Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

OPEN ACCESS

ISSN 2056-9890

# Crystal structure of di-$\mu$-iodido-bis{[bis(piperidin-1-yl)methane-$\kappa^2N,N'$]copper(I)}

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Received 11 September 2015; accepted 6 October 2015

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

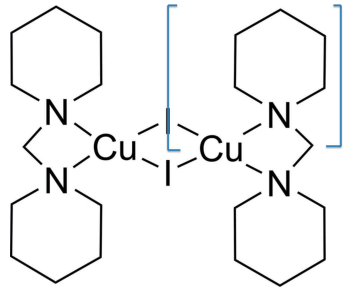
The title compound, $[Cu_2I_2(C_{11}H_{22}N_2)_2]$, crystallizes as a symmetric dimer with one quarter of the molecule in the asymmetric unit. The copper(I) atom, the iodine atom and the central methylene C atom of the di(piperidin-1-yl)methane ligand lie on a mirror plane and the complete molecule exhibits point group symmetry 2/*m*. To the best of our knowledge it is the first diamine copper(I) complex containing a four-membered chelate ring. Compared to other diamine copper(I) iodide dimers, the title compound has a short Cu···Cu distance of 2.5137 (11) Å, but a long Cu—N bond length of 2.213 (3) Å. The I—Cu—I angle [121.84 (2)°] is large, and the N—Cu—N angle = 66.61 (13)° is the smallest one found for copper(I) diamine complexes. As a result of the four-membered ring, the ligands around the copper(I) atom have an extremely distorted tetrahedral arrangement. In the crystal, there are no significant intermolecular interactions present.

**Keywords:** crystal structure; copper iodide; dimer; small ring; four-membered chelate ring..

**CCDC reference**: 1429684

## 1. Related literature

To the best of our knowledge no related diamine complexes with four-membered chelate rings are known. For diamine complexes with five-membered chelate rings, see: Haitko (1984); Garbauskas *et al.* (1986). For a bipyridine complex containing a copper(I) iodide dimer, see: Huang *et al.* (2013). For the crystal structure of the $\mu,\mu'$-diiodido-bridged dimer, with four-coordinate copper(I), *viz.* $[(py)_2CuI_2Cu(py)_2]$ (py is pyridine), see: Dyason *et al.* (1984).




## 2. Experimental

### 2.1. Crystal data

$[Cu_2I_2(C_{11}H_{22}N_2)_2]$
$M_r$ = 745.49
Orthorhombic, *Cmce*
*a* = 18.718 (4) Å
*b* = 8.4175 (15) Å
*c* = 17.074 (3) Å
*V* = 2690.1 (8) Å$^3$
*Z* = 4
Mo *K*$\alpha$ radiation
$\mu$ = 3.89 mm$^{-1}$
*T* = 173 K
0.4 × 0.3 × 0.2 mm

### 2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{min}$ = 0.256, $T_{max}$ = 0.459
38065 measured reflections
1704 independent reflections
1349 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.096

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.070
*S* = 1.07
1704 reflections
73 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.99 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.44 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—Cu1$^{i}$ | 2.5137 (11) | I1—Cu1$^{i}$ | 2.5922 (7) |
| I1—Cu1 | 2.5798 (8) | Cu1—N1 | 2.213 (3) |
| | | | |
| Cu1—I1—Cu1$^{i}$ | 58.16 (2) | N1—Cu1—I1$^{i}$ | 111.90 (7) |
| N1—Cu1—N1$^{ii}$ | 66.61 (13) | I1—Cu1—I1$^{i}$ | 121.84 (2) |
| N1—Cu1—I1 | 116.02 (7) | | |

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2015*b*); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

## Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5211).

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# supporting information

*Acta Cryst.* (2015). E**71**, m193–m194 [https://doi.org/10.1107/S2056989015018757]

## Crystal structure of di-$\mu$-iodido-bis{[bis(piperidin-1-yl)methane-$\kappa^2N,N'$]copper(I)}

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### S1. Synthesis and crystallization

The title compound was prepared by dissolving 98 mg (0.51 mmol) of CuI in 2 ml acetone under an inert argon atmosphere. Then 151 mg (0.83 mmol) of di(piperidin-1-yl)methane was added to this solution with stirring. After one week colourless crystals of the title compound were obtained.

