026 (3)	0.026 (4)	-0.001 (3)	0.010 (3)	0.002 (3)
C21	0.021 (3)	0.036 (4)	0.026 (4)	0.001 (3)	0.014 (3)	0.002 (3)
C22	0.027 (4)	0.029 (4)	0.025 (4)	-0.002 (3)	0.011 (3)	0.002 (3)
C23	0.017 (3)	0.028 (4)	0.035 (4)	0.003 (3)	0.004 (3)	0.000 (3)
C24	0.016 (3)	0.029 (4)	0.021 (3)	-0.002 (3)	0.010 (3)	-0.005 (3)
C25	0.026 (4)	0.031 (4)	0.025 (4)	0.000 (3)	0.010 (3)	-0.001 (3)
C26	0.021 (3)	0.036 (4)	0.024 (4)	-0.004 (3)	0.003 (3)	0.000 (3)
C27	0.030 (4)	0.035 (4)	0.022 (4)	-0.007 (3)	0.011 (3)	0.000 (3)
C28	0.017 (3)	0.025 (3)	0.021 (3)	-0.003 (3)	0.007 (3)	-0.004 (3)
C29	0.027 (4)	0.028 (4)	0.028 (4)	-0.005 (3)	0.013 (3)	-0.007 (3)
C30	0.021 (3)	0.027 (3)	0.033 (4)	0.001 (3)	0.006 (3)	-0.005 (3)
C31	0.018 (3)	0.025 (3)	0.029 (4)	0.001 (3)	0.002 (3)	-0.004 (3)
Cl1	0.0236 (8)	0.0311 (8)	0.0248 (8)	0.0005 (7)	0.0094 (7)	0.0002 (7)
O1	0.021 (3)	0.061 (4)	0.043 (3)	0.011 (3)	0.009 (2)	-0.001 (3)
O2	0.043 (3)	0.031 (3)	0.055 (4)	-0.014 (3)	0.008 (3)	-0.004 (3)
O3	0.034 (3)	0.114 (6)	0.052 (4)	0.008 (4)	0.010 (3)	0.052 (4)
O4	0.037 (3)	0.074 (4)	0.062 (4)	-0.021 (3)	0.024 (3)	-0.046 (4)
Cl2	0.0245 (8)	0.0293 (8)	0.0233 (8)	0.0005 (7)	0.0081 (7)	-0.0032 (7)
O5	0.035 (3)	0.103 (6)	0.070 (5)	-0.029 (4)	0.031 (3)	-0.061 (4)
O6	0.038 (3)	0.036 (3)	0.064 (4)	-0.008 (3)	0.011 (3)	-0.018 (3)
O7	0.040 (4)	0.100 (6)	0.092 (6)	0.023 (4)	0.021 (4)	0.067 (5)
O8	0.030 (3)	0.046 (3)	0.033 (3)	0.012 (2)	0.016 (2)	0.006 (2)

Geometric parameters (Å, °)

Br1—Cu1	2.3436 (10)	C4—C5	1.397 (9)
Br1—Cu2	2.9945 (11)	C5—C6	1.391 (10)
Br2—Cu2	2.3578 (10)	C5—H5	0.9300
Br2—Cu1	3.0249 (11)	C6—C7	1.403 (10)

