



Crystal structure of di- μ -iodido-bis[bis-(acetonitrile- κ N)copper(I)]

Eva Rebecca Barth,^a Christopher Götz,^a Michael Knorr^b and Carsten Strohmann^{a*}

^aFakultät für Chemie und Chemische Biologie, Technische Universität Dortmund, Otto-Hahn-Strasse 6, 44227 Dortmund, Germany, and ^bInstitut UTINAM, UMR CNRS 6213, Université de Franche-Comté, 16 Route de Gray, 25030 Besançon, France. *Correspondence e-mail: carsten.strohmann@tu-dortmund.de

Received 24 August 2015; accepted 28 September 2015

Edited by M. Weil, Vienna University of Technology, Austria

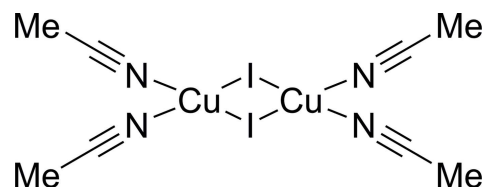
The title compound, $[\text{Cu}_2\text{I}_2(\text{CH}_3\text{CN})_4]$, exhibits a centrosymmetric Cu_2I_2 core [$\text{Cu}\cdots\text{Cu}$ distance = 2.7482 (11) Å], the Cu^{I} atoms of which are further coordinated by four molecules of acetonitrile. The Cu^{I} atom has an overall distorted tetrahedral coordination environment evidenced by $L-\text{Cu}-L$ angles ($L = \text{N}$ or I) ranging from 100.47 (10) to 117.06 (2)°. The coordination geometries of the acetonitrile ligands deviate slightly from linearity as shown by $\text{Cu}-\text{N}-\text{C}$ angles of 167.0 (2) and 172.7 (2)°. In the crystal, there are no significant hydrogen-bonding interactions present, so the crystal packing seems to be formed predominantly by van der Waals forces.

Keywords: crystal structure; copper(I) iodide complex; dimer.

CCDC reference: 1427944

1. Related literature

The title molecule is the active species used for the synthesis of luminescent compounds with $(\text{CuI})_n$ moieties, prepared by treatment with sulfur ligands. For more details of syntheses and properties of these compounds, see: Knorr *et al.* (2012, 2014, 2015). The $\text{N}-\text{Cu}-\text{N}$ angle of 100.47 (10)° in the title compound is comparable with that found in the pyridine-coordinated CuI dimer (Dyason *et al.*, 1984). For crystal structures of CuI dimers with additional diamine ligands, see: Haitko (2007); Garbaskas *et al.* (1986). The title compound represents, to the best of our knowledge, the first crystallographic characterization of CuI with acetonitrile as the only co-ligand, probably caused by the sensitive nature of the crystals. In the solid state, CuI appears as a polymer (Wyckoff & Posnjak, 1922).



2. Experimental

2.1. Crystal data

$[\text{Cu}_2\text{I}_2(\text{C}_2\text{H}_3\text{N})_4]$
 $M_r = 545.10$
Monoclinic $P2_1/c$
 $a = 7.669$ (3) Å
 $b = 14.367$ (5) Å
 $c = 7.944$ (3) Å
 $\beta = 116.957$ (5)°

$V = 780.2$ (5) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 6.66$ mm⁻¹
 $T = 173$ K
 $0.4 \times 0.3 \times 0.2$ mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2003)
 $T_{\text{min}} = 0.178$, $T_{\text{max}} = 1$

18211 measured reflections
1696 independent reflections
1628 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.056$
 $S = 1.16$
1696 reflections

76 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.70$ e Å⁻³

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS2014 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: SHELXTL (Sheldrick, 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: WM5208).

References

- Bruker (2003). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Dyason, J. C., Engelhardt, L. M., Healy, P. C. & White, A. H. (1984). *Aust. J. Chem.* **37**, 2201–2205.
- Garbaskas, M. F., Haitko, D. A. & Kasper, J. S. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 729–738.
- Haitko, D. A. (2007). *J. Coord. Chem.* **13**, 119–122.
- Knorr, M., Bonnot, A., Lappand, A., Khatyr, A., Strohmann, C., Kubicki, M. M., Rousselin, Y. & Harvey, P. D. (2015). *Inorg. Chem.* **54**, 4076–4093.

