

Redetermination of poly[di- μ_3 -iodido- $[\mu$ -1,2-*trans*-(pyridin-4-yl)ethene- κ^2 N:N']dicopper(I)]

Henry C. Neal,^a Harsha Tamtam,^a Bradley W. Smucker^{a*} and Volodymyr V. Nesterov^b

^aAustin College, 900 N Grand, Sherman, TX 75090, USA, and ^bDepartment of Chemistry, University of North Texas, 1508 W. Mulberry, Denton, TX 76201, USA. *Correspondence e-mail: bsmucker@austincollege.edu

Received 21 December 2018

Accepted 22 January 2019

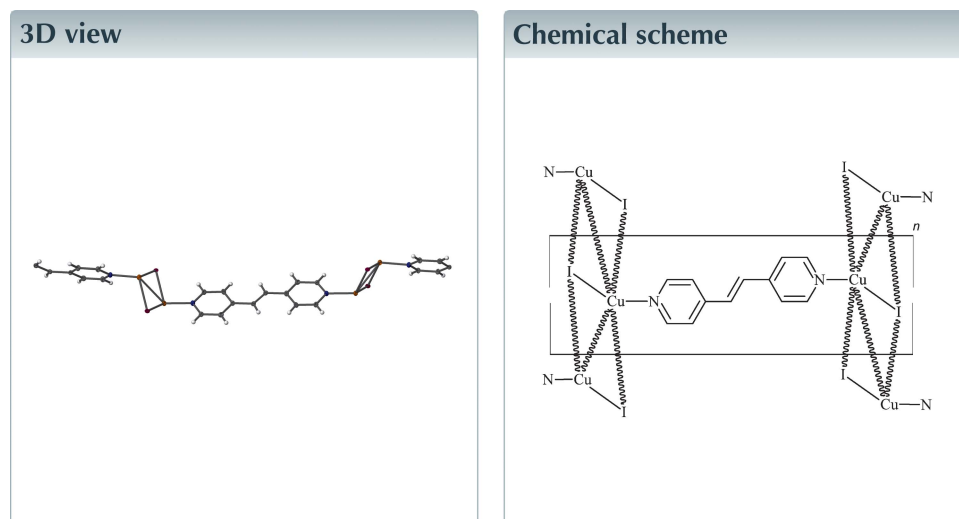
Edited by S. Bernès, Benemérita Universidad Autónoma de Puebla, México

Keywords: X-ray analysis; crystal structure; coordination polymer; redetermination.

CCDC reference: 1892770

Structural data: full structural data are available from iucrdata.iucr.org

The re-investigated structure of the title compound, $[\text{Cu}_2\text{I}_2(\text{C}_{12}\text{H}_{10}\text{N}_2)]_n$, a two-dimensional coordination polymer crystallizing with monoclinic ($P2_1/n$) symmetry, is based on data collected at 100 K, while the previously reported structure was obtained with data collected at 203 K [Blake *et al.* (1999). *Cryst. Eng.* **2**, 181–195]. The refinement of the crystal structure is greatly improved; for example, the wR_2 residual converges to 0.047 for 1532 independent data, *versus* $wR_2 = 0.179$ for 992 independent data in the 1999 study.



Structure description

The previously reported structure for the title compound (Blake *et al.*, 1999) at 203 K with $R_1 = 6.48\%$ [$I > 2\sigma(I)$] was re-investigated at 100 K (Fig. 1), producing a much more accurate refinement for the crystal structure. We were able to achieve $R_1 = 1.78\%$ and $wR_2 = 4.74\%$ (as compared with $R_1 = 6.48\%$ and $wR_2 = 17.86\%$ for the structure reported by Blake *et al.*) after collecting 1532 independent reflections for 83 refined parameters (as compared with 992 independent reflections for 82 parameters in the previously reported structure). Our completeness is 100%, a vast improvement over the reported 76.6%, and our goodness of fit is 1.073 (as compared with 1.109). We were able to achieve an R_{int} of 2.19% after collecting experimental data up to $2\theta_{\text{max}}$ angle of 54° as compared with an R_{int} of 13.48% after collecting experimental data up to $2\theta_{\text{max}}$ angle of 48° . A comparison of the improved resolution of select bond lengths between this refinement and that reported by Blake *et al.* is given in Table 1.