Cu1—N3	1.977 (5)	C6—H6	0.9300
Cu1—N1	1.998 (6)	C7—C8	1.351 (9)
Cu1—N5	2.016 (6)	C7—H7	0.9300
Cu1—O5	2.466 (6)	C9—C10	1.351 (10)
Cu2—N21	2.016 (6)	C9—H9	0.9300
Cu2—N23	1.962 (6)	C10—C11	1.414 (9)
Cu2—N25	2.013 (5)	C10—H10	0.9300
Cu2—O4	2.564 (6)	C11—H11	0.9300
N1—C1	1.345 (8)	C21—C22	1.396 (10)
N1—N2	1.374 (8)	C21—H21	0.9300
N2—C3	1.344 (9)	C22—C23	1.374 (10)
N2—C4	1.410 (8)	C22—H22	0.9300
N3—C4	1.314 (8)	C23—H23	0.9300
N3—C8	1.324 (8)	C24—C25	1.377 (10)
N4—N5	1.348 (7)	C25—C26	1.386 (10)
N4—C9	1.369 (8)	C25—H25	0.9300
N4—C8	1.427 (9)	C26—C27	1.373 (10)
N5—C11	1.314 (9)	C26—H26	0.9300
N21—C21	1.325 (8)	C27—C28	1.387 (9)
N21—N22	1.377 (7)	C27—H27	0.9300
N22—C23	1.360 (8)	C29—C30	1.373 (10)
N22—C24	1.385 (8)	C29—H29	0.9300
N23—C28	1.319 (8)	C30—C31	1.400 (9)
N23—C24	1.330 (8)	C30—H30	0.9300
N24—C29	1.356 (8)	C31—H31	0.9300
N24—C28	1.385 (9)	C11—O4	1.422 (6)
N24—N25	1.392 (8)	C11—O3	1.423 (6)
N25—C31	1.319 (8)	C11—O1	1.426 (5)
C1—C2	1.399 (10)	C11—O2	1.427 (6)
C1—H1	0.9300	C12—O7	1.419 (7)
C2—C3	1.355 (10)	C12—O5	1.420 (6)
C2—H2	0.9300	C12—O6	1.422 (6)
C3—H3	0.9300	C12—O8	1.437 (5)
Cu1—Br1—Cu2	86.84 (3)	C4—C5—H5	121.6
Cu2—Br2—Cu1	85.88 (3)	C5—C6—C7	120.8 (7)
N1—Cu1—Br1	102.00 (17)	C5—C6—H6	119.6
N3—Cu1—Br1	178.59 (16)	C7—C6—H6	119.6
N5—Cu1—Br1	100.43 (15)	C8—C7—C6	117.0 (6)
N1—Cu1—Br2	94.25 (17)	C8—C7—H7	121.5
N3—Cu1—Br2	87.83 (16)	C6—C7—H7	121.5
N5—Cu1—Br2	86.26 (16)	N3—C8—C7	122.6 (6)
Br1—Cu1—Br2	93.39 (4)	N3—C8—N4	110.6 (6)
N21—Cu2—Br2	100.95 (15)	C7—C8—N4	126.8 (6)
N23—Cu2—Br2	176.42 (17)	C10—C9—N4	106.2 (6)
N25—Cu2—Br2	101.72 (18)	C10—C9—H9	126.9
N21—Cu2—Br1	94.87 (16)	N4—C9—H9	126.9
N23—Cu2—Br1	89.69 (16)	C9—C10—C11	106.0 (6)

