

Dibromidotetrakis(1*H*-indazole- κ N²)copper(II)

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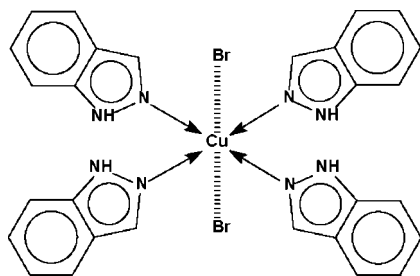
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.012$ Å; R factor = 0.061; wR factor = 0.228; data-to-parameter ratio = 17.9.

The Cu atom in the title compound, $[\text{CuBr}_2(\text{C}_7\text{H}_6\text{N}_2)_4]$, is surrounded by four N-heterocycles that define an N_4 square-planar geometry. The coordination geometry is distorted towards an elongated octahedron owing to the presence of the two Br^- anions, which are located at about 3 Å above and below the square plane. There are two independent molecules in the asymmetric unit, each with their Cu atom lying on an inversion centre.

Related literature

For related structures, see Hossaini Sadr *et al.* (2004, 2005, 2006). For related literature, see: Allen (2002).



Experimental

Crystal data

$[\text{CuBr}_2(\text{C}_7\text{H}_6\text{N}_2)_4]$
 $M_r = 695.91$
 Triclinic, $P\bar{1}$
 $a = 10.338$ (1) Å
 $b = 10.923$ (1) Å

$c = 13.730$ (1) Å
 $\alpha = 72.545$ (3)°
 $\beta = 77.329$ (3)°
 $\gamma = 73.890$ (3)°
 $V = 1405.3$ (3) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.65$ mm⁻¹

$T = 295$ (2) K
 $0.24 \times 0.21 \times 0.12$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.073$, $T_{\max} = 0.668$

13779 measured reflections
 6389 independent reflections
 2895 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.228$
 $S = 1.13$
 6389 reflections
 356 parameters

12 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.65$ e Å⁻³
 $\Delta\rho_{\min} = -1.00$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------|-----------|---------|-----------|
| Cu1—N1 | 2.027 (5) | Cu2—N5 | 2.024 (7) |
| Cu1—N3 | 2.008 (6) | Cu2—N7 | 2.023 (6) |
| Cu1—Br1 | 3.033 (1) | Cu2—Br2 | 2.980 (1) |

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2226).

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supplementary materials

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Dibromidotetrakis(1*H*-indazole- κ N²)copper(II)

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Comment

Unlike benzimidazole, which affords a number of adducts with metal salts, indazole furnishes only few complexes (Cambridge Structural Database, Version 5.28; Allen, 2002). The present study of the copper dibromide adduct (I) follows previous studies on Cu complexes of pyrazole-based N-heterocycles (Hossaini Sadr *et al.*, 2005; 2006).

Two independent $[\text{Cu}(\text{C}_7\text{H}_6\text{N}_2)_4]^{2+}2\text{Br}^-$ formula units comprise the asymmetric unit in (I), each with the Cu atom situated on a center of inversion. Complex (I) is formally a salt (Fig. 1) owing to the large distance of the Br ions (more than 3 Å) above and below the N₄ square plane defined by the four N-heterocycles. In the corresponding imidazole adduct, one Br atom is covalently bonded whereas the other is uncoordinated, so that the geometry is a square pyramid (Hossaini Sadr *et al.*, 2004).

Experimental

Copper dibromide (0.05 g, 0.25 mmol) and indazole (0.12 g, 1 mmol) were dissolved in acetone (25 ml). Slow evaporation of the filtered solution yielded crystals.

Refinement

The C- and N-bound H atoms were placed in calculated positions and included in the refinement in the riding-model approximation with N—H = 0.86 Å and C—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) 1.2U_{\text{eq}}(\text{C},\text{N})$. The vibrations of the Cu atoms appeared elongated in the directions of the weakly associated Br anions and, accordingly, the displacement factors were restrained to be nearly isotropic. The final difference Fourier map had a maximum and minimum residual density peaks at 1.35 Å from Br1 and Br2, respectively {AU to confirm this}.

Figures

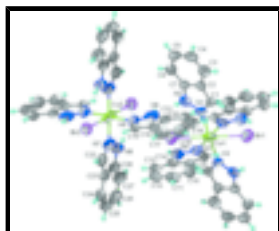


Fig. 1. Molecular structures of the two independent molecules of $[\text{Cu}(\text{C}_7\text{H}_6\text{N}_2)_4]^{2+} 2\text{Br}^-$ (I) showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radius. Each of the Cu atoms is located on a crystallographic center of inversion. The Cu...Br interactions are denoted by dashed lines.