Analysis of the crystal packing shows that molecules in the crystal form staggered sheets (Fig. 2). Equidistant intermolecular contacts $\text{Cu1}\cdots\text{Cu1}$ [2.7852 (4) Å] and $\text{I1}\cdots\text{I1}$ [4.0743 (1) Å] link these sheets along the b -axis direction and form stacks (Fig. 3).

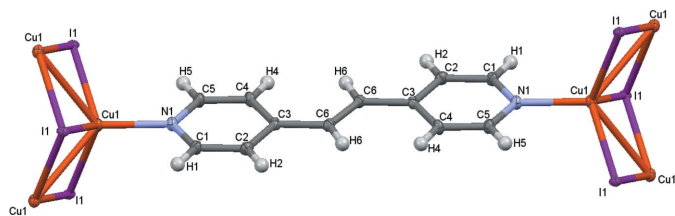


Figure 1
Ellipsoid plot (50% probability level for all non-hydrogen atoms) of the title compound with additional Cu–I fragments included to indicate the directionality of the two-dimensional coordination polymer.

Synthesis and crystallization

Following the general procedure for making copper(I)-pyridine-iodide clusters (Parmeggiani & Sacchetti, 2012), an acetonitrile solution of copper(I) iodide, ascorbic acid, and potassium iodide was added to a thin tube and layered first with acetonitrile then with an acetonitrile solution of 1,2-di(pyridin-4-yl)ethylene. Large yello–orange crystals were present after 1 week.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Single crystal X-ray data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source as well as a low-temperature Oxford Cryostream 800 liquid nitrogen cooling system at 100 (2) K. The data collection strategy was calculated within *CrysAlis PRO* (Rigaku OD, 2018) to ensure desired data redundancy and percent completeness.

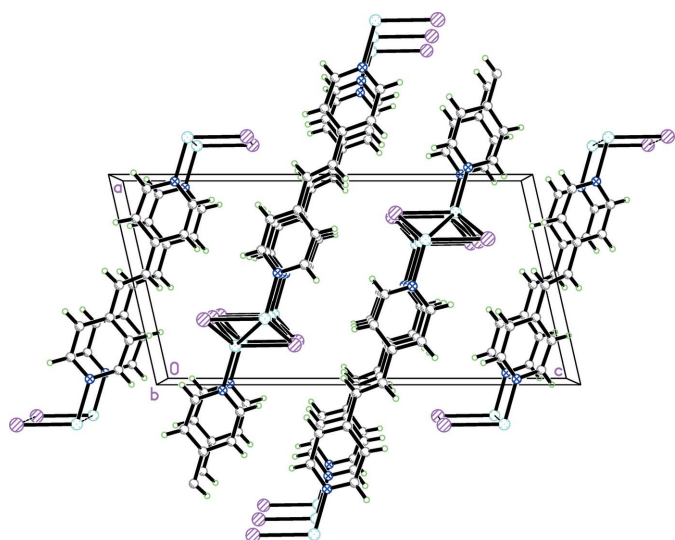


Figure 2
Fragment of the crystal packing along the *b*-axis direction.

Table 1

Comparison of some bond lengths (Å) in the reported refinement and the refinement published by Blake *et al.* (1999).

Bond	This structure	Structure of Blake <i>et al.</i>
Cu1–I1	2.6200 (4)	2.6314 (16)
Cu1···Cu1 ⁱ	2.7852 (4)	2.8182 (17)
Cu1–N1	2.039 (2)	2.055 (8)
C6=C6 ⁱⁱ	1.329 (5)	1.31 (2)
N1–C1	1.344 (4)	1.360 (14)
N1–C5	1.343 (4)	1.331 (15)

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

Table 2

Experimental details.

