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## Key indicators

Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.010$  Å  
 $R$  factor = 0.044  
 $wR$  factor = 0.114  
Data-to-parameter ratio = 14.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis( $\mu$ -4-nitropyridine  $N$ -oxide- $\kappa^2\text{O}:\text{O}$ )-  
bis[dibromocopper(II)]

The title compound,  $[\text{Cu}_2\text{Br}_4(\text{C}_5\text{H}_4\text{N}_2\text{O}_3)_2]$ , is a centrosymmetric dimer that contains a central planar  $\text{Cu}_2\text{O}_2$  rhombus with the O atom of the  $N$ -oxide group bridging two Cu atoms [ $\text{Cu}-\text{O}-\text{Cu} = 109.08$  (19) $^\circ$  and  $\text{O}-\text{Cu}-\text{O} = 70.92$  (19) $^\circ$ ]. The two-dimensional sheet structure is built up *via* semi-coordinate intermolecular  $\text{Cu}\cdots\text{Br}$  bonds [3.226 (1) and 3.810 (1) Å] and weak hydrogen bonding [ $\text{C}\cdots\text{Br} = 3.733$  (7), 3.781 (7) and 3.830 (7) Å].

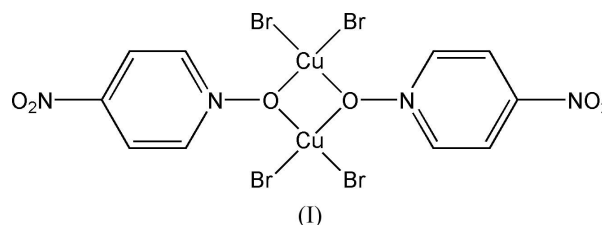
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## Comment

The molecule of the title compound, (I), lies on a center of inversion at  $(-x, 1-y, 1-z)$ . As shown in Fig. 1, the central core consists of a  $\text{Cu}_2\text{O}_2$  rhombus with the O atoms of the  $N$ -oxide ligand bridging the two Cu atoms. The  $\text{Cu}-\text{O}-\text{Cu}$  angles are  $109.08$  (19) $^\circ$  and  $\text{O}-\text{Cu}-\text{O}$  angles are  $70.92$  (19) $^\circ$ . The  $\text{CuBr}_2$  planes are both inclined at  $10.8$  (1) $^\circ$  to the central  $\text{Cu}_2\text{O}_2$  planar core. The perpendicular  $N$ -oxide ligands are also tilted out of the plane of the central core by  $71.6$  (2) $^\circ$ . The terminal nitro groups are almost coplanar with the pyridine rings [8.5 (1.5) $^\circ$ ], indicating extended conjugation of the aromatic system.



The extended two-dimensional system is more complicated. There are two semi-coordinate  $\text{Cu}\cdots\text{Br}$  bonds that complete the Cu coordination sphere, *viz.*  $\text{Cu1}-\text{Br1}^{\text{ii}}$  [3.226 (1) Å; symmetry code: (ii)  $\frac{1}{2}-x, y-\frac{1}{2}, z$ ] and  $\text{Cu1}-\text{Br1}^{\text{iii}}$

