

## Bis(2,2'-bipyridine-1 $\kappa^2$ N,N')- $\mu$ -bromido-1:2 $\kappa^2$ Br-tribromido-2 $\kappa^3$ Br-copper(II)-mercury(II)

Yong-Min Lee,<sup>a</sup> Hae-Wook Ryu,<sup>a</sup> Sung-Nak Choi,<sup>a</sup> Jae Soo Choi<sup>b</sup> and Sung Kwon Kang<sup>b\*</sup>

<sup>a</sup>Department of Chemistry and Institute of Functionalized Chemical Materials, Pusan National University, Pusan 609-735, Republic of Korea, and <sup>b</sup>Department of Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea  
Correspondence e-mail: skkang@cnu.ac.kr

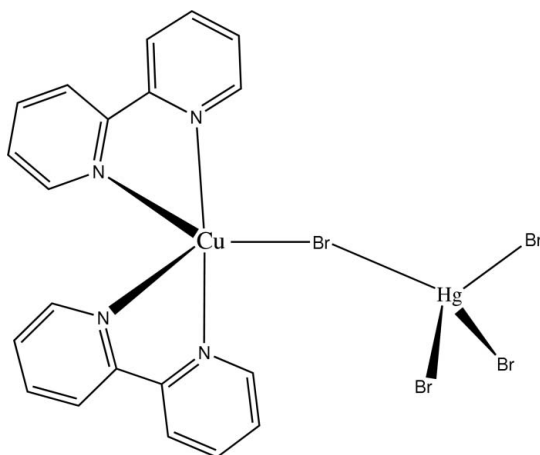
Received 18 May 2007; accepted 14 June 2007

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.018$  Å;  $R$  factor = 0.060;  $wR$  factor = 0.110; data-to-parameter ratio = 17.4.

In the title compound,  $[\text{CuHgBr}_4(\text{C}_{10}\text{H}_8\text{N}_2)_2]$ , the  $\text{Cu}^{\text{II}}$  atom is coordinated by four N atoms of two bidentate 2,2'-bipyridine ligands and one Br atom of a tetrabromidomercurate anion in a distorted trigonal-bipyramidal geometry. The Br atom occupies an equatorial position and bridges the  $\text{Cu}^{\text{II}}$  and Hg atoms, with Hg—Br distances of 2.7503 (15) Å, longer by more than 0.15 Å than the terminal Hg—Br bonds. Weak  $\pi$ - $\pi$  interactions between symmetry-related pyridine rings stabilize the packing; the shortest C—C distance between two parallel aromatic rings of bipy ligands is 3.491 (9) Å.

### Related literature

For general background see: Majumdar *et al.* (1998); Leznoff *et al.* (2003); Choudhury *et al.* (1994); Oh *et al.* (2006); Addison *et al.* (1984). For related structures see: Song *et al.* (2004); Schunk & Thewalt (2001); Zheng *et al.* (2002).



### Experimental

#### Crystal data

$[\text{CuHgBr}_4(\text{C}_{10}\text{H}_8\text{N}_2)_2]$   
 $M_r = 896.14$   
 Monoclinic,  $P2_1/n$   
 $a = 8.5510$  (6) Å  
 $b = 15.522$  (4) Å  
 $c = 18.056$  (2) Å  
 $\beta = 92.784$  (8)°

$V = 2393.8$  (7) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 13.99$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 0.23 × 0.2 × 0.2 mm

#### Data collection

Enraf-Nonius CAD-4 diffractometer  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\text{min}} = 0.050$ ,  $T_{\text{max}} = 0.059$   
 6320 measured reflections

4705 independent reflections  
 2406 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.057$   
 3 standard reflections every 400 reflections  
 intensity decay: none

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.110$   
 $S = 0.99$   
 4705 reflections  
 271 parameters

156 restraints  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.93$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.13$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

|         |             |         |             |
|---------|-------------|---------|-------------|
| Br1—Cu1 | 2.632 (2)   | Br3—Hg1 | 2.5512 (14) |
| Br1—Hg1 | 2.7502 (15) | Br4—Hg1 | 2.5780 (14) |
| Br2—Hg1 | 2.6008 (15) |         |             |

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).

This work was supported by a grant from the Ministry of Commerce, Industry and Energy, and the Korea Industrial Technology Foundation. X-ray data were collected at the Center for Research Facilities in Chungnam National University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN3049).