Crystal data	
Chemical formula	[Cu ₂ I ₂ (C ₁₂ H ₁₀ N ₂)]
<i>M_r</i>	563.1
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.4695 (3), 4.0743 (1), 18.6048 (6)
β (°)	102.878 (4)
<i>V</i> (Å ³)	699.75 (4)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	7.43
Crystal size (mm)	0.09 × 0.03 × 0.02
Data collection	
Diffractometer	Rigaku XtaLAB Synergy, Dual-flex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T</i> _{min} , <i>T</i> _{max}	0.604, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	4364, 1532, 1435
<i>R</i> _{int}	0.022
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.641
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.018, 0.047, 1.07
No. of reflections	1532
No. of parameters	83
H-atom treatment	H-atom parameters constrained
$\Delta\rho$ _{max} , $\Delta\rho$ _{min} (e Å ⁻³)	0.46, -0.70

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009) and *PLATON* (Spek, 2009).

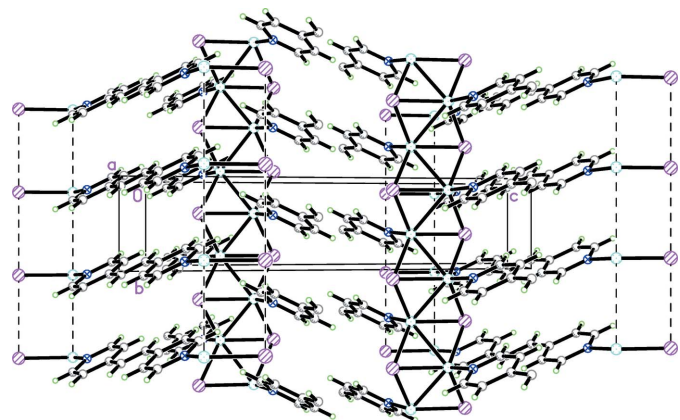


Figure 3
Fragment of the crystal packing along the *a*-axis direction. Dashed lines indicate intermolecular Cu···Cu and I···I contacts.

Acknowledgements

We acknowledge the NSF MRI Program (CHE-1726652) and the UNT for supporting the acquisition of the Rigaku XtaLAB Synergy-S X-ray diffractometer.

Funding information

Funding for this research was provided by: National Science Foundation.

References

- Blake, A. J., Brooks, N. R., Champness, N. R., Cooke, P. A., Crew, M., Deveson, A. M., Hanton, L. R., Hubberstey, P., Fenske, D. & Schröder, M. (1999). *Cryst. Eng.* **2**, 181–195.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Parmeggiani, F. & Sacchetti, A. (2012). *J. Chem. Educ.* **89**, 946–949.
- Rigaku, OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, England.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

full crystallographic data

IUCrData (2019). 4, x190122 [https://doi.org/10.1107/S2414314619001226]

Redetermination of poly[di- μ_3 -iodido- $[\mu$ -1,2-*trans*-(pyridin-4-yl)ethene- κ^2 N:N']dicopper(I)]

Henry C. Neal, Harsha Tamtam, Bradley W. Smucker and Volodymyr V. Nesterov

Poly[di- μ_3 -iodido- $[\mu$ -1,2-*trans*-(pyridin-4-yl)ethene- κ^2 N:N']dicopper(I)]

Crystal data

[Cu₂I₂(C₁₂H₁₀N₂)]