- Knorr, M., Guyon, F., Khatyr, A., Strohmann, C., Allain, M., Aly, A. M., Lapprand, A., Fortin, D. & Harvey, P. D. (2012). *Inorg. Chem.* **51**, 9917–9934.
- Knorr, M., Khatyr, A., Dini Aleo, A., El Yaagoubi, A., Strohmann, C., Kubicki, M. M., Rousselin, Y., Aly, A. M., Fortin, D., Lapprand, A. & Harvey, P. D. (2014). *Cryst. Growth Des.* **14**, 5373–5387.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **A71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wyckoff, R. W. G. & Posnjak, E. (1922). *J. Am. Chem. Soc.* **44**, 30–36.

supporting information

Acta Cryst. (2015). E71, m189–m190 [doi:10.1107/S2056989015018149]

Crystal structure of di- μ -iodido-bis[bis(acetonitrile- κ N)copper(I)]

Eva Rebecca Barth, Christopher Golz, Michael Knorr and Carsten Strohmann

S1. Synthesis and crystallization

The title compound occurred as a byproduct from the synthesis of copper(I) iodide compounds (see: *Related literature*). CuI was dissolved in acetonitrile and treated with an excess of sulfur ligands (*i.e.* dimethyl sulfide). After stirring, the solution was stored in a refrigerator over night, followed by keeping it in a freezer (Knorr *et al.*, 2015). In addition to the crystallized CuI compounds, the title compound could be isolated in traces.

S2. Refinement

Methyl hydrogen atoms were set geometrically and refined as a rotating group with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

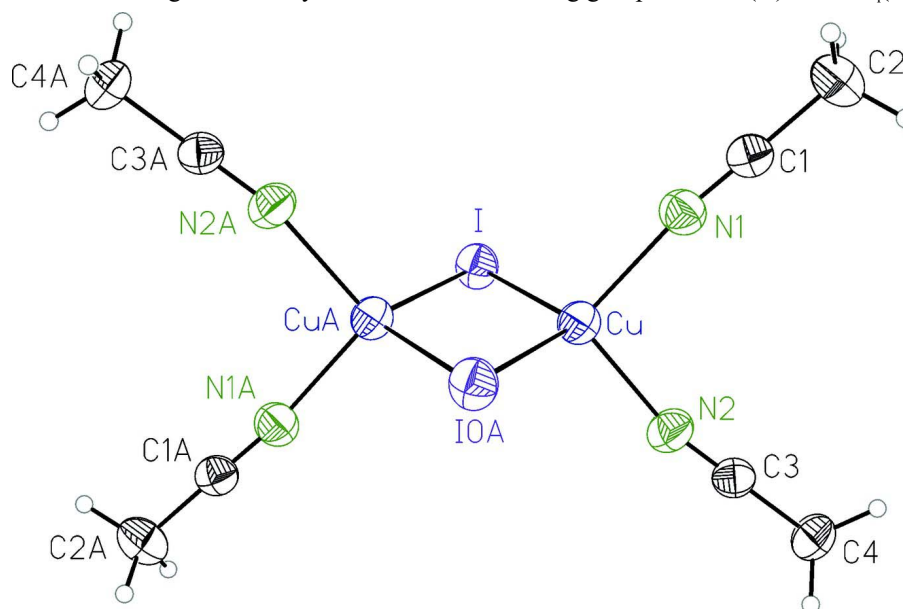


Figure 1

The molecular structure of the title compound with anisotropic displacement ellipsoids drawn at the 50% probability level.