### References

- Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.  
 Choudhury, S., Deb, A. K. & Goswami, S. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1305–1310.  
 Enraf-Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.  
 Leznoff, D. B., Draper, N. D. & Batchelor, R. J. (2003). *Polyhedron*, **22**, 1735–1743.  
 Majumdar, P., Ghosh, A. K., Falvello, L. R., Peng, S.-M. & Goswami, S. (1998). *Inorg. Chem.* **37**, 1651–1654.  
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

- Oh, M.-J., Lee, Y.-M., Lee, S. J., Kang, S. K. & Choi, S.-N. (2006). *Acta Cryst. C* **62**, m51–m53.
- Schunk, A. & Thewalt, U. (2001). *Z. Anorg. Allg. Chem.* **627**, 797–802.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Song, J., Mao, J., Zeng, H. & Dong, Z. (2004). *Eur. J. Inorg. Chem.* pp. 538–543.
- Zheng, Y.-Q., Liu, W.-H. & Lin, J.-L. (2002). *Z. Anorg. Allg. Chem.* **628**, 620–624.

**supplementary materials**

*Acta Cryst.* (2007). E63, m1952-m1953 [ doi:10.1107/S160053680702925X ]

## Bis(2,2'-bipyridine-1 $\kappa^2$ N,N')- $\mu$ -bromido-1:2 $\kappa^2$ Br-tribromido-2 $\kappa^3$ Br-copper(II)mercury(II)

Y.-M. Lee, H.-W. Ryu, S.-N. Choi, J. S. Choi and S. K. Kang

### Comment

The metal ion assisted exchange reaction strategy for the synthesis of bis and tris-chelated copper(II) complexes with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) has been developed by Majumdar *et al.*, 1998 and Choudhury *et al.*, 1994; for example, the reaction of Cu(phen)Cl<sub>2</sub> with 2 moles of Ag(phen)<sub>2</sub><sup>+</sup> produces a pure tris Cu(phen)<sub>3</sub><sup>2+</sup> cation where two chlorides are transferred from Cu(II) to Ag(I), whereas two phen ligands transferred from Ag(I) to Cu(II). The main driving force for this exchange reaction is presumably the great affinity of Ag(I) toward the halide ion. The Hg(II) assisted exchange reaction was also used for the preparation of a dimeric complex containing (bipy)<sub>2</sub>CuCl<sub>2</sub> units and linear, neutral HgCl<sub>2</sub> building blocks; the Hg(II) center in this compound increases structural dimension by accepting chloride ligand from the Cu(II) center in a bridging fashion (Leznoff *et al.*, 2003). Recently, we reported the crystal structure of Tris(1,10-phenanthroline)copper(II) di- $\mu$ -iodo-bis(diiodomercurate) dimethyl sulfoxide monohydrate which is produced from the Hg<sup>II</sup> ion assisted exchange reaction between Cu(phen)I<sub>2</sub> and Hg(phen)I<sub>2</sub> (Oh, *et al.*, 2006).

In this work, we tested the reaction of Cu(bipy)Br<sub>2</sub> with Hg(bipy)Br<sub>2</sub> with a hope to observe a similar type of tris-chelated Cu<sup>II</sup> complex to be produced since the Hg<sup>II</sup> has stronger affinity toward the halide ion and is softer Lewis acid than Cu<sup>II</sup>. As expected, the transfer of the bipy ligand is observed in this reaction. However, the complete transfer of Br atoms from Cu<sup>II</sup> to Hg<sup>II</sup> does not occur; a bimetallic and bridged complex (bipy)<sub>2</sub>Cu—Br—HgBr<sub>3</sub>(I) was produced instead of the formation of an ion pair complex [Cu(bipy)<sub>3</sub>][HgBr<sub>4</sub>].

