

## 4,5-Dihydro-3a,5a-diazoniapyrene triiodidocuprate(I)

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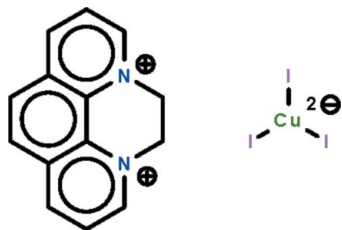
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å;  $R$  factor = 0.028;  $wR$  factor = 0.065; data-to-parameter ratio = 20.4.

In the dianion of the title salt,  $(\text{C}_{14}\text{H}_{12}\text{N}_2)[\text{CuI}_3]$ , the  $\text{Cu}^{\text{I}}$  atom is coordinated by three  $\text{I}^-$  ions that define a nearly trigonal-planar geometry; the  $\text{Cu}^{\text{I}}$  atom lies 0.1407 (6) Å out of the plane. With the exception of the methylene C atoms, the dication is essentially planar (r.m.s deviation = 0.067 Å). The most significant interaction between the ions is a  $\text{C}-\text{H}\cdots\text{I}$  contact.

### Related literature

For studies of the triiodidocuprate(I) di-anion, see: Mishra *et al.* (2008); Su *et al.* (2003). For background to the phenanthroline di-cation as a template for the construction of thiocyanatocuprate(I) polymers, see: Yue *et al.* (2010). For information on the Cambridge Structural Database, see: Allen (2002).



### Experimental

#### Crystal data

$(\text{C}_{14}\text{H}_{12}\text{N}_2)[\text{CuI}_3]$   
 $M_r = 652.50$   
Monoclinic,  $P2_1/n$   
 $a = 7.6018$  (6) Å  
 $b = 15.0917$  (12) Å  
 $c = 14.2776$  (12) Å  
 $\beta = 98.903$  (1)°

$V = 1618.2$  (2) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 7.06$  mm<sup>-1</sup>  
 $T = 100$  K  
0.20 × 0.20 × 0.02 mm

#### Data collection

Bruker SMART APEX  
diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.332$ ,  $T_{\max} = 0.872$

14984 measured reflections  
3701 independent reflections  
3065 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.055$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.065$   
 $S = 1.05$   
3701 reflections  
181 parameters

6 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.73$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.82$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cu—I1	2.5336 (7)	Cu—I3	2.5025 (7)
Cu—I2	2.5254 (7)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C13}-\text{H13b}\cdots\text{I2}$	0.99	3.06	3.969 (4)	154

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5714).

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## supporting information

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**4,5-Dihydro-3a,5a-diazoniapyrene triiodocuprate(I)**

**Di Wu, Peng-Chao Hao, Yun-Yin Niu, Seik Weng Ng and Edward R. T. Tiekink**

**S1. Comment**

Organic-inorganic hybrid compounds containing the triiodocuprate(I) anion have been the subject of recent investigations (Mishra *et al.*, 2008; Su *et al.*, 2003). While the phenanthroline di-cation has proved to be a suitable template for the construction of a thiocyanatocuprate(I) polymer (Yue *et al.*, 2010), crystal structures containing the phenanthroline template are relatively scarce (Allen, 2002). In this communication the crystal structure of a new triiodocuprate(I) complex containing the 5,6-dihydrodipyrazino(1,2,3,4-*lmn*)-1,10-phenanthroline dication, *i.e.* (I), is described.

The crystallographic asymmetric unit of (I), comprises a di-cation and a di-anion, Fig. 1. The 14 non-hydrogen atoms comprising the aromatic part of the di-cation are effectively planar with a r.m.s. deviation = 0.067 Å; the maximum deviations of 0.090 (5) and -0.117 (4) Å are found for the C10 and N1 atoms, respectively. The C13 and C14 atoms lie 0.267 (5) and -0.480 (5) Å out of this plane, respectively. In the di-anion, the Cu—I distances lie in a relatively narrow range (Table 1) and the Cu atom lies 0.1407 (6) Å above the trigonal plane defined by the iodido atoms.