Dibromidotetrakis(1*H*-indazole- κ N²)copper(II)

Crystal data

| | |
|---|---|
| [CuBr ₂ (C ₇ H ₆ N ₂) ₄] | $Z = 2$ |
| $M_r = 695.91$ | $F_{000} = 694$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.645 \text{ Mg m}^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation |
| $a = 10.338 (1) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $b = 10.923 (1) \text{ \AA}$ | Cell parameters from 7166 reflections |
| $c = 13.730 (1) \text{ \AA}$ | $\theta = 3.2\text{--}27.5^\circ$ |
| $\alpha = 72.545 (3)^\circ$ | $\mu = 3.65 \text{ mm}^{-1}$ |
| $\beta = 77.329 (3)^\circ$ | $T = 295 (2) \text{ K}$ |
| $\gamma = 73.890 (3)^\circ$ | Prism, blue |
| $V = 1405.3 (3) \text{ \AA}^3$ | $0.24 \times 0.21 \times 0.12 \text{ mm}$ |

Data collection

| | |
|---|--|
| Rigaku R-AXIS RAPID diffractometer | 6389 independent reflections |
| Radiation source: fine-focus sealed tube | 2895 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.046$ |
| Detector resolution: $10.000 \text{ pixels mm}^{-1}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| $T = 295(2) \text{ K}$ | $\theta_{\text{min}} = 3.2^\circ$ |
| ω scans | $h = -13 \rightarrow 13$ |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | $k = -11 \rightarrow 14$ |
| $T_{\text{min}} = 0.073$, $T_{\text{max}} = 0.668$ | $l = -17 \rightarrow 17$ |
| 13779 measured reflections | |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | H-atom parameters constrained |
| $wR(F^2) = 0.228$ | $w = 1/[\sigma^2(F_o^2) + (0.1018P)^2 + 0.0608P]$ |
| $S = 1.13$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 6389 reflections | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 356 parameters | $\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$ |
| 12 restraints | $\Delta\rho_{\text{min}} = -1.00 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 1997), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| | Extinction coefficient: $0.008 (2)$ |

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|-------------|----------------------------------|
| Br1 | 0.62566 (10) | 0.25866 (8) | 0.41676 (7) | 0.1011 (4) |
| Br2 | -0.25176 (8) | 0.40169 (7) | 1.09777 (6) | 0.0840 (3) |
| Cu1 | 0.5000 | 0.5000 | 0.5000 | 0.0843 (5) |
| Cu2 | 0.0000 | 0.5000 | 1.0000 | 0.1230 (8) |
| N1 | 0.5411 (5) | 0.3924 (6) | 0.6427 (4) | 0.0636 (14) |
| N2 | 0.5199 (6) | 0.4347 (6) | 0.7267 (5) | 0.0774 (16) |
| H2N | 0.4877 | 0.5155 | 0.7291 | 0.093* |
| N3 | 0.3196 (6) | 0.4493 (7) | 0.5367 (4) | 0.0748 (17) |
| N4 | 0.2108 (6) | 0.5102 (6) | 0.5891 (5) | 0.0803 (17) |
| H4N | 0.2071 | 0.5797 | 0.6078 | 0.096* |
| N5 | 0.0567 (9) | 0.3532 (6) | 0.9272 (5) | 0.093 (2) |
| N6 | 0.1763 (9) | 0.3169 (7) | 0.8743 (6) | 0.100 (2) |
| H6N | 0.2408 | 0.3579 | 0.8604 | 0.120* |
| N7 | -0.0951 (9) | 0.6246 (6) | 0.8816 (5) | 0.090 (2) |
| N8 | -0.0317 (7) | 0.7102 (6) | 0.8075 (5) | 0.0885 (19) |
| H8N | 0.0514 | 0.7141 | 0.8031 | 0.106* |
| C1 | 0.5920 (6) | 0.2639 (6) | 0.6683 (4) | 0.0569 (15) |
| H1 | 0.6170 | 0.2106 | 0.6226 | 0.068* |
| C2 | 0.6029 (6) | 0.2195 (6) | 0.7719 (5) | 0.0591 (15) |
| C3 | 0.6478 (8) | 0.0951 (8) | 0.8374 (6) | 0.084 (2) |
| H3 | 0.6801 | 0.0206 | 0.8120 | 0.101* |
| C4 | 0.6428 (7) | 0.0863 (9) | 0.9382 (6) | 0.090 (3) |
| H4 | 0.6683 | 0.0038 | 0.9828 | 0.108* |
| C5 | 0.6006 (8) | 0.1974 (10) | 0.9777 (6) | 0.091 (3) |
| H5 | 0.6017 | 0.1881 | 1.0471 | 0.109* |
| C6 | 0.5577 (7) | 0.3201 (9) | 0.9148 (6) | 0.086 (2) |
| H6 | 0.5296 | 0.3945 | 0.9404 | 0.103* |
| C7 | 0.5573 (6) | 0.3298 (6) | 0.8111 (4) | 0.0592 (15) |
| C8 | 0.2874 (6) | 0.3499 (7) | 0.5225 (5) | 0.0630 (16) |
| H8 | 0.3460 | 0.2906 | 0.4871 | 0.076* |
| C9 | 0.1562 (6) | 0.3431 (7) | 0.5663 (4) | 0.0604 (16) |
| C10 | 0.0743 (8) | 0.2577 (8) | 0.5751 (6) | 0.086 (2) |
| H10 | 0.1071 | 0.1862 | 0.5461 | 0.104* |
| C11 | -0.0530 (8) | 0.2800 (9) | 0.6261 (7) | 0.091 (2) |
| H11 | -0.1082 | 0.2229 | 0.6327 | 0.109* |
| C12 | -0.1034 (7) | 0.3866 (9) | 0.6692 (6) | 0.084 (2) |
| H12 | -0.1923 | 0.4004 | 0.7035 | 0.101* |
| C13 | -0.0257 (7) | 0.4712 (8) | 0.6621 (6) | 0.0763 (19) |
| H13 | -0.0599 | 0.5420 | 0.6919 | 0.092* |
| C14 | 0.1048 (6) | 0.4501 (6) | 0.6102 (5) | 0.0581 (15) |
| C15 | -0.0112 (7) | 0.2676 (7) | 0.9321 (5) | 0.0622 (16) |
| H15 | -0.1001 | 0.2704 | 0.9658 | 0.075* |
| C16 | 0.0607 (6) | 0.1736 (6) | 0.8832 (5) | 0.0578 (15) |
| C17 | 0.0283 (10) | 0.0657 (9) | 0.8687 (7) | 0.096 (3) |
| H17 | -0.0571 | 0.0472 | 0.8945 | 0.116* |