The Cu—Hg distance is 4.196 (2) Å, indicating there is no metal-metal interaction between the two metal centers. The coordination geometry around Cu<sup>II</sup> atom can be described as distorted trigonal bipyramidal with the axial positions occupied by the N12 and N13 atoms of bipy ligands (N12—Cu—N13 177 (4) °) (Fig. 1). The  $\tau$  value, which is an angular structural parameter as an index of trigonality, is calculated to be 0.83, which means this is closer to trigonal bipyramidal than square pyramidal structure (Addison *et al.*, 1984). One of the equatorial positions is occupied by Br1 atom which then bridges Cu and Hg metals. The Cu—N bond distances range from 1.977 (9) to 2.052 (10) Å which are well within the reported bond distances in Cu—Hg oligomers (1.961 – 2.139 Å) containing bipy ligands (Song *et al.*, 2004). The equatorial Cu—N distances are a little longer than those in the axial Cu—N as usual in trigonal bipyramidal complexes. N24—Cu—Br1 angle (127.8 (3) °) is opened by HgBr<sub>3</sub> group from normal angle 120 ° to reduce the steric hindrance. On the other hand, N1—Cu—Br1 angle is closed to 101.3 (3) °. The bridging Hg—Br1 distance in (I) is longer than three terminal Hg—Br bonds by more than 0.15 Å (2.7503 (15) Å for bridging bromide and 2.5512 – 2.6008 Å for terminal bromide). This kind of elongation has been also observed in [Cu(en)<sub>2</sub>][HgBr<sub>4</sub>] complex (Schunk & Thewalt, 2001) and Cu—Hg oligomers, [Cu<sub>2</sub>(bipy)<sub>4</sub>HgBr<sub>4</sub>][Hg<sub>2</sub>Br<sub>6</sub>] and [Cu<sub>2</sub>(bipy)<sub>4</sub>Hg<sub>2</sub>Br<sub>6</sub>][Hg<sub>4</sub>Br<sub>10</sub>] (Song *et al.*, 2004).

There is weak slipped  $\pi$ - $\pi$  interaction between the pyridine ring (N1) and its symmetry related one with an interplanar distance of 3.438 Å and a centroid to centroid distance of 3.699 Å resulting in an offset of 21.6%. Such  $\pi$ - $\pi$  interactions

## supplementary materials

between pyridine rings have been known in various Cu<sup>II</sup> complexes containing bipy and phen ligands (Song *et al.*, 2004; Zheng *et al.*, 2002).

### Experimental

The precursor compounds 2,2'-bipyridinedibromomercury(II), Hg(bipy)Br<sub>2</sub>, and 2,2'-bipyridinedibromocopper(II), Cu(bipy)Br<sub>2</sub>, were prepared as following; mercuric bromide (1.08 g; 3.00 mmol) was dissolved in 50 ml of ethanol and then, to this solution, 2,2'-bipyridine (0.484 g; 3.10 mmol) was added. The white crystallines of Hg(bipy)Br<sub>2</sub> produced were immediately filtered, washed with cold ethanol and dried under vacuum; the yield was 88.9%. Analysis calculated for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>HgBr<sub>2</sub>: C 23.25; H 1.56; N 5.42%; found C 23.19; H 1.60; N 5.49%. Cupric bromide (0.670 g; 3.00 mmol) was dissolved in 50 ml of ethanol and then, to this solution, 2,2'-bipyridine (0.484 g; 3.10 mmol) was added. The mixture reacted at room temperature with stirring for 5 hrs. The dark orange precipitates produced were filtered, washed with cold ethanol and then dried under vacuum. The yield was 89.6%. Analysis calculated for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>CuBr<sub>2</sub>: C 31.65; H 2.12; N 7.38%; found C 31.49; H 2.23; N 7.31%.

Hg(bipy)Br<sub>2</sub> (0.431 g; 1.14 mmol) and Cu(bipy)Br<sub>2</sub> (0.578 g; 1.14 mmol) were dissolved in 10 ml of dimethylsulfoxide respectively, and then two solutions were mixed and stirred for 2 hrs. at room temperature. The dark green crystals of the title compound produced were collected, washed with cold ethanol and dimethylsulfoxide successively and then dried under vacuum. Analysis calculated for C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>CuHgBr<sub>4</sub>: C 27.67; H 1.86; N 3.23%; found C 27.12; H 2.04; N 3.44%.

### Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Figures

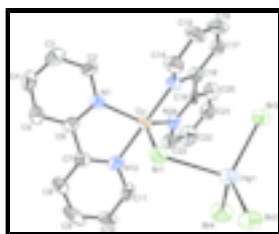


Fig. 1. Molecular structure of (I), showing the atom-numbering scheme. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

### Bis(2,2'-bipyridine-1κ<sup>2</sup>N,N')-m-bromido-1:2κ<sup>2</sup>Br-tribromido-2κ<sup>3</sup>Br-copper(II)mercury(II)

#### Crystal data

[CuHgBr<sub>4</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]

$M_r = 896.14$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 8.5510(6)$  Å

$F_{000} = 1652$

$D_x = 2.487$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 25 reflections

$\theta = 11.3\text{--}14.1^\circ$

$b = 15.522 (4) \text{ \AA}$   
 $c = 18.056 (2) \text{ \AA}$   
 $\beta = 92.784 (8)^\circ$   
 $V = 2393.8 (7) \text{ \AA}^3$   
 $Z = 4$

$\mu = 13.99 \text{ mm}^{-1}$   
 $T = 295 (2) \text{ K}$   
 Block, green  
 $0.23 \times 0.2 \times 0.2 \text{ mm}$

*Data collection*

Enraf-Nonius CAD-4  
 diffractometer  
 non-profiled  $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.050$ ,  $T_{\max} = 0.059$   
 6320 measured reflections  
 4705 independent reflections  
 2406 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.057$

$\theta_{\max} = 26^\circ$   
 $\theta_{\min} = 2.3^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -2 \rightarrow 19$   
 $l = -2 \rightarrow 22$   
 3 standard reflections  
 every 400 reflections  
 intensity decay: none

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.060$   
 $wR(F^2) = 0.110$   
 $S = 0.99$   
 4705 reflections  
 271 parameters  
 156 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.93 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -1.13 \text{ e \AA}^{-3}$   
 Extinction correction: none

*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.

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

|    | <i>x</i>     | <i>y</i>   | <i>z</i>   | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|------------|------------|----------------------------------|
| C2 | -0.0322 (14) | 0.6419 (8) | 0.5219 (7) | 0.040 (3)                        |
| H2 | 0.0485       | 0.6813     | 0.5306     | 0.048*                           |
| C3 | -0.0552 (13) | 0.5794 (9) | 0.5747 (7) | 0.045 (4)                        |
| H3 | 0.0087       | 0.5763     | 0.6178     | 0.054*                           |

