

## Redetermination of bis(2,2'-bipyridine)iodocopper(II) triiodide

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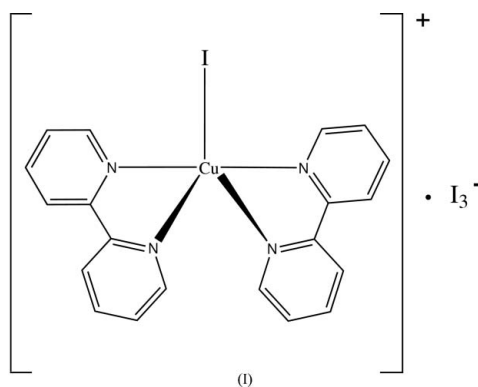
## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.011$  Å  
 $R$  factor = 0.044  
 $wR$  factor = 0.095  
Data-to-parameter ratio = 21.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

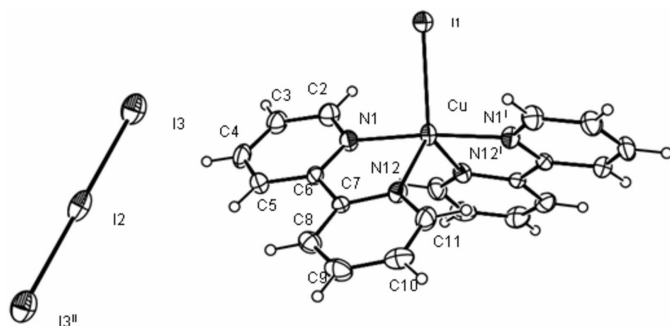
The crystal structure of the title compound,  $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2]\text{I}_3$ , has been reported previously [Freckmann & Tebbe (1981), *Acta Cryst.* **A37**, C-228], but full results were not published. The cation and anion possess crystallographically imposed  $C_2$  and  $C_i$  symmetry, respectively. The  $\text{Cu}^{\text{II}}$  atom is coordinated by four N atoms of two bidentate 2,2'-bipyridine ligands and one I atom in a distorted trigonal-bipyramidal geometry. The I atom occupies an equatorial position. In the crystal packing, the aryl rings of adjacent bipyridine ligands stack along the  $c$  axis to form zigzag chains, with  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{N}$  separations in the range 3.365–3.713 Å.

## Comment

The  $\text{Ag}^{\text{I}}$ -assisted exchange reaction strategy for the synthesis of bis- and tris-chelated copper(II) and ruthenium(II) complexes has been developed by Majumdar *et al.* (1998). For example, the reaction of  $\text{Cu}(\text{L})\text{Cl}_2$  with two moles of  $\text{AgL}'_2^+$  [ $\text{L}$  is 1,10-phenanthroline (phen) and  $\text{L}'$  is 2,2'-bipyridine (bipy)] produces the  $\text{Cu}(\text{LL}')^+$  cation, where two  $\text{Cl}^-$  anions have been transferred from  $\text{Cu}^{\text{II}}$  to  $\text{Ag}^{\text{I}}$  and two  $\text{L}'$  ligands have been transferred from  $\text{Ag}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$  (Deb *et al.*, 1991; Kakoti *et al.*, 1992; Majumdar *et al.*, 1998). The main driving force for these exchange reactions is presumably the great affinity of  $\text{Ag}^{\text{I}}$  towards the halide ion. In the present work, we tested the  $\text{Cu}(\text{bipy})\text{I}_2$ – $\text{Zn}(\text{bipy})\text{I}_2$  pair, in the hope of observing this type of exchange reaction occurring between two metal(II) compounds. The stability of 3d metal(II) ions to bidentate  $N$ -donor ligands such as ethylenediamine increases in the series  $\text{Ba}^{2+}$ – $\text{Cu}^{2+}$ , but decreases sharply with  $\text{Zn}^{2+}$  (Siegel & McCormick, 1970), and one can expect that the greater affinity of  $\text{Cu}^{\text{II}}$  than  $\text{Zn}^{\text{II}}$  towards the bipy ligand might induce the transfer of the bipy ligand from  $\text{Zn}(\text{bipy})\text{I}_2$  to  $\text{Cu}(\text{bipy})\text{I}_2$ .

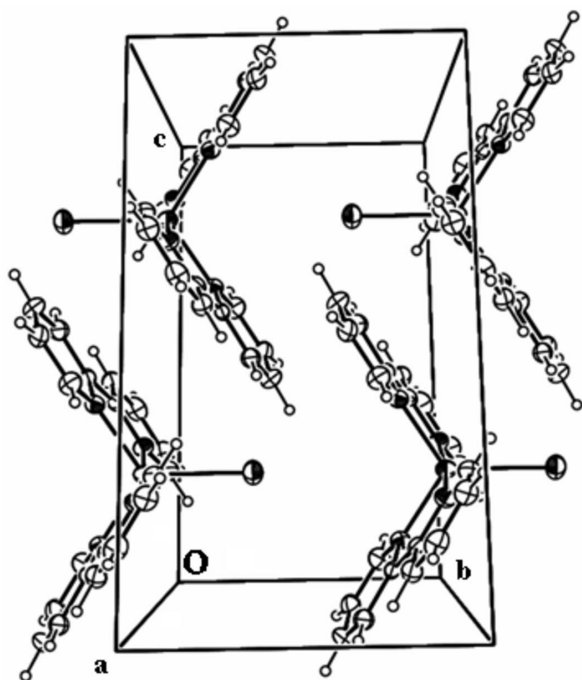


The ion-pair complex  $[\text{Cu}(\text{bipy})_2\text{I}]\text{I}_3$  was produced from the reaction between  $\text{Cu}(\text{bipy})\text{I}_2$  and  $\text{Zn}(\text{bipy})\text{I}_2$ . Showing