supplementary materials

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|-----|--------------|-------------|------------|-------------|
| C18 | 0.1251 (14) | -0.0105 (9) | 0.8162 (8) | 0.108 (3) |
| H18 | 0.1061 | -0.0843 | 0.8069 | 0.130* |
| C19 | 0.2487 (11) | 0.0154 (10) | 0.7764 (7) | 0.104 (3) |
| H19 | 0.3122 | -0.0410 | 0.7408 | 0.124* |
| C20 | 0.2836 (7) | 0.1224 (9) | 0.7868 (6) | 0.088 (2) |
| H20 | 0.3684 | 0.1409 | 0.7577 | 0.105* |
| C21 | 0.1863 (6) | 0.2026 (6) | 0.8430 (4) | 0.0564 (14) |
| C22 | -0.2200 (10) | 0.6462 (7) | 0.8630 (6) | 0.086 (2) |
| H22 | -0.2851 | 0.5999 | 0.9022 | 0.103* |
| C23 | -0.2393 (9) | 0.7522 (7) | 0.7731 (6) | 0.080 (2) |
| C24 | -0.3451 (10) | 0.8178 (9) | 0.7148 (8) | 0.103 (3) |
| H24 | -0.4286 | 0.7942 | 0.7328 | 0.124* |
| C25 | -0.3207 (13) | 0.9197 (9) | 0.6288 (7) | 0.112 (3) |
| H25 | -0.3900 | 0.9653 | 0.5893 | 0.135* |
| C26 | -0.1982 (13) | 0.9552 (10) | 0.6004 (7) | 0.113 (3) |
| H26 | -0.1866 | 1.0240 | 0.5423 | 0.135* |
| C27 | -0.0951 (11) | 0.8941 (8) | 0.6536 (6) | 0.104 (3) |
| H27 | -0.0121 | 0.9187 | 0.6346 | 0.124* |
| C28 | -0.1185 (9) | 0.7895 (7) | 0.7408 (6) | 0.080 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|-------------|------------|-------------|--------------|-------------|
| Br1 | 0.1416 (8) | 0.0637 (6) | 0.0882 (6) | 0.0001 (5) | -0.0230 (5) | -0.0221 (4) |
| Br2 | 0.0917 (6) | 0.0649 (5) | 0.0874 (6) | -0.0117 (4) | -0.0083 (4) | -0.0166 (4) |
| Cu1 | 0.0608 (7) | 0.1132 (11) | 0.0637 (7) | -0.0366 (7) | -0.0251 (6) | 0.0265 (7) |
| Cu2 | 0.232 (2) | 0.0513 (8) | 0.0766 (8) | 0.0341 (10) | -0.0776 (11) | -0.0246 (6) |
| N1 | 0.054 (3) | 0.085 (4) | 0.051 (3) | -0.021 (3) | -0.012 (2) | -0.007 (3) |
| N2 | 0.070 (3) | 0.069 (4) | 0.083 (4) | -0.011 (3) | -0.020 (3) | -0.003 (3) |
| N3 | 0.064 (3) | 0.086 (5) | 0.057 (3) | -0.012 (3) | -0.015 (3) | 0.007 (3) |
| N4 | 0.087 (4) | 0.073 (4) | 0.080 (4) | -0.021 (3) | -0.021 (3) | -0.011 (3) |
| N5 | 0.134 (6) | 0.056 (4) | 0.067 (4) | 0.023 (4) | -0.027 (4) | -0.016 (3) |
| N6 | 0.151 (7) | 0.067 (4) | 0.097 (5) | -0.041 (5) | -0.055 (5) | -0.002 (4) |
| N7 | 0.151 (6) | 0.042 (3) | 0.072 (4) | 0.002 (4) | -0.044 (4) | -0.010 (3) |
| N8 | 0.122 (5) | 0.058 (4) | 0.089 (4) | -0.008 (4) | -0.050 (4) | -0.011 (3) |
| C1 | 0.064 (3) | 0.054 (4) | 0.045 (3) | -0.007 (3) | -0.014 (3) | -0.004 (3) |