N25—Cu2—Br1	85.04 (16)	C9—C10—H10	127.0
Br2—Cu2—Br1	93.88 (3)	C11—C10—H10	127.0
N3—Cu1—N1	78.6 (2)	N5—C11—C10	110.4 (6)
N3—Cu1—N5	78.9 (2)	N5—C11—H11	124.8
N1—Cu1—N5	157.5 (2)	C10—C11—H11	124.8
N23—Cu2—N25	78.4 (2)	N21—C21—C22	111.6 (6)
N23—Cu2—N21	78.9 (2)	N21—C21—H21	124.2
N25—Cu2—N21	157.3 (2)	C22—C21—H21	124.2
C1—N1—N2	103.5 (5)	C23—C22—C21	105.0 (6)
C1—N1—Cu1	142.6 (5)	C23—C22—H22	127.5
N2—N1—Cu1	113.8 (4)	C21—C22—H22	127.5
C3—N2—N1	112.2 (5)	N22—C23—C22	107.8 (6)
C3—N2—C4	131.8 (6)	N22—C23—H23	126.1
N1—N2—C4	116.0 (5)	C22—C23—H23	126.1
C4—N3—C8	121.5 (6)	N23—C24—C25	121.0 (6)
C4—N3—Cu1	118.9 (4)	N23—C24—N22	112.1 (6)
C8—N3—Cu1	119.3 (5)	C25—C24—N22	126.9 (6)
N5—N4—C9	111.5 (6)	C24—C25—C26	117.5 (7)
N5—N4—C8	118.5 (5)	C24—C25—H25	121.3
C9—N4—C8	129.9 (6)	C26—C25—H25	121.3
C11—N5—N4	105.8 (5)	C27—C26—C25	121.7 (7)
C11—N5—Cu1	141.6 (5)	C27—C26—H26	119.1
N4—N5—Cu1	112.6 (4)	C25—C26—H26	119.1
C21—N21—N22	105.5 (5)	C26—C27—C28	116.5 (6)
C21—N21—Cu2	142.3 (5)	C26—C27—H27	121.7
N22—N21—Cu2	112.0 (4)	C28—C27—H27	121.7
C23—N22—N21	110.0 (5)	N23—C28—N24	112.6 (6)
C23—N22—C24	132.1 (6)	N23—C28—C27	122.0 (6)
N21—N22—C24	117.9 (5)	N24—C28—C27	125.3 (6)
C28—N23—C24	121.1 (6)	N24—C29—C30	108.4 (6)
C28—N23—Cu2	119.8 (5)	N24—C29—H29	125.8
C24—N23—Cu2	119.0 (4)	C30—C29—H29	125.8
C29—N24—C28	134.5 (6)	C29—C30—C31	105.2 (6)
C29—N24—N25	109.0 (6)	C29—C30—H30	127.4
C28—N24—N25	116.4 (5)	C31—C30—H30	127.4
C31—N25—N24	106.2 (5)	N25—C31—C30	111.1 (7)
C31—N25—Cu2	140.8 (5)	N25—C31—H31	124.4
N24—N25—Cu2	112.9 (4)	C30—C31—H31	124.4
N1—C1—C2	111.2 (6)	O4—C11—O3	108.8 (5)
N1—C1—H1	124.4	O4—C11—O1	108.6 (4)
C2—C1—H1	124.4	O3—C11—O1	110.2 (4)
C3—C2—C1	105.9 (6)	O4—C11—O2	107.7 (4)
C3—C2—H2	127.1	O3—C11—O2	109.7 (4)
C1—C2—H2	127.1	O1—C11—O2	111.8 (4)
N2—C3—C2	107.2 (6)	C11—O4—Cu2	138.2 (3)
N2—C3—H3	126.4	O7—C12—O5	109.1 (5)
C2—C3—H3	126.4	O7—C12—O6	110.0 (4)
N3—C4—C5	121.1 (6)	O5—C12—O6	107.7 (4)