**Figure 1**

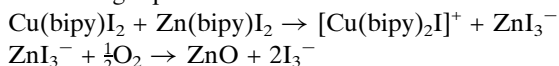
The molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. [Symmetry codes: (I)  $-x, y, \frac{1}{2} - z$ ; (II)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ .]



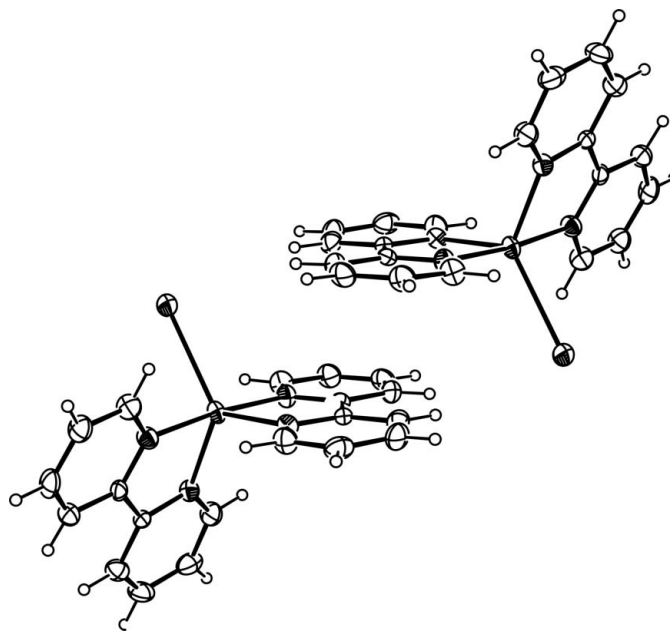
**Figure 2**

The crystal packing of (I), viewed along the *a* axis. The  $I_3^-$  anions have been omitted for clarity.

different behaviour from that observed in the exchange reaction of  $Cu^{II}$  chloride compounds with  $AgCl$  (Majumdar *et al.*, 1998), the oxidation of the  $I^-$  anions in  $Zn(bipy)I_2$  occurs, resulting in the formation of the  $I_3^-$  anion in this reaction. The bipy ligand coordinated to the  $Zn^{II}$  centre in  $Zn(bipy)I_2$  is transferred to the  $Cu^{II}$  centre of  $Cu(bipy)I_2$ , while one  $I^-$  ligand of  $Cu(bipy)I_2$  dissociates from the  $Cu^{II}$  centre, resulting in the formation of the five-coordinated  $[Cu(bipy)_2I]^+$  cation. The dissociated  $I^-$  anion reacts with the  $Zn^{II}$  complex in the presence of dioxygen to produce the  $I_3^-$  anion. The reaction for the formation of the ion-pair complex can be described by the following equations:



The structure of the title compound, (I), has been reported previously by Freckmann & Tebbe (1981) in the non-standard



**Figure 3**

The stacking of adjacent  $[Cu(bipy)_2I]^+$  cations along the *c* axis.

setting  $I2/c$ . However, as neither atomic coordinates nor details of the experiment were published, no comparison between the two structure determinations can be made. We present here a redetermination of this structure, based on new CCD intensity data.

The  $[Cu(bipy)_2I]^+$  cation shows crystallographically imposed  $C_2$  symmetry. In the anion, atom I2 is located on a centre of symmetry to form the linear  $I_3^-$  unit. The coordination geometry about the  $Cu^{II}$  atom in the cation (Fig. 1, Table 1) can be described as distorted trigonal-bipyramidal, with the axial positions occupied by the N1 atoms of the symmetry-related bipy ligands [ $N1-Cu-N1^i$   $173.8(3)^\circ$ ; symmetry code (i)  $-x, y, \frac{1}{2} - z$ ]. The overall geometry of the  $[Cu(bipy)_2I]^+$  cation is similar to that observed in the triclinic form of  $[Cu(phen)_2I]I_3$  (Horn *et al.*, 2000).

A crystal packing diagram, viewed down the *a* axis, of the arrangement of the  $[Cu(bipy)_2I]^+$  cations is shown in Fig. 2. Adjacent cations stack along the *c* axis to form zigzag chains with  $C \cdots C$  and  $C \cdots N$  separations in the range 3.365 (10)–3.713 (10) Å (Fig. 3). The shortest distance involving I and H atoms of adjacent chains is  $I1 \cdots H8^{ii} = 3.15$  Å [symmetry code: (ii)  $-x, 1 - y, -z$ ].