| C2 | 0.058 (3) | 0.056 (4) | 0.058 (3) | -0.009 (3) | -0.009 (3) | -0.011 (3) |
| C3 | 0.097 (5) | 0.059 (4) | 0.084 (5) | -0.008 (4) | -0.021 (4) | -0.005 (4) |
| C4 | 0.077 (5) | 0.095 (6) | 0.070 (5) | -0.010 (4) | -0.021 (4) | 0.018 (4) |
| C5 | 0.083 (5) | 0.121 (8) | 0.055 (4) | -0.018 (5) | -0.016 (4) | -0.005 (5) |
| C6 | 0.078 (5) | 0.100 (6) | 0.072 (5) | -0.009 (4) | -0.011 (4) | -0.023 (4) |
| C7 | 0.055 (3) | 0.069 (4) | 0.047 (3) | -0.013 (3) | -0.009 (3) | -0.004 (3) |
| C8 | 0.051 (3) | 0.066 (4) | 0.063 (4) | -0.004 (3) | -0.003 (3) | -0.017 (3) |
| C9 | 0.051 (3) | 0.073 (4) | 0.053 (3) | -0.018 (3) | -0.009 (3) | -0.006 (3) |
| C10 | 0.084 (5) | 0.081 (5) | 0.103 (6) | -0.026 (4) | -0.009 (4) | -0.034 (4) |
| C11 | 0.076 (5) | 0.098 (7) | 0.106 (6) | -0.042 (5) | -0.028 (5) | -0.005 (5) |
| C12 | 0.059 (4) | 0.092 (6) | 0.079 (5) | -0.015 (4) | -0.001 (4) | 0.002 (4) |
| C13 | 0.068 (4) | 0.070 (5) | 0.082 (5) | -0.005 (4) | -0.006 (4) | -0.020 (4) |

| | | | | | | |
|-----|------------|-----------|-----------|------------|------------|------------|
| C14 | 0.049 (3) | 0.063 (4) | 0.060 (3) | -0.025 (3) | -0.007 (3) | 0.000 (3) |
| C15 | 0.062 (4) | 0.061 (4) | 0.056 (3) | 0.000 (3) | -0.006 (3) | -0.017 (3) |
| C16 | 0.059 (3) | 0.052 (4) | 0.057 (3) | -0.010 (3) | -0.013 (3) | -0.006 (3) |
| C17 | 0.118 (6) | 0.086 (6) | 0.096 (6) | -0.060 (6) | -0.028 (5) | 0.001 (5) |
| C18 | 0.166 (10) | 0.056 (5) | 0.117 (8) | -0.011 (6) | -0.058 (8) | -0.029 (5) |
| C19 | 0.123 (8) | 0.086 (7) | 0.094 (6) | 0.031 (6) | -0.044 (6) | -0.042 (5) |
| C20 | 0.065 (4) | 0.117 (7) | 0.077 (5) | -0.011 (4) | -0.011 (4) | -0.026 (5) |
| C21 | 0.072 (4) | 0.044 (3) | 0.054 (3) | -0.011 (3) | -0.016 (3) | -0.012 (3) |
| C22 | 0.120 (7) | 0.055 (5) | 0.073 (5) | 0.004 (4) | -0.014 (5) | -0.023 (4) |
| C23 | 0.112 (6) | 0.055 (4) | 0.068 (4) | 0.009 (4) | -0.030 (4) | -0.022 (3) |
| C24 | 0.106 (6) | 0.098 (7) | 0.104 (6) | 0.011 (5) | -0.028 (5) | -0.045 (5) |
| C25 | 0.153 (9) | 0.082 (7) | 0.087 (6) | 0.032 (6) | -0.064 (7) | -0.020 (5) |
| C26 | 0.161 (10) | 0.084 (7) | 0.074 (5) | 0.010 (7) | -0.030 (7) | -0.020 (5) |
| C27 | 0.156 (8) | 0.059 (5) | 0.087 (5) | -0.005 (5) | -0.038 (6) | -0.009 (4) |
| C28 | 0.118 (6) | 0.050 (4) | 0.069 (4) | -0.003 (4) | -0.035 (4) | -0.012 (3) |