N3—C4—N2	112.6 (6)	O7—C12—O8	108.8 (4)
C5—C4—N2	126.3 (6)	O5—C12—O8	109.4 (4)
C6—C5—C4	116.8 (6)	O6—C12—O8	111.8 (3)
C6—C5—H5	121.6	Cl2—O5—Cu1	136.7 (3)
N3—Cu1—N1—C1	-179.3 (9)	C4—N3—C8—N4	177.2 (6)
N5—Cu1—N1—C1	-175.8 (7)	Cu1—N3—C8—N4	2.6 (7)
N3—Cu1—N1—N2	-1.0 (4)	C6—C7—C8—N3	2.4 (10)
N5—Cu1—N1—N2	2.6 (9)	C6—C7—C8—N4	-178.5 (6)
C1—N1—N2—C3	0.8 (8)	N5—N4—C8—N3	-2.6 (8)
Cu1—N1—N2—C3	-178.2 (5)	C9—N4—C8—N3	-179.9 (7)
C1—N1—N2—C4	178.6 (6)	N5—N4—C8—C7	178.2 (6)
Cu1—N1—N2—C4	-0.3 (7)	C9—N4—C8—C7	0.9 (11)
N1—Cu1—N3—C4	2.3 (5)	N5—N4—C9—C10	-0.9 (8)
N5—Cu1—N3—C4	-176.3 (5)	C8—N4—C9—C10	176.6 (6)
N1—Cu1—N3—C8	177.0 (5)	N4—C9—C10—C11	1.3 (8)
N5—Cu1—N3—C8	-1.6 (5)	N4—N5—C11—C10	0.8 (8)
C9—N4—N5—C11	0.0 (8)	Cu1—N5—C11—C10	-177.9 (6)
C8—N4—N5—C11	-177.7 (6)	C9—C10—C11—N5	-1.4 (8)
C9—N4—N5—Cu1	179.2 (5)	N22—N21—C21—C22	1.1 (8)
C8—N4—N5—Cu1	1.4 (7)	Cu2—N21—C21—C22	-173.0 (6)
N3—Cu1—N5—C11	178.7 (8)	N21—C21—C22—C23	-1.4 (8)
N1—Cu1—N5—C11	175.1 (7)	N21—N22—C23—C22	-0.4 (8)
N3—Cu1—N5—N4	0.0 (4)	C24—N22—C23—C22	178.9 (7)
N1—Cu1—N5—N4	-3.5 (9)	C21—C22—C23—N22	1.0 (8)
N23—Cu2—N21—C21	177.2 (8)	C28—N23—C24—C25	-4.1 (10)
N25—Cu2—N21—C21	177.2 (7)	Cu2—N23—C24—C25	179.6 (5)
N23—Cu2—N21—N22	3.4 (4)	C28—N23—C24—N22	178.0 (6)
N25—Cu2—N21—N22	3.3 (8)	Cu2—N23—C24—N22	1.6 (7)
C21—N21—N22—C23	-0.4 (7)	C23—N22—C24—N23	-177.7 (6)
Cu2—N21—N22—C23	175.7 (4)	N21—N22—C24—N23	1.5 (8)
C21—N21—N22—C24	-179.8 (6)	C23—N22—C24—C25	4.5 (12)
Cu2—N21—N22—C24	-3.7 (7)	N21—N22—C24—C25	-176.3 (7)
N25—Cu2—N23—C28	0.7 (5)	N23—C24—C25—C26	3.2 (10)
N21—Cu2—N23—C28	-179.2 (5)	N22—C24—C25—C26	-179.3 (7)
N25—Cu2—N23—C24	177.1 (5)	C24—C25—C26—C27	-1.8 (11)
N21—Cu2—N23—C24	-2.9 (5)	C25—C26—C27—C28	1.2 (10)
C29—N24—N25—C31	0.0 (7)	C24—N23—C28—N24	-177.3 (6)
C28—N24—N25—C31	-177.8 (5)	Cu2—N23—C28—N24	-1.0 (7)
C29—N24—N25—Cu2	177.7 (4)	C24—N23—C28—C27	3.6 (10)
C28—N24—N25—Cu2	-0.1 (7)	Cu2—N23—C28—C27	179.9 (5)
N23—Cu2—N25—C31	176.2 (8)	C29—N24—C28—N23	-176.4 (7)
N21—Cu2—N25—C31	176.2 (6)	N25—N24—C28—N23	0.6 (8)
N23—Cu2—N25—N24	-0.3 (4)	C29—N24—C28—C27	2.7 (11)
N21—Cu2—N25—N24	-0.3 (9)	N25—N24—C28—C27	179.7 (6)
N2—N1—C1—C2	0.2 (7)	C26—C27—C28—N23	-2.1 (10)
Cu1—N1—C1—C2	178.7 (6)	C26—C27—C28—N24	178.9 (6)
N1—C1—C2—C3	-1.1 (8)	C28—N24—C29—C30	176.7 (7)