## supplementary materials

---

|     |               |              |             |              |
|-----|---------------|--------------|-------------|--------------|
| C4  | -0.1743 (14)  | 0.5227 (9)   | 0.5618 (7)  | 0.048 (4)    |
| H4  | -0.1925       | 0.4804       | 0.5968      | 0.057*       |
| C5  | -0.2686 (13)  | 0.5265 (8)   | 0.4980 (7)  | 0.041 (3)    |
| H5  | -0.3483       | 0.4866       | 0.4889      | 0.049*       |
| C6  | -0.2414 (12)  | 0.5917 (8)   | 0.4475 (6)  | 0.032 (3)    |
| C7  | -0.3341 (12)  | 0.6042 (8)   | 0.3783 (7)  | 0.033 (3)    |
| C8  | -0.4543 (12)  | 0.5510 (8)   | 0.3537 (7)  | 0.040 (3)    |
| H8  | -0.4795       | 0.5019       | 0.3801      | 0.049*       |
| C9  | -0.5376 (13)  | 0.5729 (9)   | 0.2877 (9)  | 0.055 (4)    |
| H9  | -0.6222       | 0.5392       | 0.2711      | 0.066*       |
| C10 | -0.4967 (12)  | 0.6420 (9)   | 0.2481 (7)  | 0.047 (4)    |
| H10 | -0.5510       | 0.6557       | 0.2037      | 0.056*       |
| C11 | -0.3745 (13)  | 0.6917 (8)   | 0.2739 (7)  | 0.038 (3)    |
| H11 | -0.3454       | 0.7393       | 0.2464      | 0.046*       |
| C14 | 0.2304 (13)   | 0.7503 (8)   | 0.4252 (7)  | 0.048 (3)    |
| H14 | 0.2351        | 0.6909       | 0.4188      | 0.057*       |
| C15 | 0.3632 (14)   | 0.7934 (10)  | 0.4513 (7)  | 0.052 (4)    |
| H15 | 0.4544        | 0.7637       | 0.4652      | 0.062*       |
| C16 | 0.3563 (14)   | 0.8814 (10)  | 0.4561 (7)  | 0.052 (4)    |
| H16 | 0.4452        | 0.9117       | 0.4725      | 0.062*       |
| C17 | 0.2216 (13)   | 0.9257 (8)   | 0.4375 (6)  | 0.040 (3)    |
| H17 | 0.2174        | 0.9855       | 0.4410      | 0.048*       |
| C18 | 0.0911 (13)   | 0.8779 (8)   | 0.4130 (7)  | 0.035 (3)    |
| C19 | -0.0611 (13)  | 0.9174 (8)   | 0.3890 (7)  | 0.035 (3)    |
| C20 | -0.0916 (14)  | 1.0046 (8)   | 0.3924 (7)  | 0.047 (4)    |
| H20 | -0.0146       | 1.0431       | 0.4093      | 0.057*       |
| C21 | -0.2390 (16)  | 1.0331 (9)   | 0.3702 (7)  | 0.053 (4)    |
| H21 | -0.2623       | 1.0915       | 0.3729      | 0.064*       |
| C22 | -0.3525 (15)  | 0.9762 (9)   | 0.3440 (8)  | 0.060 (4)    |
| H22 | -0.4511       | 0.9955       | 0.3275      | 0.072*       |
| C23 | -0.3154 (14)  | 0.8895 (9)   | 0.3432 (7)  | 0.047 (4)    |
| H23 | -0.3922       | 0.8501       | 0.3278      | 0.057*       |
| Br1 | 0.04425 (13)  | 0.64128 (9)  | 0.27693 (8) | 0.0433 (4)   |
| Br2 | 0.23547 (15)  | 0.67094 (9)  | 0.06716 (8) | 0.0511 (4)   |
| Br3 | 0.28973 (14)  | 0.86587 (9)  | 0.24357 (8) | 0.0483 (4)   |
| Br4 | -0.15949 (15) | 0.82029 (10) | 0.12790 (9) | 0.0634 (5)   |
| Cu1 | -0.10161 (15) | 0.73448 (10) | 0.37395 (9) | 0.0432 (4)   |
| Hg1 | 0.11158 (6)   | 0.76093 (3)  | 0.17075 (3) | 0.04758 (19) |
| N1  | -0.1207 (10)  | 0.6482 (6)   | 0.4588 (5)  | 0.032 (2)    |
| N12 | -0.2952 (10)  | 0.6737 (7)   | 0.3379 (5)  | 0.036 (3)    |
| N13 | 0.0957 (10)   | 0.7909 (7)   | 0.4088 (5)  | 0.041 (3)    |
| N24 | -0.1725 (11)  | 0.8604 (6)   | 0.3640 (5)  | 0.036 (3)    |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|    | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$   | $U^{13}$   | $U^{23}$  |
|----|-----------|-----------|-----------|------------|------------|-----------|
| C2 | 0.053 (7) | 0.035 (8) | 0.031 (8) | -0.001 (7) | -0.013 (6) | 0.004 (7) |
| C3 | 0.045 (8) | 0.059 (9) | 0.032 (8) | 0.014 (7)  | 0.008 (7)  | 0.001 (8) |