Geometric parameters (Å, °)

| | | | |
|----------------------|------------|---------|------------|
| Cu1—N1 | 2.027 (5) | C6—H6 | 0.9300 |
| Cu1—N3 | 2.008 (6) | C8—C9 | 1.370 (8) |
| Cu1—Br1 | 3.033 (1) | C8—H8 | 0.9300 |
| Cu2—N5 | 2.024 (7) | C9—C10 | 1.389 (10) |
| Cu2—N7 | 2.023 (6) | C9—C14 | 1.395 (9) |
| Cu2—Br2 | 2.980 (1) | C10—C11 | 1.342 (11) |
| Cu1—N3 ⁱ | 2.008 (6) | C10—H10 | 0.9300 |
| Cu1—N1 ⁱ | 2.027 (5) | C11—C12 | 1.385 (12) |
| Cu2—N7 ⁱⁱ | 2.023 (6) | C11—H11 | 0.9300 |
| Cu2—N5 ⁱⁱ | 2.024 (7) | C12—C13 | 1.354 (12) |
| N1—N2 | 1.320 (8) | C12—H12 | 0.9300 |
| N1—C1 | 1.321 (8) | C13—C14 | 1.374 (8) |
| N2—C7 | 1.400 (8) | C13—H13 | 0.9300 |
| N2—H2N | 0.8600 | C15—C16 | 1.352 (9) |
| N3—C8 | 1.298 (9) | C15—H15 | 0.9300 |
| N3—N4 | 1.320 (8) | C16—C21 | 1.378 (8) |
| N4—C14 | 1.364 (8) | C16—C17 | 1.389 (10) |
| N4—H4N | 0.8600 | C17—C18 | 1.340 (13) |
| N5—C15 | 1.295 (10) | C17—H17 | 0.9300 |
| N5—N6 | 1.312 (9) | C18—C19 | 1.347 (13) |
| N6—C21 | 1.409 (9) | C18—H18 | 0.9300 |
| N6—H6N | 0.8600 | C19—C20 | 1.368 (13) |
| N7—C22 | 1.315 (10) | C19—H19 | 0.9300 |
| N7—N8 | 1.347 (9) | C20—C21 | 1.397 (10) |
| N8—C28 | 1.359 (9) | C20—H20 | 0.9300 |
| N8—H8N | 0.8600 | C22—C23 | 1.424 (10) |
| C1—C2 | 1.377 (8) | C22—H22 | 0.9300 |
| C1—H1 | 0.9300 | C23—C28 | 1.362 (11) |
| C2—C7 | 1.388 (9) | C23—C24 | 1.399 (12) |
| C2—C3 | 1.404 (9) | C24—C25 | 1.391 (13) |