N1—N2—C3—C2	-1.5 (9)	N25—N24—C29—C30	-0.5 (7)
C4—N2—C3—C2	-178.9 (7)	N24—C29—C30—C31	0.8 (8)
C1—C2—C3—N2	1.5 (8)	N24—N25—C31—C30	0.5 (7)
C8—N3—C4—C5	3.3 (10)	Cu2—N25—C31—C30	-176.1 (6)
Cu1—N3—C4—C5	177.9 (5)	C29—C30—C31—N25	-0.8 (8)
C8—N3—C4—N2	-177.7 (6)	O3—Cl1—O4—Cu2	-112.2 (6)
Cu1—N3—C4—N2	-3.1 (7)	O1—Cl1—O4—Cu2	7.8 (8)
C3—N2—C4—N3	179.5 (7)	O2—Cl1—O4—Cu2	129.0 (6)
N1—N2—C4—N3	2.2 (8)	N23—Cu2—O4—Cl1	76.3 (7)
C3—N2—C4—C5	-1.6 (12)	N25—Cu2—O4—Cl1	-1.2 (7)
N1—N2—C4—C5	-178.9 (6)	N21—Cu2—O4—Cl1	156.3 (7)
N3—C4—C5—C6	-2.0 (10)	O7—Cl2—O5—Cu1	95.0 (8)
N2—C4—C5—C6	179.1 (7)	O6—Cl2—O5—Cu1	-145.6 (6)
C4—C5—C6—C7	1.0 (11)	O8—Cl2—O5—Cu1	-23.9 (8)
C5—C6—C7—C8	-1.2 (11)	N3—Cu1—O5—Cl2	-53.7 (7)
C4—N3—C8—C7	-3.6 (10)	N1—Cu1—O5—Cl2	-132.7 (8)
Cu1—N3—C8—C7	-178.1 (5)	N5—Cu1—O5—Cl2	25.0 (8)

(II) dibromo[2,6-bis(pyrazol-1-yl)pyridine]copper(II)*Crystal data*[CuBr₂(C₁₁H₉N₅)] $M_r = 434.58$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 11.0056 (2) \text{ \AA}$ $b = 7.8940 (1) \text{ \AA}$ $c = 15.2370 (2) \text{ \AA}$ $\beta = 93.856 (1)^\circ$ $V = 1320.77 (3) \text{ \AA}^3$ $Z = 4$ $F(000) = 836$ *Data collection*Bruker SMART 6K CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8 pixels mm⁻¹ ω and φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 1998)

 $T_{\min} = 0.206$, $T_{\max} = 0.249$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.023$ $wR(F^2) = 0.055$ $S = 1.03$

4675 reflections

172 parameters

0 restraints

10000 integrated reflections used for unit cell
measurement. $D_x = 2.186 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 10000 reflections

 $\theta = 1.8\text{--}32.9^\circ$ $\mu = 7.70 \text{ mm}^{-1}$ $T = 120 \text{ K}$

Tube, green

 $0.30 \times 0.27 \times 0.25 \text{ mm}$

24033 measured reflections

4675 independent reflections

3978 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.034$ $\theta_{\text{max}} = 32.5^\circ$, $\theta_{\text{min}} = 1.9^\circ$ $h = -16 \rightarrow 16$ $k = -11 \rightarrow 11$ $l = -23 \rightarrow 23$ Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 0.8921P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$

$$\Delta\rho_{\max} = 0.61 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The absorption correction was done with *SADABS*, μ^*r . The radius was calculated from the estimation of the crystal being a sphere ($r = 0.16 \text{ mm}$). The μ coefficient is calculated from the program *FPrime* (Program *FPrime* for Windows 1.0 for calculating real and anomalous X-ray dispersion coefficients, R-B. Von Dreele, 1994).