In the crystal structure, the ions are almost parallel (dihedral angle between the 1,10-phenanthroline and CuI<sub>3</sub> planes = 1.45 (4) °) with the closest interaction between them being a C—H···I contact, Table 2. The I3 atom lies over the (C4—C7,C11,C12) ring, with the I3···ring centroid distance = 3.5842 (19) Å and the Cu—I3···ring centroid angle = 101.22 (3)°.

**S2. Experimental**

5,6-Dihydrodipyrazino(1,2,3,4-*lmn*)-1,10-phenanthroline dibromide was synthesized by reacting 1,2-dibromoethane with 1,10-phenanthroline monohydrate. A methanol solution (10 ml) of the salt (0.37 g, 1 mmol) was mixed with a water/DMF (1:4) solution (10 ml) of cuprous iodide (0.19 g, 1 mmol). An excess of potassium iodide (0.83 g, 5 mmol) was added. The solution was filtered and the solvent allowed to evaporate slowly to furnish dark-brown crystals of the cuprate salt.

**S3. Refinement**

H-atoms were placed in calculated positions (C—H 0.95 to 0.99 Å) and were included in the refinement in the riding model approximation with  $U_{iso}(\text{H})$  set to  $1.2U_{eq}(\text{C})$ . The anisotropic displacement ellipsoid of one of the phenanthroline C-atoms (C12) was tightly restrained to be nearly isotropic.

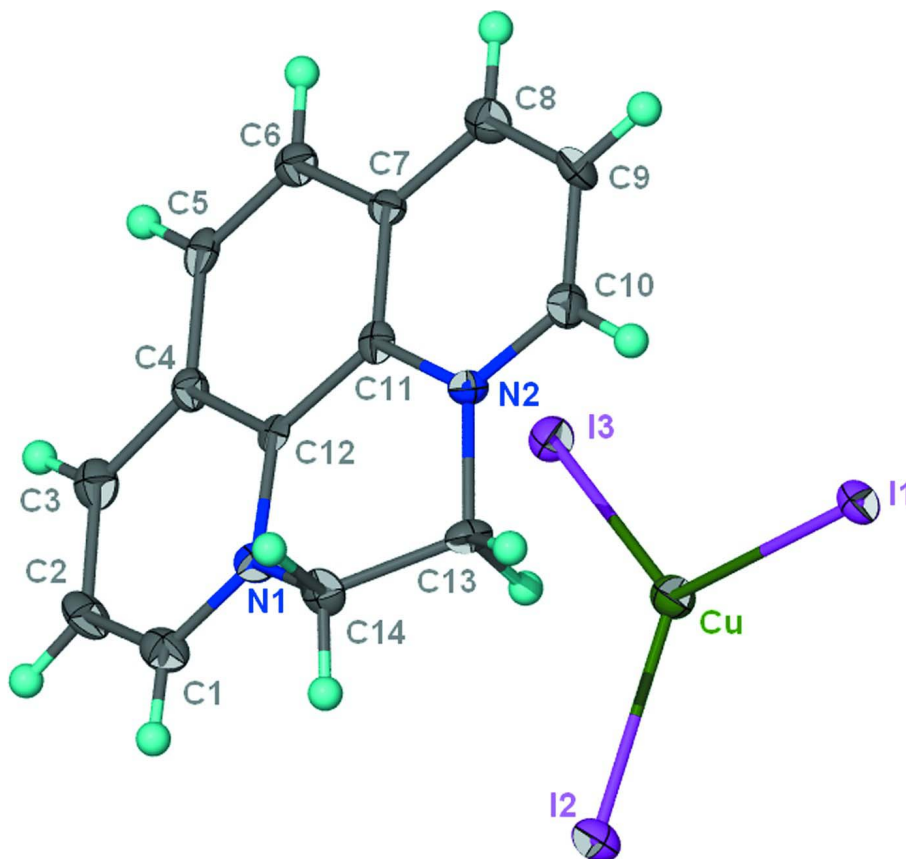


Figure 1

Displacement ellipsoid plot (Barbour, 2001) of (I) drawn at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

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##### Crystal data

(C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>)[CuI<sub>3</sub>]