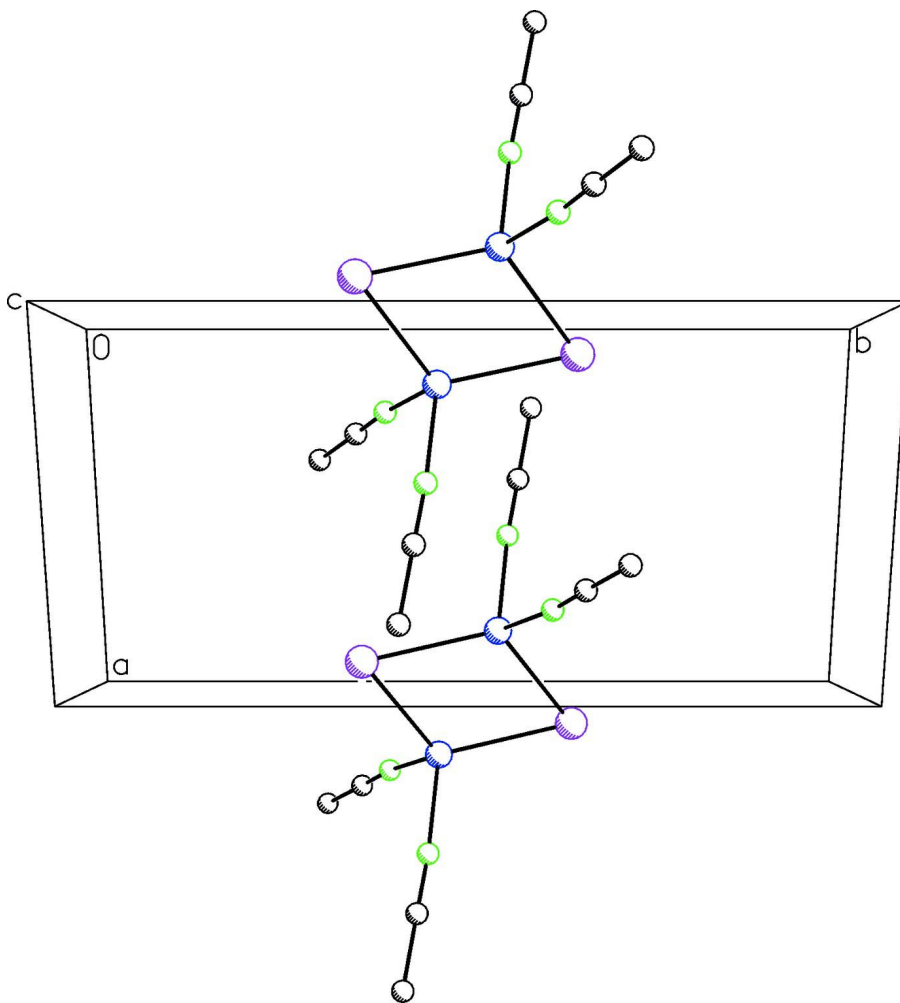


Figure 2

Part of the crystal packing of the title compound viewed along [001]. H atoms were omitted for clarity.

Di- μ -iodido-bis[bis(acetonitrile- κ N)copper(I)]

Crystal data

[Cu₂I₂(C₂H₃N)₄]

$M_r = 545.10$

Monoclinic, $P2_1/c$

$a = 7.669$ (3) Å

$b = 14.367$ (5) Å

$c = 7.944$ (3) Å

$\beta = 116.957$ (5)°

$V = 780.2$ (5) Å³

$Z = 2$

$F(000) = 504$

$D_x = 2.320$ Mg m⁻³

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

Cell parameters from 5543 reflections

$\theta = 2.8$ – 27.1 °

$\mu = 6.66$ mm⁻¹

$T = 173$ K

Block, colourless

$0.4 \times 0.3 \times 0.2$ mm

Data collection

Bruker APEXII CCD
diffractometer

Graphite monochromator
phi and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2003)

$T_{\min} = 0.178$, $T_{\max} = 1$

18211 measured reflections

1696 independent reflections
 1628 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\text{max}} = 27.0^\circ$, $\theta_{\text{min}} = 2.8^\circ$

$h = -9 \rightarrow 9$
 $k = -18 \rightarrow 18$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.056$
 $S = 1.16$
 1696 reflections
 76 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.2851P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.77 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.70 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL2014* (Sheldrick,
 2015), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0356 (10)