The data collection nominally covered over a full sphere of reciprocal space, by a combination of 3 sets of ω scans and 1 of a φ scan. Each scan was exposed for 3 s covering 0.3° in ω or φ . No sign of crystal decay was observed.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.728141 (18)	0.90095 (3)	0.113100 (14)	0.01129 (5)
Br1	0.837301 (15)	0.61243 (2)	0.115767 (11)	0.01398 (4)
Br2	0.650512 (16)	0.94056 (2)	0.254749 (11)	0.01595 (5)
N1	0.87207 (13)	1.0590 (2)	0.13190 (9)	0.0133 (3)
N2	0.90523 (13)	1.13552 (19)	0.05633 (9)	0.0124 (3)
N3	0.74678 (12)	0.98764 (19)	-0.00757 (9)	0.0110 (3)
N4	0.57702 (13)	0.83521 (19)	-0.04324 (9)	0.0119 (3)
N5	0.57788 (13)	0.80694 (19)	0.04589 (9)	0.0127 (3)
C1	0.95340 (16)	1.1111 (2)	0.19455 (12)	0.0153 (3)
H1	0.9540	1.0790	0.2533	0.018*
C2	1.03860 (16)	1.2215 (2)	0.15992 (12)	0.0159 (3)
H2	1.1042	1.2742	0.1904	0.019*
C3	1.00504 (15)	1.2353 (2)	0.07225 (12)	0.0144 (3)
H3	1.0431	1.3004	0.0313	0.017*
C4	0.83384 (15)	1.0993 (2)	-0.02140 (11)	0.0117 (3)
C5	0.84967 (16)	1.1683 (2)	-0.10355 (11)	0.0146 (3)
H5	0.9102	1.2476	-0.1123	0.018*
C6	0.76983 (16)	1.1120 (2)	-0.17227 (12)	0.0163 (3)
H6	0.7787	1.1526	-0.2288	0.020*
C7	0.67706 (16)	0.9967 (2)	-0.15862 (11)	0.0145 (3)
H7	0.6240	0.9591	-0.2046	0.017*
C8	0.66796 (15)	0.9409 (2)	-0.07314 (11)	0.0120 (3)
C9	0.48000 (15)	0.7573 (2)	-0.08654 (12)	0.0152 (3)
H9	0.4601	0.7593	-0.1468	0.018*
C10	0.41726 (15)	0.6752 (2)	-0.02408 (12)	0.0159 (3)
H10	0.3469	0.6106	-0.0334	0.019*
C11	0.48184 (15)	0.7096 (2)	0.05683 (12)	0.0150 (3)
H11	0.4600	0.6692	0.1109	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00993 (9)	0.01347 (10)	0.01054 (9)	-0.00080 (7)	0.00120 (7)	0.00041 (7)
Br1	0.01222 (8)	0.01348 (9)	0.01613 (8)	0.00164 (6)	0.00024 (6)	0.00060 (6)
Br2	0.01605 (8)	0.01973 (9)	0.01256 (8)	0.00186 (6)	0.00462 (6)	0.00079 (6)
N1	0.0134 (6)	0.0151 (7)	0.0114 (6)	-0.0011 (5)	0.0019 (5)	-0.0002 (5)
N2	0.0113 (6)	0.0141 (7)	0.0118 (6)	-0.0005 (5)	0.0016 (5)	0.0005 (5)
N3	0.0104 (6)	0.0113 (7)	0.0114 (6)	0.0005 (5)	0.0009 (5)	-0.0010 (5)
N4	0.0099 (6)	0.0132 (7)	0.0127 (6)	0.0002 (5)	0.0004 (5)	-0.0006 (5)
N5	0.0117 (6)	0.0144 (7)	0.0122 (6)	0.0010 (5)	0.0023 (5)	0.0005 (5)
C1	0.0147 (7)	0.0174 (8)	0.0136 (7)	-0.0005 (6)	0.0000 (6)	-0.0022 (6)
C2	0.0132 (7)	0.0154 (8)	0.0189 (8)	0.0009 (6)	-0.0012 (6)	-0.0051 (7)
C3	0.0111 (7)	0.0125 (8)	0.0199 (8)	0.0002 (6)	0.0023 (6)	-0.0021 (6)
C4	0.0101 (7)	0.0121 (8)	0.0132 (7)	0.0018 (6)	0.0015 (5)	-0.0013 (6)
C5	0.0144 (7)	0.0152 (8)	0.0145 (7)	-0.0006 (6)	0.0032 (6)	0.0018 (6)
C6	0.0178 (8)	0.0187 (9)	0.0127 (8)	0.0021 (7)	0.0028 (6)	0.0025 (6)
C7	0.0141 (7)	0.0171 (8)	0.0121 (7)	0.0017 (6)	-0.0001 (6)	-0.0010 (6)
C8	0.0105 (7)	0.0115 (8)	0.0142 (7)	0.0014 (6)	0.0017 (5)	-0.0016 (6)
C9	0.0112 (7)	0.0149 (8)	0.0189 (8)	0.0018 (6)	-0.0017 (6)	-0.0041 (6)
C10	0.0110 (7)	0.0127 (8)	0.0239 (9)	0.0004 (6)	0.0007 (6)	-0.0033 (7)
C11	0.0123 (7)	0.0125 (8)	0.0204 (8)	0.0006 (6)	0.0036 (6)	0.0000 (6)