*M<sub>r</sub>* = 652.50

Monoclinic, *P*2<sub>1</sub>/*n*

Hall symbol: -*P* 2<sub>1</sub>yn

*a* = 7.6018 (6) Å

*b* = 15.0917 (12) Å

*c* = 14.2776 (12) Å

$\beta$  = 98.903 (1)°

*V* = 1618.2 (2) Å<sup>3</sup>

*Z* = 4

*F*(000) = 1192

*D<sub>x</sub>* = 2.678 Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda$  = 0.71073 Å

Cell parameters from 4486 reflections

$\theta$  = 2.9–28.1°

$\mu$  = 7.06 mm<sup>-1</sup>

*T* = 100 K

Plate, brown

0.20 × 0.20 × 0.02 mm

##### Data collection

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

*T<sub>min</sub>* = 0.332, *T<sub>max</sub>* = 0.872

14984 measured reflections

3701 independent reflections

3065 reflections with *I* > 2σ(*I*)

$R_{\text{int}} = 0.055$   
 $\theta_{\text{max}} = 27.5^\circ$ ,  $\theta_{\text{min}} = 2.0^\circ$   
 $h = -9 \rightarrow 9$

$k = -19 \rightarrow 19$   
 $l = -18 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.065$   
 $S = 1.05$   
 3701 reflections  
 181 parameters  
 6 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 1.1596P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.73 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.82 \text{ e } \text{\AA}^{-3}$

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.66182 (4)	0.44391 (2)	0.12230 (2)	0.01428 (8)
I2	0.67359 (4)	0.43433 (2)	0.42229 (2)	0.01632 (9)
I3	0.49833 (4)	0.19901 (2)	0.24528 (2)	0.01604 (9)
Cu	0.62612 (8)	0.35182 (4)	0.26653 (4)	0.01510 (14)
N1	0.1049 (5)	0.3718 (3)	0.3535 (3)	0.0130 (8)
N2	0.1521 (5)	0.4112 (3)	0.1658 (3)	0.0119 (8)
C1	0.0995 (6)	0.3503 (3)	0.4439 (3)	0.0160 (10)
H1	0.1218	0.3950	0.4911	0.019*
C2	0.0627 (6)	0.2657 (3)	0.4704 (3)	0.0169 (10)
H2	0.0668	0.2510	0.5354	0.020*
C3	0.0196 (6)	0.2024 (3)	0.4013 (3)	0.0165 (10)
H3	-0.0120	0.1443	0.4182	0.020*
C4	0.0223 (6)	0.2236 (3)	0.3056 (3)	0.0126 (9)
C5	-0.0244 (6)	0.1603 (3)	0.2316 (3)	0.0133 (10)
H5	-0.0615	0.1025	0.2464	0.016*
C6	-0.0163 (6)	0.1820 (3)	0.1401 (3)	0.0140 (10)
H6	-0.0494	0.1394	0.0916	0.017*
C7	0.0411 (6)	0.2679 (3)	0.1155 (3)	0.0110 (9)
C8	0.0559 (6)	0.2916 (3)	0.0224 (3)	0.0154 (10)
H8	0.0228	0.2505	-0.0277	0.019*
C9	0.1181 (6)	0.3739 (3)	0.0029 (3)	0.0145 (10)
H9	0.1255	0.3906	-0.0605	0.017*
C10	0.1702 (6)	0.4327 (3)	0.0771 (3)	0.0148 (10)
H10	0.2190	0.4886	0.0645	0.018*
C11	0.0871 (6)	0.3306 (3)	0.1873 (3)	0.0109 (9)
C12	0.0725 (6)	0.3089 (3)	0.2834 (3)	0.0096 (9)
C13	0.2245 (6)	0.4716 (3)	0.2442 (3)	0.0126 (10)
H13A	0.2214	0.5333	0.2206	0.015*
H13B	0.3500	0.4559	0.2678	0.015*
C14	0.1165 (6)	0.4646 (3)	0.3240 (3)	0.0140 (10)
H14A	0.1729	0.5006	0.3785	0.017*