supplementary materials

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| C3—C4 | 1.348 (11) | C24—H24 | 0.9300 |
| C3—H3 | 0.9300 | C25—C26 | 1.368 (14) |
| C4—C5 | 1.398 (12) | C25—H25 | 0.9300 |
| C4—H4 | 0.9300 | C26—C27 | 1.330 (13) |
| C5—C6 | 1.372 (11) | C26—H26 | 0.9300 |
| C5—H5 | 0.9300 | C27—C28 | 1.415 (11) |
| C6—C7 | 1.396 (9) | C27—H27 | 0.9300 |
| N3—Cu1—N3 ⁱ | 180.0 (4) | C5—C6—C7 | 118.0 (8) |
| N3—Cu1—N1 | 88.2 (2) | C5—C6—H6 | 121.0 |
| N3 ⁱ —Cu1—N1 | 91.8 (2) | C7—C6—H6 | 121.0 |
| N3—Cu1—N1 ⁱ | 91.8 (2) | C2—C7—C6 | 121.1 (6) |
| N3 ⁱ —Cu1—N1 ⁱ | 88.2 (2) | C2—C7—N2 | 104.9 (6) |
| N1—Cu1—N1 ⁱ | 180.00 (16) | C6—C7—N2 | 133.9 (7) |
| N3—Cu1—Br1 ⁱ | 90.3 (2) | N3—C8—C9 | 111.5 (6) |
| N3 ⁱ —Cu1—Br1 ⁱ | 89.7 (2) | N3—C8—H8 | 124.2 |
| N1—Cu1—Br1 ⁱ | 89.84 (18) | C9—C8—H8 | 124.2 |
| N1 ⁱ —Cu1—Br1 ⁱ | 90.16 (18) | C8—C9—C10 | 134.8 (7) |
| N3—Cu1—Br1 | 89.7 (2) | C8—C9—C14 | 105.7 (6) |
| N3 ⁱ —Cu1—Br1 | 90.3 (2) | C10—C9—C14 | 119.6 (6) |
| N1—Cu1—Br1 | 90.16 (18) | C11—C10—C9 | 119.0 (8) |
| N1 ⁱ —Cu1—Br1 | 89.84 (18) | C11—C10—H10 | 120.5 |
| Br1 ⁱ —Cu1—Br1 | 180.00 (3) | C9—C10—H10 | 120.5 |
| N7 ⁱⁱ —Cu2—N7 | 180.000 (2) | C10—C11—C12 | 121.1 (7) |
| N7 ⁱⁱ —Cu2—N5 ⁱⁱ | 91.3 (2) | C10—C11—H11 | 119.5 |
| N7—Cu2—N5 ⁱⁱ | 88.7 (2) | C12—C11—H11 | 119.5 |
| N7 ⁱⁱ —Cu2—N5 | 88.7 (2) | C13—C12—C11 | 121.2 (7) |
| N7—Cu2—N5 | 91.3 (2) | C13—C12—H12 | 119.4 |
| N5 ⁱⁱ —Cu2—N5 | 180.000 (2) | C11—C12—H12 | 119.4 |
| N7 ⁱⁱ —Cu2—Br2 | 89.4 (2) | C12—C13—C14 | 118.6 (8) |
| N7—Cu2—Br2 | 90.6 (2) | C12—C13—H13 | 120.7 |
| N5 ⁱⁱ —Cu2—Br2 | 92.4 (3) | C14—C13—H13 | 120.7 |
| N5—Cu2—Br2 | 87.6 (3) | N4—C14—C13 | 135.3 (7) |
| N7 ⁱⁱ —Cu2—Br2 ⁱⁱ | 90.6 (2) | N4—C14—C9 | 104.2 (5) |
| N7—Cu2—Br2 ⁱⁱ | 89.4 (2) | C13—C14—C9 | 120.6 (6) |
| N5 ⁱⁱ —Cu2—Br2 ⁱⁱ | 87.6 (3) | N5—C15—C16 | 112.9 (6) |
| N5—Cu2—Br2 ⁱⁱ | 92.4 (3) | N5—C15—H15 | 123.6 |
| Br2—Cu2—Br2 ⁱⁱ | 180.00 (3) | C16—C15—H15 | 123.6 |
| N2—N1—C1 | 107.6 (5) | C15—C16—C21 | 106.6 (6) |
| N2—N1—Cu1 | 127.4 (5) | C15—C16—C17 | 132.2 (7) |
| C1—N1—Cu1 | 125.0 (5) | C21—C16—C17 | 121.2 (7) |
| N1—N2—C7 | 110.5 (6) | C18—C17—C16 | 117.3 (8) |
| N1—N2—H2N | 124.8 | C18—C17—H17 | 121.3 |
| C7—N2—H2N | 124.8 | C16—C17—H17 | 121.3 |
| C8—N3—N4 | 106.6 (6) | C17—C18—C19 | 122.6 (9) |