Geometric parameters (Å, °)

Cu1—Br1	2.5740 (3)	C1—H1	0.9300
Cu1—Br2	2.3946 (3)	C2—C3	1.366 (2)
Cu1—N1	2.0218 (15)	C2—H2	0.9300
Cu1—N3	1.9854 (14)	C3—H3	0.9300
Cu1—N5	2.0264 (15)	C4—C5	1.387 (2)
N1—C1	1.329 (2)	C5—C6	1.394 (3)
N1—N2	1.371 (2)	C5—H5	0.9300
N2—C3	1.360 (2)	C6—C7	1.394 (3)
N2—C4	1.406 (2)	C6—H6	0.9300
N3—C4	1.329 (2)	C7—C8	1.385 (2)
N3—C8	1.331 (2)	C7—H7	0.9300
N4—C9	1.363 (2)	C9—C10	1.375 (3)
N4—N5	1.376 (2)	C9—H9	0.9300
N4—C8	1.402 (2)	C10—C11	1.407 (3)
N5—C11	1.327 (2)	C10—H10	0.9300
C1—C2	1.408 (3)	C11—H11	0.9300
N3—Cu1—N1	77.86 (6)	C3—C2—H2	127.1
N3—Cu1—N5	77.87 (6)	C1—C2—H2	127.1
N1—Cu1—N5	154.50 (6)	N2—C3—C2	106.88 (16)
N3—Cu1—Br2	148.76 (4)	N2—C3—H3	126.6
N1—Cu1—Br2	96.62 (4)	C2—C3—H3	126.6
N5—Cu1—Br2	100.07 (4)	N3—C4—C5	122.62 (16)