H14B            -0.0047                    0.4882                    0.3029                    0.017\*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
I1	0.01585 (16)	0.01624 (17)	0.01116 (15)	0.00100 (12)	0.00336 (12)	0.00077 (12)
I2	0.01971 (17)	0.01736 (17)	0.01211 (15)	0.00023 (13)	0.00313 (12)	-0.00156 (12)
I3	0.01528 (16)	0.01722 (17)	0.01553 (16)	-0.00182 (12)	0.00215 (12)	0.00031 (12)
Cu	0.0145 (3)	0.0173 (3)	0.0134 (3)	0.0010 (2)	0.0021 (2)	-0.0004 (2)
N1	0.0086 (19)	0.019 (2)	0.0107 (19)	0.0034 (16)	-0.0015 (15)	0.0011 (16)
N2	0.011 (2)	0.014 (2)	0.0104 (19)	-0.0011 (15)	0.0006 (16)	-0.0021 (15)
C1	0.016 (3)	0.019 (3)	0.013 (2)	0.004 (2)	0.0004 (19)	0.0003 (19)
C2	0.019 (3)	0.022 (3)	0.009 (2)	0.005 (2)	0.002 (2)	0.004 (2)
C3	0.015 (2)	0.017 (3)	0.018 (2)	0.002 (2)	0.004 (2)	0.002 (2)
C4	0.010 (2)	0.015 (2)	0.013 (2)	0.0014 (18)	0.0027 (18)	0.0013 (18)
C5	0.007 (2)	0.015 (2)	0.018 (2)	0.0005 (18)	0.0022 (18)	0.0038 (19)
C6	0.011 (2)	0.014 (2)	0.016 (2)	0.0016 (18)	0.0020 (19)	-0.0015 (19)
C7	0.009 (2)	0.013 (2)	0.011 (2)	0.0007 (18)	0.0011 (17)	-0.0016 (18)
C8	0.014 (2)	0.017 (3)	0.015 (2)	0.0033 (19)	0.0025 (19)	-0.0017 (19)
C9	0.018 (3)	0.018 (3)	0.009 (2)	0.000 (2)	0.0046 (19)	0.0003 (19)
C10	0.012 (2)	0.020 (3)	0.012 (2)	0.0003 (19)	0.0013 (19)	0.004 (2)
C11	0.008 (2)	0.013 (2)	0.012 (2)	0.0025 (17)	0.0009 (17)	0.0034 (18)
C12	0.0033 (19)	0.013 (2)	0.012 (2)	0.0025 (16)	0.0008 (16)	-0.0009 (17)
C13	0.014 (2)	0.011 (2)	0.012 (2)	-0.0016 (18)	-0.0024 (18)	-0.0007 (18)
C14	0.017 (3)	0.010 (2)	0.016 (2)	0.0032 (19)	0.006 (2)	-0.0020 (18)

*Geometric parameters (Å, °)*

Cu—I1	2.5336 (7)	C5—C6	1.357 (6)
Cu—I2	2.5254 (7)	C5—H5	0.9500
Cu—I3	2.5025 (7)	C6—C7	1.429 (6)
N1—C1	1.337 (6)	C6—H6	0.9500
N1—C12	1.375 (6)	C7—C8	1.398 (6)
N1—C14	1.470 (6)	C7—C11	1.399 (6)
N2—C10	1.336 (6)	C8—C9	1.373 (7)
N2—C11	1.366 (6)	C8—H8	0.9500
N2—C13	1.481 (6)	C9—C10	1.391 (6)
C1—C2	1.374 (7)	C9—H9	0.9500
C1—H1	0.9500	C10—H10	0.9500
C2—C3	1.376 (7)	C11—C12	1.431 (6)
C2—H2	0.9500	C13—C14	1.507 (6)
C3—C4	1.406 (6)	C13—H13A	0.9900
C3—H3	0.9500	C13—H13B	0.9900
C4—C12	1.394 (6)	C14—H14A	0.9900
C4—C5	1.428 (7)	C14—H14B	0.9900
I3—Cu—I2	124.13 (3)	C11—C7—C6	118.9 (4)
I3—Cu—I1	119.69 (2)	C9—C8—C7	120.3 (4)