$M_r = 563.1$

Monoclinic, $P2_1/n$

$a = 9.4695$ (3) Å

$b = 4.0743$ (1) Å

$c = 18.6048$ (6) Å

$\beta = 102.878$ (4)°

$V = 699.75$ (4) Å³

$Z = 2$

$F(000) = 520$

$D_x = 2.673$ Mg m⁻³

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

Cell parameters from 3630 reflections

$\theta = 2.3$ – 31.1 °

$\mu = 7.43$ mm⁻¹

$T = 100$ K

Plate, clear light yellow

$0.09 \times 0.03 \times 0.02$ mm

Data collection

Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet X-ray Source

Mirror monochromator

ω scans

Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2018)

$T_{\min} = 0.604$, $T_{\max} = 1.000$

4364 measured reflections

1532 independent reflections

1435 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 27.1$ °, $\theta_{\min} = 2.2$ °

$h = -12 \rightarrow 12$

$k = -5 \rightarrow 5$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.047$

$S = 1.07$

1532 reflections

83 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.7134P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.46$ e Å⁻³

$\Delta\rho_{\min} = -0.70$ e Å⁻³

Extinction correction: SHELXL2018 (Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0016 (3)

Special details

Refinement. Single crystal X-ray data were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source as well as a low-temperature Oxford Cryostream 800 liquid nitrogen cooling system at 100 (2) K. The data collection strategy was calculated within *CrysAlis PRO* (Rigaku OD, 2018; Table 2) to ensure desired data redundancy and percent completeness. All non-hydrogen atoms were refined anisotropically using *SHELXL* (Sheldrick, 2015b) and the space group was unambiguously verified by *PLATON* (Spek, 2009). All H atoms were attached *via* the riding model at calculated positions, with calculated isotropic displacement parameters.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.68604 (2)	0.62004 (4)	0.84525 (2)	0.01014 (9)
Cu1	0.68200 (4)	0.62033 (8)	0.70399 (2)	0.01281 (10)
N1	0.4696 (2)	0.5974 (5)	0.65013 (12)	0.0123 (5)
C1	0.3630 (3)	0.7307 (7)	0.67755 (14)	0.0141 (5)
H1	0.387165	0.831271	0.723539	0.017*
C2	0.2186 (3)	0.7258 (7)	0.64066 (15)	0.0149 (6)
H2	0.148556	0.821387	0.661890	0.018*
C3	0.1788 (3)	0.5767 (7)	0.57138 (14)	0.0115 (5)
C4	0.2899 (3)	0.4386 (7)	0.54285 (14)	0.0139 (5)
H4	0.269163	0.338118	0.496805	0.017*
C5	0.4311 (3)	0.4528 (7)	0.58375 (14)	0.0138 (5)
H5	0.503348	0.356747	0.564167	0.017*
C6	0.0256 (3)	0.5728 (7)	0.53223 (15)	0.0122 (5)
H6	−0.040426	0.680460	0.554244	0.015*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01214 (11)	0.00854 (12)	0.01046 (11)	−0.00082 (6)	0.00406 (7)	0.00027 (6)
Cu1	0.01037 (17)	0.0149 (2)	0.01267 (17)	−0.00004 (12)	0.00152 (13)	−0.00116 (13)
N1	0.0103 (10)	0.0145 (12)	0.0116 (10)	−0.0003 (9)	0.0013 (8)	−0.0003 (9)
C1	0.0137 (13)	0.0161 (14)	0.0116 (12)	0.0018 (11)	0.0011 (10)	−0.0024 (11)
C2	0.0136 (13)	0.0155 (14)	0.0166 (13)	0.0020 (11)	0.0053 (10)	−0.0017 (11)
C3	0.0099 (12)	0.0129 (13)	0.0117 (12)	−0.0014 (10)	0.0021 (10)	0.0024 (10)
C4	0.0137 (13)	0.0178 (14)	0.0095 (11)	−0.0012 (11)	0.0013 (10)	−0.0023 (11)
C5	0.0115 (12)	0.0168 (14)	0.0132 (12)	0.0013 (11)	0.0028 (10)	−0.0010 (11)
C6	0.0109 (12)	0.0130 (13)	0.0135 (12)	0.0008 (10)	0.0042 (9)	0.0017 (10)