|     |            |             |             |             |             |             |
|-----|------------|-------------|-------------|-------------|-------------|-------------|
| C4  | 0.048 (8)  | 0.048 (9)   | 0.048 (9)   | -0.002 (7)  | 0.013 (7)   | 0.013 (8)   |
| C5  | 0.046 (8)  | 0.028 (7)   | 0.050 (9)   | 0.003 (6)   | 0.008 (7)   | 0.003 (7)   |
| C6  | 0.034 (6)  | 0.036 (7)   | 0.026 (7)   | 0.007 (6)   | 0.009 (6)   | -0.005 (6)  |
| C7  | 0.018 (6)  | 0.044 (8)   | 0.036 (8)   | 0.005 (6)   | -0.001 (6)  | -0.005 (7)  |
| C8  | 0.027 (6)  | 0.040 (8)   | 0.055 (9)   | -0.006 (6)  | 0.008 (7)   | -0.012 (8)  |
| C9  | 0.021 (6)  | 0.053 (10)  | 0.090 (12)  | -0.004 (7)  | -0.004 (8)  | -0.026 (9)  |
| C10 | 0.024 (6)  | 0.069 (10)  | 0.045 (9)   | -0.008 (7)  | -0.015 (6)  | -0.005 (8)  |
| C11 | 0.037 (7)  | 0.037 (8)   | 0.041 (8)   | 0.005 (6)   | 0.002 (6)   | 0.019 (7)   |
| C14 | 0.049 (7)  | 0.035 (8)   | 0.058 (8)   | 0.000 (7)   | -0.013 (7)  | 0.001 (8)   |
| C15 | 0.029 (7)  | 0.072 (11)  | 0.054 (9)   | -0.012 (7)  | -0.007 (7)  | -0.007 (9)  |
| C16 | 0.032 (7)  | 0.081 (11)  | 0.042 (8)   | -0.005 (8)  | -0.007 (7)  | -0.010 (9)  |
| C17 | 0.058 (8)  | 0.031 (8)   | 0.033 (8)   | -0.012 (7)  | 0.011 (7)   | -0.005 (7)  |
| C18 | 0.045 (7)  | 0.028 (7)   | 0.033 (7)   | -0.012 (6)  | 0.002 (6)   | -0.003 (7)  |
| C19 | 0.046 (7)  | 0.022 (7)   | 0.037 (8)   | -0.014 (6)  | 0.009 (6)   | 0.012 (7)   |
| C20 | 0.048 (8)  | 0.041 (9)   | 0.054 (9)   | 0.000 (7)   | 0.009 (7)   | 0.000 (8)   |
| C21 | 0.075 (9)  | 0.034 (8)   | 0.051 (9)   | -0.004 (8)  | 0.003 (8)   | 0.002 (8)   |
| C22 | 0.045 (8)  | 0.060 (10)  | 0.075 (11)  | 0.020 (8)   | 0.001 (8)   | 0.016 (9)   |
| C23 | 0.049 (8)  | 0.047 (9)   | 0.045 (9)   | 0.008 (7)   | -0.007 (7)  | 0.007 (8)   |
| Br1 | 0.0431 (7) | 0.0393 (8)  | 0.0472 (9)  | -0.0010 (6) | -0.0027 (7) | 0.0004 (7)  |
| Br2 | 0.0544 (8) | 0.0526 (9)  | 0.0454 (9)  | 0.0121 (7)  | -0.0085 (7) | -0.0070 (8) |
| Br3 | 0.0541 (8) | 0.0498 (9)  | 0.0405 (8)  | -0.0093 (7) | -0.0039 (7) | -0.0001 (8) |
| Br4 | 0.0496 (8) | 0.0680 (11) | 0.0706 (11) | 0.0113 (8)  | -0.0187 (8) | 0.0091 (10) |
| Cu1 | 0.0354 (8) | 0.0371 (10) | 0.0552 (11) | -0.0115 (8) | -0.0170 (7) | 0.0115 (9)  |
| Hg1 | 0.0466 (3) | 0.0477 (4)  | 0.0472 (3)  | 0.0045 (3)  | -0.0103 (2) | -0.0044 (3) |
| N1  | 0.036 (5)  | 0.024 (6)   | 0.035 (6)   | -0.001 (5)  | -0.002 (5)  | -0.006 (5)  |
| N12 | 0.027 (5)  | 0.044 (7)   | 0.035 (6)   | 0.004 (5)   | -0.007 (5)  | 0.007 (6)   |
| N13 | 0.029 (5)  | 0.052 (7)   | 0.041 (7)   | -0.012 (5)  | -0.009 (5)  | 0.007 (6)   |
| N24 | 0.040 (6)  | 0.029 (6)   | 0.039 (6)   | 0.001 (5)   | 0.002 (5)   | 0.008 (5)   |

*Geometric parameters (Å, °)*

|         |            |         |             |
|---------|------------|---------|-------------|
| C2—N1   | 1.341 (13) | C16—C17 | 1.370 (16)  |
| C2—C3   | 1.380 (16) | C16—H16 | 0.9300      |
| C2—H2   | 0.9300     | C17—C18 | 1.394 (14)  |
| C3—C4   | 1.357 (16) | C17—H17 | 0.9300      |
| C3—H3   | 0.9300     | C18—N13 | 1.353 (14)  |
| C4—C5   | 1.375 (16) | C18—C19 | 1.484 (15)  |
| C4—H4   | 0.9300     | C19—N24 | 1.361 (13)  |
| C5—C6   | 1.388 (16) | C19—C20 | 1.380 (16)  |
| C5—H5   | 0.9300     | C20—C21 | 1.377 (16)  |
| C6—N1   | 1.363 (13) | C20—H20 | 0.9300      |
| C6—C7   | 1.460 (15) | C21—C22 | 1.379 (17)  |
| C7—N12  | 1.353 (14) | C21—H21 | 0.9300      |
| C7—C8   | 1.375 (15) | C22—C23 | 1.383 (17)  |
| C8—C9   | 1.399 (17) | C22—H22 | 0.9300      |
| C8—H8   | 0.9300     | C23—N24 | 1.339 (13)  |
| C9—C10  | 1.346 (17) | C23—H23 | 0.9300      |
| C9—H9   | 0.9300     | Br1—Cu1 | 2.632 (2)   |
| C10—C11 | 1.363 (15) | Br1—Hg1 | 2.7502 (15) |