### S2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.99 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

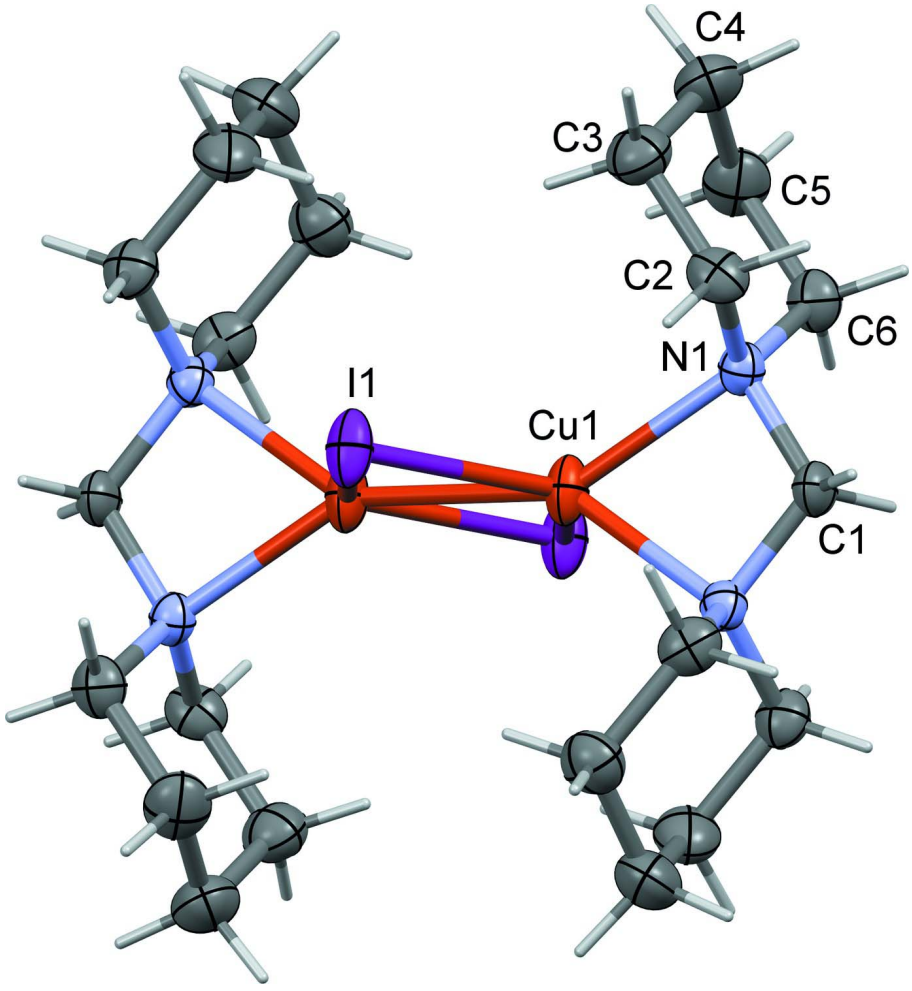


**Figure 1**

Molecular structure of the title compound, with atom labelling. The displacement ellipsoids are drawn at the 50% probability level.