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| C8—N3—Cu1 | 129.2 (5) | C17—C18—H18 | 118.7 |
| N4—N3—Cu1 | 124.0 (6) | C19—C18—H18 | 118.7 |
| N3—N4—C14 | 112.1 (6) | C18—C19—C20 | 121.9 (8) |
| N3—N4—H4N | 124.0 | C18—C19—H19 | 119.1 |
| C14—N4—H4N | 124.0 | C20—C19—H19 | 119.1 |
| C15—N5—N6 | 105.9 (6) | C19—C20—C21 | 117.1 (7) |
| C15—N5—Cu2 | 127.4 (6) | C19—C20—H20 | 121.5 |
| N6—N5—Cu2 | 126.4 (7) | C21—C20—H20 | 121.5 |
| N5—N6—C21 | 111.7 (7) | C16—C21—C20 | 119.8 (6) |
| N5—N6—H6N | 124.1 | C16—C21—N6 | 102.9 (6) |
| C21—N6—H6N | 124.1 | C20—C21—N6 | 137.2 (7) |
| C22—N7—N8 | 108.1 (6) | N7—C22—C23 | 108.8 (8) |
| C22—N7—Cu2 | 131.1 (6) | N7—C22—H22 | 125.6 |
| N8—N7—Cu2 | 120.6 (6) | C23—C22—H22 | 125.6 |
| N7—N8—C28 | 110.0 (7) | C28—C23—C24 | 118.2 (8) |
| N7—N8—H8N | 125.0 | C28—C23—C22 | 105.7 (7) |
| C28—N8—H8N | 125.0 | C24—C23—C22 | 136.1 (10) |
| N1—C1—C2 | 110.9 (6) | C25—C24—C23 | 117.5 (10) |
| N1—C1—H1 | 124.6 | C25—C24—H24 | 121.2 |
| C2—C1—H1 | 124.6 | C23—C24—H24 | 121.2 |
| C1—C2—C7 | 106.1 (5) | C26—C25—C24 | 122.1 (9) |
| C1—C2—C3 | 134.0 (7) | C26—C25—H25 | 119.0 |
| C7—C2—C3 | 119.9 (6) | C24—C25—H25 | 119.0 |
| C4—C3—C2 | 118.4 (8) | C27—C26—C25 | 121.9 (10) |
| C4—C3—H3 | 120.8 | C27—C26—H26 | 119.0 |
| C2—C3—H3 | 120.8 | C25—C26—H26 | 119.0 |
| C3—C4—C5 | 122.1 (7) | C26—C27—C28 | 116.4 (10) |
| C3—C4—H4 | 119.0 | C26—C27—H27 | 121.8 |
| C5—C4—H4 | 119.0 | C28—C27—H27 | 121.8 |
| C6—C5—C4 | 120.4 (7) | N8—C28—C23 | 107.4 (7) |
| C6—C5—H5 | 119.8 | N8—C28—C27 | 128.8 (9) |
| C4—C5—H5 | 119.8 | C23—C28—C27 | 123.8 (8) |
| N3—Cu1—N1—N2 | -93.9 (5) | C5—C6—C7—N2 | 179.1 (7) |
| N3 ⁱ —Cu1—N1—N2 | 86.1 (5) | N1—N2—C7—C2 | -0.1 (7) |
| Br1 ⁱ —Cu1—N1—N2 | -3.6 (5) | N1—N2—C7—C6 | 178.9 (7) |
| Br1—Cu1—N1—N2 | 176.4 (5) | N4—N3—C8—C9 | -0.4 (8) |
| N3—Cu1—N1—C1 | 84.4 (5) | Cu1—N3—C8—C9 | 174.8 (4) |
| N3 ⁱ —Cu1—N1—C1 | -95.6 (5) | N3—C8—C9—C10 | -178.6 (8) |
| Br1 ⁱ —Cu1—N1—C1 | 174.6 (5) | N3—C8—C9—C14 | 0.5 (7) |
| Br1—Cu1—N1—C1 | -5.4 (5) | C8—C9—C10—C11 | 178.9 (7) |
| C1—N1—N2—C7 | -0.5 (7) | C14—C9—C10—C11 | -0.2 (11) |
| Cu1—N1—N2—C7 | 178.0 (4) | C9—C10—C11—C12 | 0.4 (13) |
| N1—Cu1—N3—C8 | -91.4 (6) | C10—C11—C12—C13 | -0.7 (13) |
| N1 ⁱ —Cu1—N3—C8 | 88.6 (6) | C11—C12—C13—C14 | 0.7 (12) |
| Br1 ⁱ —Cu1—N3—C8 | 178.8 (6) | N3—N4—C14—C13 | 178.6 (7) |
| Br1—Cu1—N3—C8 | -1.2 (6) | N3—N4—C14—C9 | 0.3 (7) |
| N1—Cu1—N3—N4 | 83.0 (5) | C12—C13—C14—N4 | -178.6 (7) |