I2—Cu—I1	115.25 (3)	C9—C8—H8	119.9
C1—N1—C12	120.5 (4)	C7—C8—H8	119.9
C1—N1—C14	121.3 (4)	C8—C9—C10	119.3 (4)
C12—N1—C14	117.5 (4)	C8—C9—H9	120.4
C10—N2—C11	121.5 (4)	C10—C9—H9	120.4
C10—N2—C13	119.1 (4)	N2—C10—C9	120.6 (4)
C11—N2—C13	118.9 (4)	N2—C10—H10	119.7
N1—C1—C2	121.9 (5)	C9—C10—H10	119.7
N1—C1—H1	119.0	N2—C11—C7	119.7 (4)
C2—C1—H1	119.0	N2—C11—C12	120.2 (4)
C1—C2—C3	119.0 (4)	C7—C11—C12	120.0 (4)
C1—C2—H2	120.5	N1—C12—C4	119.8 (4)
C3—C2—H2	120.5	N1—C12—C11	120.6 (4)
C2—C3—C4	120.0 (5)	C4—C12—C11	119.7 (4)
C2—C3—H3	120.0	N2—C13—C14	110.3 (4)
C4—C3—H3	120.0	N2—C13—H13A	109.6
C12—C4—C3	118.5 (4)	C14—C13—H13A	109.6
C12—C4—C5	119.6 (4)	N2—C13—H13B	109.6
C3—C4—C5	121.8 (4)	C14—C13—H13B	109.6
C6—C5—C4	120.5 (4)	H13A—C13—H13B	108.1
C6—C5—H5	119.8	N1—C14—C13	110.3 (4)
C4—C5—H5	119.8	N1—C14—H14A	109.6
C5—C6—C7	121.2 (4)	C13—C14—H14A	109.6
C5—C6—H6	119.4	N1—C14—H14B	109.6
C7—C6—H6	119.4	C13—C14—H14B	109.6
C8—C7—C11	118.5 (4)	H14A—C14—H14B	108.1
C8—C7—C6	122.6 (4)		
C12—N1—C1—C2	0.3 (7)	C8—C7—C11—N2	-2.8 (7)
C14—N1—C1—C2	170.3 (4)	C6—C7—C11—N2	176.2 (4)
N1—C1—C2—C3	-4.0 (7)	C8—C7—C11—C12	179.6 (4)
C1—C2—C3—C4	3.1 (7)	C6—C7—C11—C12	-1.4 (7)
C2—C3—C4—C12	1.2 (7)	C1—N1—C12—C4	4.2 (6)
C2—C3—C4—C5	-178.9 (4)	C14—N1—C12—C4	-166.2 (4)
C12—C4—C5—C6	1.5 (7)	C1—N1—C12—C11	-176.8 (4)
C3—C4—C5—C6	-178.4 (4)	C14—N1—C12—C11	12.8 (6)
C4—C5—C6—C7	0.8 (7)	C3—C4—C12—N1	-4.8 (6)
C5—C6—C7—C8	178.1 (4)	C5—C4—C12—N1	175.2 (4)
C5—C6—C7—C11	-0.9 (7)	C3—C4—C12—C11	176.1 (4)
C11—C7—C8—C9	1.5 (7)	C5—C4—C12—C11	-3.8 (6)
C6—C7—C8—C9	-177.6 (4)	N2—C11—C12—N1	7.2 (6)
C7—C8—C9—C10	1.5 (7)	C7—C11—C12—N1	-175.3 (4)
C11—N2—C10—C9	1.8 (7)	N2—C11—C12—C4	-173.9 (4)
C13—N2—C10—C9	174.2 (4)	C7—C11—C12—C4	3.7 (6)
C8—C9—C10—N2	-3.2 (7)	C10—N2—C13—C14	150.5 (4)
C10—N2—C11—C7	1.2 (7)	C11—N2—C13—C14	-36.9 (6)
C13—N2—C11—C7	-171.2 (4)	C1—N1—C14—C13	146.4 (4)
C10—N2—C11—C12	178.8 (4)	C12—N1—C14—C13	-43.3 (5)

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C13—N2—C11—C12	6.4 (6)	N2—C13—C14—N1	53.7 (5)
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*Hydrogen-bond geometry (Å, °)*

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<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C13—H13b···I2	0.99	3.06	3.969 (4)	154

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