Geometric parameters (\AA , $^\circ$)

I1—Cu1	2.6200 (4)	C2—H2	0.9300
I1—Cu1 ⁱ	2.6563 (4)	C2—C3	1.399 (4)
I1—Cu1 ⁱⁱ	2.6582 (4)	C3—C4	1.398 (4)
Cu1—Cu1 ⁱ	2.7852 (4)	C3—C6	1.472 (4)
Cu1—Cu1 ⁱⁱ	2.7852 (4)	C4—H4	0.9300
Cu1—N1	2.039 (2)	C4—C5	1.384 (4)
N1—C1	1.344 (4)	C5—H5	0.9300

N1—C5	1.343 (4)	C6—C6 ⁱⁱⁱ	1.329 (5)
C1—H1	0.9300	C6—H6	0.9300
C1—C2	1.386 (4)		
Cu1—I1—Cu1 ⁱ	63.719 (10)	C5—N1—C1	117.0 (2)
Cu1—I1—Cu1 ⁱⁱ	63.694 (10)	N1—C1—H1	118.4
Cu1 ⁱ —I1—Cu1 ⁱⁱ	100.106 (12)	N1—C1—C2	123.2 (2)
I1—Cu1—I1 ⁱⁱ	116.327 (13)	C2—C1—H1	118.4
I1—Cu1—I1 ⁱ	116.263 (13)	C1—C2—H2	120.1
I1 ⁱⁱ —Cu1—I1 ⁱ	100.105 (13)	C1—C2—C3	119.7 (3)
I1—Cu1—Cu1 ⁱ	58.776 (13)	C3—C2—H2	120.1
I1 ⁱ —Cu1—Cu1 ⁱⁱ	125.749 (19)	C2—C3—C6	119.6 (2)
I1 ⁱⁱ —Cu1—Cu1 ⁱⁱ	57.506 (9)	C4—C3—C2	117.0 (2)
I1 ⁱⁱ —Cu1—Cu1 ⁱ	125.731 (19)	C4—C3—C6	123.4 (2)
I1—Cu1—Cu1 ⁱⁱ	58.820 (13)	C3—C4—H4	120.3
I1 ⁱ —Cu1—Cu1 ⁱ	57.487 (9)	C5—C4—C3	119.4 (2)
Cu1 ⁱ —Cu1—Cu1 ⁱⁱ	94.010 (19)	C5—C4—H4	120.3
N1—Cu1—I1 ⁱⁱ	110.72 (7)	N1—C5—C4	123.7 (3)
N1—Cu1—I1	106.57 (6)	N1—C5—H5	118.2
N1—Cu1—I1 ⁱ	106.46 (6)	C4—C5—H5	118.2
N1—Cu1—Cu1 ⁱⁱ	127.29 (7)	C3—C6—H6	117.5
N1—Cu1—Cu1 ⁱ	122.60 (7)	C6 ⁱⁱⁱ —C6—C3	124.9 (3)
C1—N1—Cu1	122.50 (18)	C6 ⁱⁱⁱ —C6—H6	117.5
C5—N1—Cu1	120.53 (18)		
Cu1—N1—C1—C2	178.0 (2)	C2—C3—C4—C5	0.5 (4)
Cu1—N1—C5—C4	-177.6 (2)	C2—C3—C6—C6 ⁱⁱⁱ	-177.1 (3)
N1—C1—C2—C3	0.0 (5)	C3—C4—C5—N1	-0.9 (5)
C1—N1—C5—C4	0.8 (4)	C4—C3—C6—C6 ⁱⁱⁱ	3.2 (5)
C1—C2—C3—C4	-0.1 (4)	C5—N1—C1—C2	-0.3 (4)
C1—C2—C3—C6	-179.8 (3)	C6—C3—C4—C5	-179.8 (3)

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x, -y+1, -z+1$.