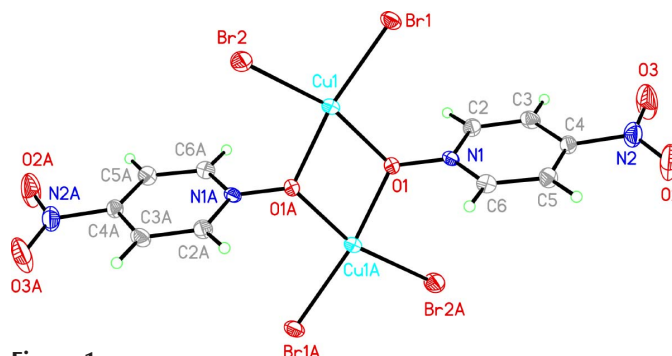
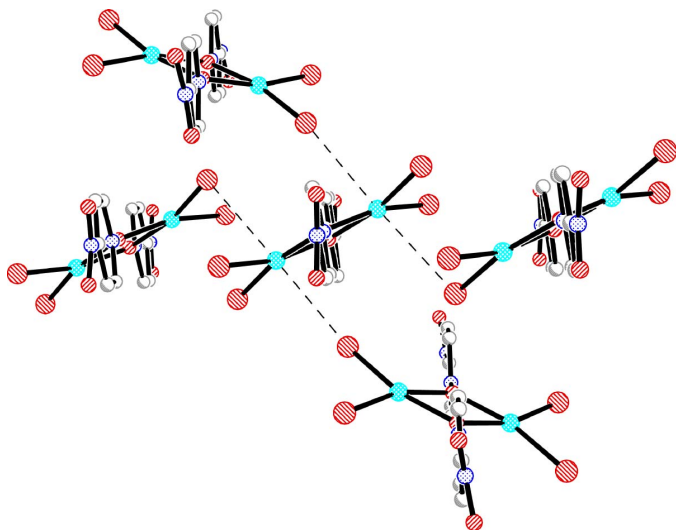
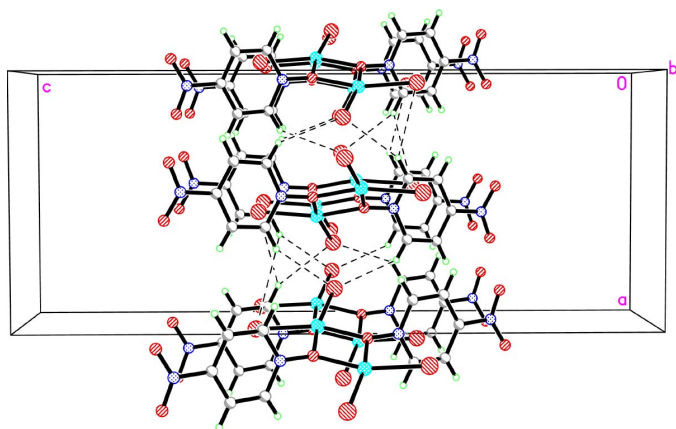


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids. The suffix A indicates the symmetry code  $(-x, 1-y, 1-z)$ .


**Figure 2**

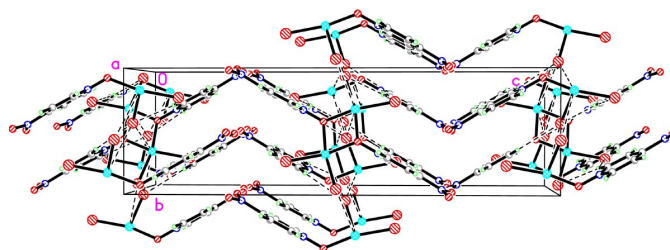
The complete coordination sphere around the Cu centers for the central molecule only. Dashed lines indicate semi-coordinate bonding. H atoms have been omitted for clarity.


**Figure 3**

Hydrogen bonding (dashed lines) within the extended sheet.

[3.810 (1) Å; symmetry code: (iii)  $-x, 2 - y, 1 - z$ ; see Table 1 for the complete geometrical parameters], resulting in a very distorted octahedron which is shown in Fig. 2. This semi-coordinate Cu $\cdots$ Br bonding links the Cu<sub>2</sub>O<sub>2</sub>Br<sub>4</sub> units into a sheet structure parallel to the (001) plane in the unit cell. The inorganic core is sheathed by the 4-nitropyridine groups, which also hold the sheet together *via* non-classical bifurcated hydrogen bonding (see Table 2) between C6 and Br1<sup>i</sup> and Br2<sup>i</sup> [symmetry code: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$ ] and a weak interaction between C2 and Br1<sup>ii</sup>. This synthon is shown in Fig. 3. The terminal nitro groups on adjacent sheets interdigitate and form a herring-bone pattern (Fig. 4).

There are relatively few *N*-oxide dihalo copper(II) structures in the Cambridge Structural Database (Version 5.26; Allen, 2002). Excluding solvent-coordinated or internally coordinated copper systems there are only nine reports: CSD refcode CUCPYO (Schäfer *et al.*, 1965), CUCPYO11 (Sager *et al.*, 1967), DURYIY (Nepveu *et al.*, 1986), HULZOD (Ivashevskaja *et al.*, 2002), PHPYOC, PYOCDB (Watson & Johnson, 1971), QQQBWD, QQQBWG, QQQBWJ (Kidd *et*


**Figure 4**

Packing of (I) viewed down the *a* axis.

*al.*, 1967). Only DURYIY and PYOCDB are bromo species, the remainder are all chloro-substituted. The title compound, (I), has many similarities to the above compounds.

## Experimental

A 1:1 solution of 4-nitropyridine *N*-oxide and CuBr<sub>2</sub> in ethanol was left to slowly evaporate over 7 d. Just before complete dryness, the product formed as red plates in *ca* 60% yield.