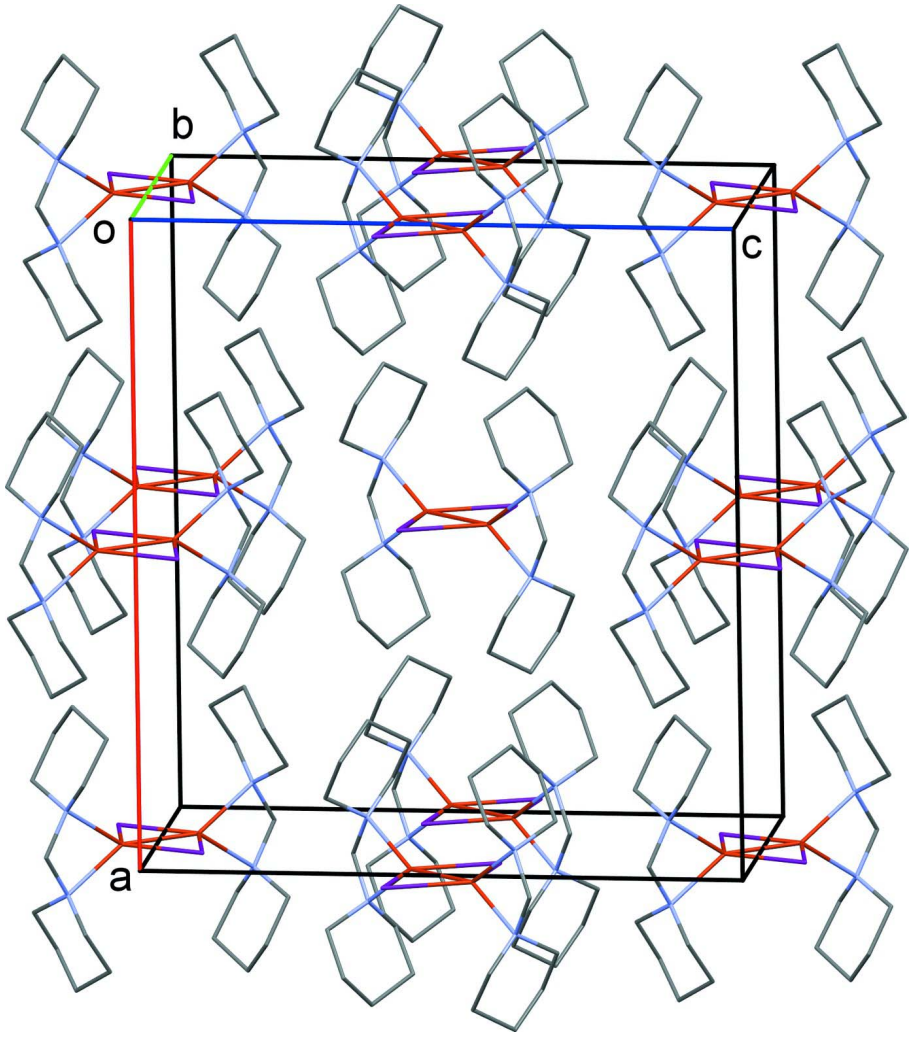


**Figure 2**

Crystal packing of the title compound viewed along *b* axis. H-atoms have been omitted for clarity.

**Di-$\mu$-iodido-bis{[bis(piperidin-1-yl)methane-$\kappa^2N,N'$]copper(I)}**

*Crystal data*

$[Cu_2I_2(C_{11}H_{22}N_2)_2]$
$M_r = 745.49$
Orthorhombic, *Cmce*
$a = 18.718$ (4) Å
$b = 8.4175$ (15) Å
$c = 17.074$ (3) Å
$V = 2690.1$ (8) Å$^3$
$Z = 4$
$F(000) = 1472$
$D_x = 1.841$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 38065 reflections
$\theta = 2.2$–$28.2°$
$\mu = 3.89$ mm$^{-1}$
$T = 173$ K
Block, colourless
0.4 × 0.3 × 0.2 mm

*Data collection*

Bruker APEXII CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.256$, $T_{max} = 0.459$