Special details

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

Refinement. 1. Fixed U_{iso} At 1.5 times of: All C(H,H,H) groups 2.a Idealized Me refined as rotating group: C2(H2A,H2B,H2C), C4(H4A,H4B,H4C)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2924 (4)	0.35511 (17)	0.2436 (4)	0.0327 (5)
C2	0.3602 (5)	0.3046 (2)	0.1258 (5)	0.0477 (7)
H2A	0.3147	0.2400	0.1117	0.072*
H2B	0.5035	0.3057	0.1851	0.072*
H2C	0.3081	0.3341	0.0012	0.072*
C3	0.5869 (4)	0.43439 (18)	0.8689 (4)	0.0327 (5)
C4	0.7870 (4)	0.4169 (2)	1.0081 (4)	0.0440 (6)
H4A	0.7881	0.3711	1.1000	0.066*
H4B	0.8464	0.4750	1.0734	0.066*
H4C	0.8617	0.3927	0.9451	0.066*
Cu	0.17322 (5)	0.46160 (2)	0.52217 (4)	0.03798 (12)
I	-0.09223 (2)	0.36402 (2)	0.57402 (3)	0.03945 (11)
N1	0.2374 (3)	0.39446 (16)	0.3335 (3)	0.0386 (5)
N2	0.4306 (3)	0.44856 (16)	0.7589 (3)	0.0402 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0351 (13)	0.0281 (12)	0.0329 (13)	-0.0024 (9)	0.0137 (11)	0.0016 (9)
C2	0.0589 (18)	0.0430 (15)	0.0494 (17)	-0.0014 (13)	0.0318 (15)	-0.0063 (13)
C3	0.0348 (13)	0.0328 (12)	0.0294 (11)	-0.0015 (10)	0.0137 (10)	0.0003 (10)
C4	0.0323 (13)	0.0523 (17)	0.0381 (14)	0.0054 (12)	0.0077 (11)	0.0013 (12)
Cu	0.03422 (19)	0.0400 (2)	0.03415 (19)	0.00505 (13)	0.01066 (14)	-0.00146 (13)

I	0.03990 (14)	0.03205 (13)	0.04649 (15)	0.00095 (6)	0.01965 (10)	0.00337 (6)
N1	0.0407 (12)	0.0370 (12)	0.0369 (12)	0.0027 (10)	0.0164 (10)	-0.0009 (10)
N2	0.0345 (12)	0.0438 (13)	0.0353 (11)	0.0002 (10)	0.0096 (10)	0.0007 (10)

Geometric parameters (Å, °)

C1—C2	1.454 (4)	C4—H4B	0.9800
C1—N1	1.132 (4)	C4—H4C	0.9800
C2—H2A	0.9800	Cu—Cu ⁱ	2.7482 (11)
C2—H2B	0.9800	Cu—I ⁱ	2.6108 (10)
C2—H2C	0.9800	Cu—I	2.6532 (8)
C3—C4	1.450 (3)	Cu—N1	2.022 (2)
C3—N2	1.137 (3)	Cu—N2	2.025 (2)
C4—H4A	0.9800	I—Cu ⁱ	2.6108 (10)
N1—C1—C2	179.2 (3)	I—Cu—Cu ⁱ	57.78 (3)
C1—C2—H2A	109.5	I ⁱ —Cu—Cu ⁱ	59.286 (14)
C1—C2—H2B	109.5	I ⁱ —Cu—I	117.06 (2)
C1—C2—H2C	109.5	N1—Cu—Cu ⁱ	129.99 (7)
H2A—C2—H2B	109.5	N1—Cu—I	108.95 (7)
H2A—C2—H2C	109.5	N1—Cu—I ⁱ	110.27 (7)
H2B—C2—H2C	109.5	N1—Cu—N2	100.47 (10)
N2—C3—C4	179.4 (3)	N2—Cu—Cu ⁱ	129.41 (8)
C3—C4—H4A	109.5	N2—Cu—I	107.48 (8)
C3—C4—H4B	109.5	N2—Cu—I ⁱ	111.28 (7)
C3—C4—H4C	109.5	Cu ⁱ —I—Cu	62.94 (2)
H4A—C4—H4B	109.5	C1—N1—Cu	172.7 (2)
H4A—C4—H4C	109.5	C3—N2—Cu	167.0 (2)
H4B—C4—H4C	109.5		

Symmetry code: (i) $-x, -y+1, -z+1$.