N3—Cu1—Br1	104.03 (4)	N3—C4—N2	111.67 (14)
N1—Cu1—Br1	100.58 (4)	C5—C4—N2	125.71 (16)
N5—Cu1—Br1	92.76 (4)	C4—C5—C6	116.24 (16)
Br2—Cu1—Br1	107.203 (10)	C4—C5—H5	121.9
C1—N1—N2	105.22 (14)	C6—C5—H5	121.9
C1—N1—Cu1	140.90 (13)	C7—C6—C5	121.81 (16)
N2—N1—Cu1	113.77 (11)	C7—C6—H6	119.1
C3—N2—N1	111.26 (14)	C5—C6—H6	119.1
C3—N2—C4	131.82 (15)	C8—C7—C6	116.62 (16)
N1—N2—C4	116.92 (14)	C8—C7—H7	121.7
C4—N3—C8	120.36 (15)	C6—C7—H7	121.7
C4—N3—Cu1	119.73 (11)	N3—C8—C7	122.23 (16)
C8—N3—Cu1	119.81 (12)	N3—C8—N4	111.38 (14)
C9—N4—N5	110.96 (14)	C7—C8—N4	126.37 (16)
C9—N4—C8	131.61 (15)	N4—C9—C10	106.92 (16)
N5—N4—C8	117.35 (14)	N4—C9—H9	126.5
C11—N5—N4	105.39 (14)	C10—C9—H9	126.5
C11—N5—Cu1	141.15 (12)	C9—C10—C11	105.55 (15)
N4—N5—Cu1	113.00 (10)	C9—C10—H10	127.2
N1—C1—C2	110.82 (16)	C11—C10—H10	127.2
N1—C1—H1	124.6	N5—C11—C10	111.17 (16)
C2—C1—H1	124.6	N5—C11—H11	124.4
C3—C2—C1	105.81 (16)	C10—C11—H11	124.4
N3—Cu1—N1—C1	-176.2 (2)	Cu1—N1—C1—C2	175.94 (15)
N5—Cu1—N1—C1	165.68 (17)	N1—C1—C2—C3	0.2 (2)
Br2—Cu1—N1—C1	35.0 (2)	N1—N2—C3—C2	0.86 (19)
Br1—Cu1—N1—C1	-74.0 (2)	C4—N2—C3—C2	-179.01 (17)
N3—Cu1—N1—N2	-0.80 (11)	C1—C2—C3—N2	-0.65 (19)
N5—Cu1—N1—N2	-18.9 (2)	C8—N3—C4—C5	-2.0 (3)
Br2—Cu1—N1—N2	-149.61 (11)	Cu1—N3—C4—C5	-178.21 (13)
Br1—Cu1—N1—N2	101.45 (11)	C8—N3—C4—N2	178.29 (15)
C1—N1—N2—C3	-0.71 (19)	Cu1—N3—C4—N2	2.04 (19)
Cu1—N1—N2—C3	-177.72 (11)	C3—N2—C4—N3	177.16 (17)
C1—N1—N2—C4	179.19 (15)	N1—N2—C4—N3	-2.7 (2)
Cu1—N1—N2—C4	2.17 (18)	C3—N2—C4—C5	-2.6 (3)
Br2—Cu1—N3—C4	81.95 (15)	N1—N2—C4—C5	177.56 (16)
Br1—Cu1—N3—C4	-98.78 (12)	N3—C4—C5—C6	-1.0 (3)
Br2—Cu1—N3—C8	-94.32 (14)	N2—C4—C5—C6	178.75 (16)
Br1—Cu1—N3—C8	84.96 (13)	C4—C5—C6—C7	1.8 (3)
N1—Cu1—N3—C4	-0.74 (12)	C5—C6—C7—C8	0.1 (3)
N5—Cu1—N3—C4	171.40 (14)	C4—N3—C8—C7	4.2 (3)
N1—Cu1—N3—C8	-177.00 (14)	Cu1—N3—C8—C7	-179.61 (13)
N5—Cu1—N3—C8	-4.87 (13)	C4—N3—C8—N4	-174.38 (14)
C9—N4—N5—C11	0.78 (19)	Cu1—N3—C8—N4	1.86 (19)
C8—N4—N5—C11	177.90 (15)	C6—C7—C8—N3	-3.2 (3)
C9—N4—N5—Cu1	174.68 (11)	C6—C7—C8—N4	175.11 (16)
C8—N4—N5—Cu1	-8.20 (18)	C9—N4—C8—N3	-179.27 (17)

N3—Cu1—N5—C11	177.3 (2)	N5—N4—C8—N3	4.3 (2)
N1—Cu1—N5—C11	-164.57 (17)	C9—N4—C8—C7	2.3 (3)
Br2—Cu1—N5—C11	-34.4 (2)	N5—N4—C8—C7	-174.13 (16)
Br1—Cu1—N5—C11	73.57 (19)	N5—N4—C9—C10	-0.61 (19)
N3—Cu1—N5—N4	6.73 (11)	C8—N4—C9—C10	-177.19 (17)
N1—Cu1—N5—N4	24.8 (2)	N4—C9—C10—C11	0.20 (19)
Br2—Cu1—N5—N4	154.95 (10)	N4—N5—C11—C10	-0.64 (19)
Br1—Cu1—N5—N4	-97.03 (11)	Cu1—N5—C11—C10	-171.68 (14)
N2—N1—C1—C2	0.3 (2)	C9—C10—C11—N5	0.3 (2)