38065 measured reflections
1704 independent reflections
1349 reflections with $I > 2\sigma(I)$
$R_{int} = 0.096$
$\theta_{max} = 28.2°$, $\theta_{min} = 2.2°$
$h = -24 \rightarrow 24$
$k = -11 \rightarrow 11$
$l = -22 \rightarrow 22$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.070$
$S = 1.07$
1704 reflections
73 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.6685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.99$ e Å$^{-3}$
$\Delta\rho_{min} = -0.44$ e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| I1 | 0.5000 | 0.70816 (3) | 0.58360 (2) | 0.03716 (12) |
| Cu1 | 0.5000 | 0.40635 (6) | 0.55733 (3) | 0.03283 (16) |
| N1 | 0.56490 (13) | 0.2603 (3) | 0.63824 (16) | 0.0259 (5) |
| C1 | 0.5000 | 0.1792 (5) | 0.6679 (3) | 0.0299 (10) |
| H1A | 0.5000 | 0.0670 | 0.6505 | 0.036* |
| H1B | 0.5000 | 0.1806 | 0.7259 | 0.036* |
| C2 | 0.60139 (18) | 0.3498 (4) | 0.70093 (19) | 0.0333 (7) |
| H2A | 0.6165 | 0.2756 | 0.7427 | 0.040* |
| H2B | 0.5677 | 0.4274 | 0.7241 | 0.040* |
| C3 | 0.66608 (19) | 0.4367 (4) | 0.6694 (2) | 0.0444 (9) |
| H3A | 0.6504 | 0.5176 | 0.6310 | 0.053* |
| H3B | 0.6905 | 0.4924 | 0.7129 | 0.053* |
| C4 | 0.7177 (2) | 0.3238 (5) | 0.6306 (3) | 0.0497 (10) |
| H4A | 0.7382 | 0.2510 | 0.6702 | 0.060* |
| H4B | 0.7573 | 0.3844 | 0.6064 | 0.060* |
| C5 | 0.6785 (2) | 0.2285 (5) | 0.5680 (2) | 0.0460 (9) |
| H5A | 0.6628 | 0.3006 | 0.5255 | 0.055* |
| H5B | 0.7114 | 0.1490 | 0.5451 | 0.055* |
| C6 | 0.61428 (18) | 0.1448 (4) | 0.60214 (19) | 0.0333 (8) |
| H6A | 0.5891 | 0.0858 | 0.5603 | 0.040* |
| H6B | 0.6302 | 0.0674 | 0.6421 | 0.040* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| I1 | 0.0678 (3) | 0.02108 (15) | 0.02262 (17) | 0.000 | 0.000 | −0.00298 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cu1 | 0.0540 (4) | 0.0219 (3) | 0.0225 (3) | 0.000 | 0.000 | 0.0030 (2) |
| N1 | 0.0293 (13) | 0.0222 (11) | 0.0262 (13) | 0.0010 (10) | 0.0021 (11) | −0.0001 (10) |
| C1 | 0.032 (3) | 0.028 (2) | 0.029 (3) | 0.000 | 0.000 | 0.0092 (18) |
| C2 | 0.0359 (19) | 0.0369 (17) | 0.0271 (17) | 0.0032 (14) | −0.0048 (14) | −0.0078 (14) |
| C3 | 0.040 (2) | 0.041 (2) | 0.052 (2) | −0.0066 (16) | −0.0035 (17) | −0.0046 (17) |
| C4 | 0.036 (2) | 0.051 (2) | 0.062 (3) | −0.0062 (17) | 0.0047 (19) | 0.0075 (19) |
| C5 | 0.043 (2) | 0.047 (2) | 0.048 (2) | 0.0054 (18) | 0.0177 (17) | 0.0000 (18) |
