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# The copper(II) complexes di-$\mu$-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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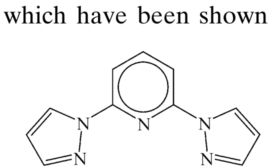
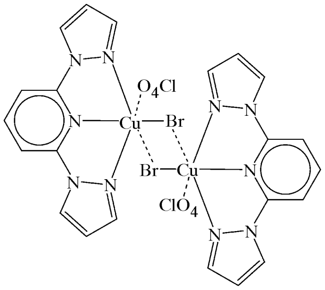
The two title compounds, di-$\mu$-bromo-bis{[2,6-bis(pyrazol-1-yl-$\kappa N^2$)pyridine-$\kappa N$](perchlorato-$\kappa O$)copper(II)}, $[Cu_2Br_2(ClO_4)_2(C_{11}H_9N_5)_2]$, (I), and [2,6-bis(pyrazol-1-yl)pyridine]dibromocopper(II), $[CuBr_2(C_{11}H_9N_5)]$, (II), were synthesized by only slight modifications of the same reaction; compound (II) was formed by adding one molar equivalent of pyrazole ($C_3N_2H_4$) to the reaction mixture of (I). Compound (I) is a bromo-bridged dinuclear copper(II) compound stabilized by weak interactions with the perchlorate anions ($ClO_4^-$), while (II) is a related mononuclear species, which has a distorted square-pyramidal geometry.

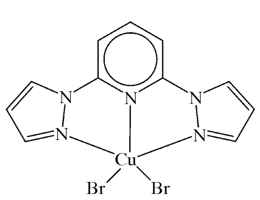
## Comment

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.


bppy

The bromine-bridged dicopper complex $[Cu_2Br_2(ClO_4)_2(bppy)_2]$ (I), and the monocopper complex $[CuBr_2(bppy)]$, (II), were prepared *via* essentially the same route, except that pyrazole was added to the reaction mixture that yielded (II).


(I)


(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 $ClO_4^-$ 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 $ClO_4^-$ 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 $CuN_3Br$ 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],

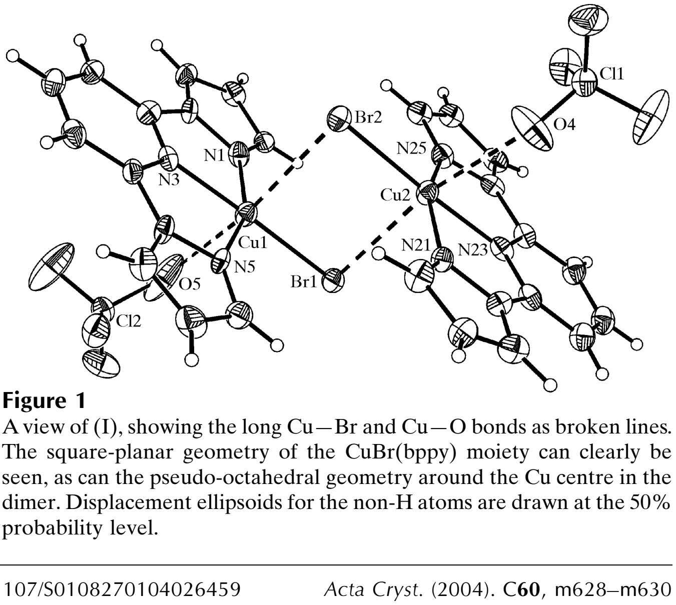


**Figure 1**
A view of (I), showing the long Cu—Br and Cu—O bonds as broken lines. The square-planar geometry of the CuBr(bppy) moiety can clearly be seen, as can the pseudo-octahedral geometry around the Cu centre in the dimer. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability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

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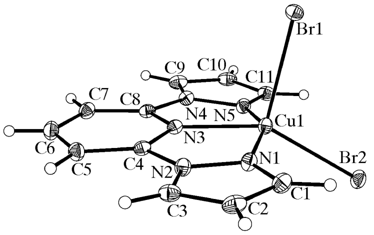

**Figure 2**
A view of (II), showing the square-pyramidal geometry around the Cu centre. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

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 anistropic 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-cordinate 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 $Cu(ClO_4)_2·6H_2O$ (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 $Cu(ClO_4)_2·6H_2O$, 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*

$[Cu_2Br_2(ClO_4)_2(C_{11}H_9N_5)_2]$
$M_r = 908.26$
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) Å$^3$
$Z = 2$

$D_x = 2.089$ 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
$\omega$ and $\varphi$ 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 $I > 2\sigma(I)$
$R_{int} = 0.092$
$\theta_{max} = 32.5°$
$h = -11 \rightarrow 11$
$k = -22 \rightarrow 22$
$l = -19 \rightarrow 18$

*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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.66$ e Å$^{-3}$
$\Delta\rho_{min} = -1.13$ 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*

$[CuBr_2(C_{11}H_9N_5)]$
$M_r = 434.58$
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) Å$^3$
$Z = 4$

$D_x = 2.186$ 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
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.206$, $T_{\max} = 0.249$
24 033 measured reflections
4675 independent reflections
3978 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 32.5°$
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -23 \rightarrow 23$

*Refinement*

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

**Table 2**
Selected geometric parameters (Å, °) 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 (C—H = 0.93 Å), with isotropic displacement parameters fixed at 120% of the $U_{\rm eq}$ 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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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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