### Crystal data

[Cu<sub>2</sub>Br<sub>4</sub>(C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 726.92  
 Orthorhombic, *Pbca*  
*a* = 10.044 (2) Å  
*b* = 7.2816 (15) Å  
*c* = 25.006 (5) Å  
*V* = 1828.9 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.640 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 5682 reflections  
 $\theta$  = 2.6–27.0°  
 $\mu$  = 11.10 mm<sup>-1</sup>  
*T* = 297 (2) K  
 Plate, red  
 0.44 × 0.15 × 0.01 mm

### Data collection

Bruker–Siemens SMART APEX diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2001)  
*T<sub>min</sub>* = 0.081, *T<sub>max</sub>* = 0.898  
 24047 measured reflections

1654 independent reflections  
 1400 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.080  
 $\theta_{\max}$  = 25.2°  
*h* = −12 → 12  
*k* = −8 → 8  
*l* = −30 → 30

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.044  
*wR*(*F*<sup>2</sup>) = 0.114  
*S* = 1.07  
 1654 reflections  
 118 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 9.3212P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.92 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Br1—Cu1	2.3403 (10)	Cu1—O1 <sup>i</sup>	2.034 (4)
Br2—Cu1	2.3178 (11)	Cu1—Br1 <sup>ii</sup>	3.2261 (11)
Cu1—O1	1.982 (4)	Cu1—Br1 <sup>iii</sup>	3.8103 (12)
O1—Cu1—O1 <sup>i</sup>	70.92 (19)	Br2—Cu1—Br1 <sup>ii</sup>	110.31 (4)
O1—Cu1—Br2	162.07 (13)	Br1—Cu1—Br1 <sup>ii</sup>	88.09 (3)
O1 <sup>i</sup> —Cu1—Br2	93.35 (12)	O1—Cu1—Br1 <sup>iii</sup>	84.98 (13)
O1—Cu1—Br1	97.70 (13)	O1 <sup>i</sup> —Cu1—Br1 <sup>iii</sup>	115.93 (13)
O1 <sup>i</sup> —Cu1—Br1	166.38 (13)	Br2—Cu1—Br1 <sup>iii</sup>	94.74 (4)
Br2—Cu1—Br1	98.93 (4)	Br1—Cu1—Br1 <sup>iii</sup>	69.07 (3)
O1—Cu1—Br1 <sup>ii</sup>	76.86 (13)	Br1 <sup>ii</sup> —Cu1—Br1 <sup>iii</sup>	148.65 (3)
O1 <sup>i</sup> —Cu1—Br1 <sup>ii</sup>	82.11 (13)	Cu1—O1—Cu1 <sup>i</sup>	109.08 (19)

Symmetry codes: (i)  $-x, 1 - y, 1 - z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, z$ ; (iii)  $-x, 2 - y, 1 - z$ .

**Table 2**  
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6–H6A $\cdots$ Br1 <sup>iv</sup>	0.93	2.89	3.733 (7)	151
C6–H6A $\cdots$ Br2 <sup>iv</sup>	0.93	3.06	3.781 (7)	136
C2–H2A $\cdots$ Br1 <sup>ii</sup>	0.93	3.05	3.830 (7)	143

Symmetry codes: (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, z$ ; (iv)  $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$ .

All H atoms were positioned geometrically and refined using a riding model, with  $U_{\text{iso}}(\text{H})$  values constrained to be  $1.2U_{\text{eq}}$  of the carrier atom and  $C-H = 0.93$  Å. There are large residuals of *ca*  $1.92 \text{ e } \text{Å}^{-3}$  approximately  $1.1$  Å from Br2 and Br1. These are due to imperfectly corrected absorption effects and could not be eliminated.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.  
 Bruker (2001). *SMART* (Version 5.626), *SAINT-Plus* (Version 6.36a), *SADABS* (Version 2.05) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.  
 Ivashevskaja, S. N., Aleshina, L. A., Andreev, V. P., Nizhnik, Y. P. & Chernyshev, V. V. (2002). *Acta Cryst.* **E58**, m721–m723.  
 Kidd, M. R., Sager, R. S. & Watson, W. H. (1967). *Inorg. Chem.* **6**, 946–950.  
 Sager, R. S., Williams, R. J. & Watson, W. H. (1967). *Inorg. Chem.* **6**, 951–955.  
 Schäfer, H. L., Morrow, J. C. & Smith, H. M. (1965). *J. Chem. Phys.* **42**, 504–508.  
 Nepveu, F., Astheimer, H., Paulus, H. & Haase, W. (1986). *J. Coord. Chem.* **14**, 269–274.  
 Watson, W. H. & Johnson, D. R. (1971). *J. Coord. Chem.* **1**, 145–153.