| C6 | 0.040 (2) | 0.0289 (16) | 0.0314 (18) | 0.0033 (14) | 0.0023 (15) | −0.0046 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—Cu1$^{i}$ | 2.5137 (11) | C2—H2A | 0.9900 |
| I1—Cu1 | 2.5798 (8) | C2—H2B | 0.9900 |
| I1—Cu1$^{i}$ | 2.5922 (7) | C3—C4 | 1.509 (5) |
| Cu1—N1 | 2.213 (3) | C3—H3A | 0.9900 |
| Cu1—N1$^{ii}$ | 2.213 (3) | C3—H3B | 0.9900 |
| Cu1—I1$^{i}$ | 2.5922 (7) | C4—C5 | 1.526 (6) |
| N1—C6 | 1.476 (4) | C4—H4A | 0.9900 |
| N1—C2 | 1.477 (4) | C4—H4B | 0.9900 |
| N1—C1 | 1.483 (3) | C5—C6 | 1.509 (5) |
| C1—N1$^{ii}$ | 1.483 (3) | C5—H5A | 0.9900 |
| C1—H1A | 0.9900 | C5—H5B | 0.9900 |
| C1—H1B | 0.9900 | C6—H6A | 0.9900 |
| C2—C3 | 1.513 (5) | C6—H6B | 0.9900 |
| | | | |
| Cu1—I1—Cu1$^{i}$ | 58.16 (2) | C3—C2—H2B | 109.4 |
| N1—Cu1—N1$^{ii}$ | 66.61 (13) | H2A—C2—H2B | 108.0 |
| N1—Cu1—Cu1$^{i}$ | 146.59 (7) | C4—C3—C2 | 111.4 (3) |
| N1$^{ii}$—Cu1—Cu1$^{i}$ | 146.59 (7) | C4—C3—H3A | 109.4 |
| N1—Cu1—I1 | 116.02 (7) | C2—C3—H3A | 109.4 |
| N1$^{ii}$—Cu1—I1 | 116.01 (7) | C4—C3—H3B | 109.4 |
| Cu1$^{i}$—Cu1—I1 | 61.17 (2) | C2—C3—H3B | 109.4 |
| N1—Cu1—I1$^{i}$ | 111.90 (7) | H3A—C3—H3B | 108.0 |
| N1$^{ii}$—Cu1—I1$^{i}$ | 111.90 (7) | C3—C4—C5 | 109.3 (3) |
| Cu1$^{i}$—Cu1—I1$^{i}$ | 60.67 (3) | C3—C4—H4A | 109.8 |
| I1—Cu1—I1$^{i}$ | 121.84 (2) | C5—C4—H4A | 109.8 |
| C6—N1—C2 | 110.4 (2) | C3—C4—H4B | 109.8 |
| C6—N1—C1 | 110.6 (3) | C5—C4—H4B | 109.8 |
| C2—N1—C1 | 111.5 (3) | H4A—C4—H4B | 108.3 |
| C6—N1—Cu1 | 116.7 (2) | C6—C5—C4 | 111.0 (3) |
| C2—N1—Cu1 | 115.02 (19) | C6—C5—H5A | 109.4 |
| C1—N1—Cu1 | 91.11 (18) | C4—C5—H5A | 109.4 |
| N1$^{ii}$—C1—N1 | 110.0 (3) | C6—C5—H5B | 109.4 |
| N1$^{ii}$—C1—H1A | 109.7 | C4—C5—H5B | 109.4 |
| N1—C1—H1A | 109.7 | H5A—C5—H5B | 108.0 |
| N1$^{ii}$—C1—H1B | 109.7 | N1—C6—C5 | 110.6 (3) |
| N1—C1—H1B | 109.7 | N1—C6—H6A | 109.5 |
| H1A—C1—H1B | 108.2 | C5—C6—H6A | 109.5 |

| | | | |
|---|---|---|---|
| N1—C2—C3 | 111.0 (3) | N1—C6—H6B | 109.5 |
| N1—C2—H2A | 109.4 | C5—C6—H6B | 109.5 |
| C3—C2—H2A | 109.4 | H6A—C6—H6B | 108.1 |
| N1—C2—H2B | 109.4 | | |
| | | | |
| C6—N1—C1—N1$^{ii}$ | −128.9 (3) | C2—C3—C4—C5 | 54.5 (4) |
| C2—N1—C1—N1$^{ii}$ | 107.7 (3) | C3—C4—C5—C6 | −55.1 (4) |
| Cu1—N1—C1—N1$^{ii}$ | −9.8 (3) | C2—N1—C6—C5 | −59.2 (4) |
| C6—N1—C2—C3 | 58.5 (3) | C1—N1—C6—C5 | 176.9 (3) |
| C1—N1—C2—C3 | −178.0 (3) | Cu1—N1—C6—C5 | 74.6 (3) |
| Cu1—N1—C2—C3 | −76.1 (3) | C4—C5—C6—N1 | 57.9 (4) |
| N1—C2—C3—C4 | −56.9 (4) | | |

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, *y*, *z*.