## Experimental

The precursor compound  $[Cu(bipy)I_2]$  was prepared as follows. 2,2'-Bipyridine (0.812 g, 5.2 mmol) in ethanol–triethyl orthoformate (5:1 v/v, 60 ml) was slowly added to  $Cu(NO_3)_2 \cdot 3H_2O$  (1.208 g, 5 mmol) dissolved in ethanol (60 ml), and then additional 2,2'-bipyridine (0.484 g, 3.1 mmol) was added to the mixture. The light-blue precipitate was filtered, washed with cold EtOH and dried under a vacuum to give  $[Cu(bipy)(NO_3)_2]$ .  $[Cu(bipy)I_2]$  was prepared by reaction of  $[Cu(bipy)(NO_3)_2]$  (1.31 g, 3 mmol) with NaI (0.899 g, 6 mmol) dissolved in ethanol (60 ml). The resulting olive-green precipitate was filtered, washed with cold EtOH and dried under a vacuum in a glove

box (yield 70.2%). Analysis calculated for  $C_{10}H_8N_2CuI_2$ : C 25.36, H 1.70, N 5.92%; found: C 25.19, H 1.92, N 5.79%. The precursor compound  $[Zn(bipy)I_2]$  was prepared as follows. Zinc(II) iodide (0.670 g, 2.099 mmol) was dissolved in ethanol (50 ml) and then 2,2'-bipyridine (0.345 g, 2.2 mmol) was added to the solution. The white precipitate which formed was filtered, washed with cold EtOH and dried under a vacuum in a glove box (yield 90.1%). Analysis calculated for  $C_{10}H_8N_2ZnI_2$ : C 25.27, H 1.70, N 5.89%; found: C 25.31, H 1.62, N 5.62%. The compounds  $[Cu(bipy)I_2]$  (0.237 g, 0.55 mmol) and  $[Zn(bipy)I_2]$  (0.238 g, 0.5 mmol) were mixed and dissolved in dimethyl sulfoxide (10 ml). The mixture was allowed to react at room temperature and stirred vigorously for 1 h. Dark-purple crystals of  $[Cu(bipy)_2I]_3$ , (I), suitable for X-ray analysis were isolated by filtration, washed several times with cold ethanol and dried in a vacuum desiccator.

Crystal data

$[CuI(C_{20}H_{16}N_4)]_3$   $D_x = 2.353 \text{ Mg m}^{-3}$   
 $M_r = 883.51$  Mo  $K\alpha$  radiation  
 Monoclinic,  $C2/c$  Cell parameters from 25 reflections  
 $a = 26.353(3) \text{ \AA}$   $\theta = 11.5\text{--}14.3^\circ$   
 $b = 7.3649(7) \text{ \AA}$   $\mu = 5.84 \text{ mm}^{-1}$   
 $c = 14.8434(16) \text{ \AA}$   $T = 295(2) \text{ K}$   
 $\beta = 120.057(10)^\circ$  Block, dark purple  
 $V = 2493.5(5) \text{ \AA}^3$   $0.23 \times 0.20 \times 0.20 \text{ mm}$   
 $Z = 4$

Data collection

Enraf–Nonius CAD-4  $R_{int} = 0.023$   
 diffractometer  $\theta_{max} = 27.5^\circ$   
 Non-profiled  $\omega/2\theta$  scans  $h = -34 \rightarrow 29$   
 Absorption correction:  $\psi$  scan  $k = 0 \rightarrow 9$   
 (North *et al.*, 1968)  $l = 0 \rightarrow 19$   
 $T_{min} = 0.265$ ,  $T_{max} = 0.305$  3 standard reflections  
 2972 measured reflections every 400 reflections  
 2856 independent reflections intensity decay: 4%  
 1927 reflections with  $I > 2\sigma(I)$

Refinement

Refinement on  $F^2$   $w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 8.6223P]$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$  where  $P = (F_o^2 + 2F_c^2)/3$   
 $wR(F^2) = 0.095$   $(\Delta/\sigma)_{max} < 0.001$   
 $S = 1.01$   $\Delta\rho_{max} = 1.26 \text{ e \AA}^{-3}$   
 2856 reflections  $\Delta\rho_{min} = -0.80 \text{ e \AA}^{-3}$   
 134 parameters  
 H-atom parameters constrained

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

I1—Cu	2.6630 (13)	Cu—N1	1.991 (5)
I2—I3	2.9238 (7)	Cu—N12	2.086 (5)
N1 <sup>1</sup> —Cu—N1	173.8 (3)	N1—Cu—I1	93.11 (16)
N1—Cu—N12	80.4 (2)	N12—Cu—I1	123.10 (14)
N12—Cu—N12 <sup>1</sup>	113.8 (3)		

Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ .

The H atoms of the 2,2'-bipyridine ligand were positioned geometrically and constrained to ride on their attached atoms, with  $C-H = 0.93 \text{ \AA}$  and  $U_{iso}(H) = 1.2U_{eq}(C)$ . The largest residuals in the final difference map were  $0.88 \text{ \AA}$  from atom I3 and  $0.91 \text{ \AA}$  from atom I1.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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