supplementary materials

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| N1 ⁱ —Cu1—N3—N4 | -97.0 (5) | C12—C13—C14—C9 | -0.5 (10) |
| Br1 ⁱ —Cu1—N3—N4 | -6.8 (5) | C8—C9—C14—N4 | -0.5 (7) |
| Br1—Cu1—N3—N4 | 173.2 (5) | C10—C9—C14—N4 | 178.9 (6) |
| C8—N3—N4—C14 | 0.1 (7) | C8—C9—C14—C13 | -179.1 (6) |
| Cu1—N3—N4—C14 | -175.4 (4) | C10—C9—C14—C13 | 0.2 (10) |
| N7 ⁱⁱ —Cu2—N5—C15 | 91.4 (7) | N6—N5—C15—C16 | -0.1 (8) |
| N7—Cu2—N5—C15 | -88.6 (7) | Cu2—N5—C15—C16 | -173.3 (4) |
| Br2—Cu2—N5—C15 | 2.0 (6) | N5—C15—C16—C21 | -0.2 (8) |
| Br2 ⁱⁱ —Cu2—N5—C15 | -178.0 (6) | N5—C15—C16—C17 | -179.4 (7) |
| N7 ⁱⁱ —Cu2—N5—N6 | -80.5 (6) | C15—C16—C17—C18 | -179.4 (8) |
| N7—Cu2—N5—N6 | 99.5 (6) | C21—C16—C17—C18 | 1.5 (11) |
| Br2—Cu2—N5—N6 | -170.0 (6) | C16—C17—C18—C19 | -1.3 (14) |
| Br2 ⁱⁱ —Cu2—N5—N6 | 10.0 (6) | C17—C18—C19—C20 | -0.2 (15) |
| C15—N5—N6—C21 | 0.3 (8) | C18—C19—C20—C21 | 1.5 (13) |
| Cu2—N5—N6—C21 | 173.7 (4) | C15—C16—C21—C20 | -179.5 (6) |
| N5 ⁱⁱ —Cu2—N7—C22 | -92.2 (7) | C17—C16—C21—C20 | -0.2 (10) |
| N5—Cu2—N7—C22 | 87.8 (7) | C15—C16—C21—N6 | 0.4 (7) |
| Br2—Cu2—N7—C22 | 0.3 (7) | C17—C16—C21—N6 | 179.7 (6) |
| Br2 ⁱⁱ —Cu2—N7—C22 | -179.7 (7) | C19—C20—C21—C16 | -1.3 (11) |
| N5 ⁱⁱ —Cu2—N7—N8 | 83.4 (6) | C19—C20—C21—N6 | 178.9 (7) |
| N5—Cu2—N7—N8 | -96.6 (6) | N5—N6—C21—C16 | -0.4 (7) |
| Br2—Cu2—N7—N8 | 175.8 (5) | N5—N6—C21—C20 | 179.4 (8) |
| Br2 ⁱⁱ —Cu2—N7—N8 | -4.2 (5) | N8—N7—C22—C23 | -0.7 (8) |
| C22—N7—N8—C28 | 0.8 (8) | Cu2—N7—C22—C23 | 175.2 (5) |
| Cu2—N7—N8—C28 | -175.7 (5) | N7—C22—C23—C28 | 0.4 (8) |
| N2—N1—C1—C2 | 0.9 (7) | N7—C22—C23—C24 | 178.5 (8) |
| Cu1—N1—C1—C2 | -177.6 (4) | C28—C23—C24—C25 | -1.7 (11) |
| N1—C1—C2—C7 | -1.0 (7) | C22—C23—C24—C25 | -179.7 (8) |
| N1—C1—C2—C3 | 179.1 (7) | C23—C24—C25—C26 | 0.6 (14) |
| C1—C2—C3—C4 | -179.0 (7) | C24—C25—C26—C27 | 0.0 (15) |
| C7—C2—C3—C4 | 1.1 (11) | C25—C26—C27—C28 | 0.5 (14) |
| C2—C3—C4—C5 | -3.0 (12) | N7—N8—C28—C23 | -0.5 (8) |
| C3—C4—C5—C6 | 2.4 (12) | N7—N8—C28—C27 | 178.6 (7) |
| C4—C5—C6—C7 | 0.2 (11) | C24—C23—C28—N8 | -178.4 (7) |
| C1—C2—C7—C6 | -178.5 (6) | C22—C23—C28—N8 | 0.1 (8) |
| C3—C2—C7—C6 | 1.4 (10) | C24—C23—C28—C27 | 2.4 (11) |
| C1—C2—C7—N2 | 0.6 (7) | C22—C23—C28—C27 | -179.1 (7) |
| C3—C2—C7—N2 | -179.4 (6) | C26—C27—C28—N8 | 179.2 (8) |
| C5—C6—C7—C2 | -2.0 (10) | C26—C27—C28—C23 | -1.7 (13) |

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

Fig. 1