## supplementary materials

---

|             |            |             |             |
|-------------|------------|-------------|-------------|
| C10—H10     | 0.9300     | Br2—Hg1     | 2.6008 (15) |
| C11—N12     | 1.340 (13) | Br3—Hg1     | 2.5512 (14) |
| C11—H11     | 0.9300     | Br4—Hg1     | 2.5780 (14) |
| C14—N13     | 1.334 (13) | Cu1—N13     | 1.977 (9)   |
| C14—C15     | 1.382 (15) | Cu1—N12     | 1.987 (9)   |
| C14—H14     | 0.9300     | Cu1—N1      | 2.047 (10)  |
| C15—C16     | 1.370 (18) | Cu1—N24     | 2.052 (10)  |
| C15—H15     | 0.9300     |             |             |
| N1—C2—C3    | 123.0 (12) | N24—C19—C20 | 121.4 (12)  |
| N1—C2—H2    | 118.5      | N24—C19—C18 | 114.7 (10)  |
| C3—C2—H2    | 118.5      | C20—C19—C18 | 123.9 (11)  |
| C4—C3—C2    | 117.8 (12) | C21—C20—C19 | 118.4 (13)  |
| C4—C3—H3    | 121.1      | C21—C20—H20 | 120.8       |
| C2—C3—H3    | 121.1      | C19—C20—H20 | 120.8       |
| C3—C4—C5    | 121.4 (13) | C20—C21—C22 | 120.8 (13)  |
| C3—C4—H4    | 119.3      | C20—C21—H21 | 119.6       |
| C5—C4—H4    | 119.3      | C22—C21—H21 | 119.6       |
| C4—C5—C6    | 118.1 (12) | C21—C22—C23 | 118.0 (13)  |
| C4—C5—H5    | 120.9      | C21—C22—H22 | 121.0       |
| C6—C5—H5    | 120.9      | C23—C22—H22 | 121.0       |
| N1—C6—C5    | 121.4 (11) | N24—C23—C22 | 122.1 (13)  |
| N1—C6—C7    | 114.7 (11) | N24—C23—H23 | 118.9       |
| C5—C6—C7    | 123.9 (12) | C22—C23—H23 | 118.9       |
| N12—C7—C8   | 120.3 (11) | Cu1—Br1—Hg1 | 102.40 (6)  |
| N12—C7—C6   | 115.5 (10) | N13—Cu1—N12 | 177.8 (4)   |
| C8—C7—C6    | 124.2 (12) | N13—Cu1—N1  | 98.6 (4)    |
| C7—C8—C9    | 118.1 (13) | N12—Cu1—N1  | 80.8 (4)    |
| C7—C8—H8    | 121.0      | N13—Cu1—N24 | 81.3 (4)    |
| C9—C8—H8    | 121.0      | N12—Cu1—N24 | 100.7 (4)   |
| C10—C9—C8   | 120.8 (12) | N1—Cu1—N24  | 130.9 (4)   |
| C10—C9—H9   | 119.6      | N13—Cu1—Br1 | 91.8 (3)    |
| C8—C9—H9    | 119.6      | N12—Cu1—Br1 | 86.3 (3)    |
| C9—C10—C11  | 119.0 (12) | N1—Cu1—Br1  | 101.3 (3)   |
| C9—C10—H10  | 120.5      | N24—Cu1—Br1 | 127.8 (3)   |
| C11—C10—H10 | 120.5      | Br3—Hg1—Br4 | 115.60 (5)  |
| N12—C11—C10 | 121.6 (12) | Br3—Hg1—Br2 | 117.37 (5)  |
| N12—C11—H11 | 119.2      | Br4—Hg1—Br2 | 111.58 (5)  |
| C10—C11—H11 | 119.2      | Br3—Hg1—Br1 | 102.23 (5)  |
| N13—C14—C15 | 122.2 (13) | Br4—Hg1—Br1 | 103.59 (5)  |
| N13—C14—H14 | 118.9      | Br2—Hg1—Br1 | 104.19 (5)  |
| C15—C14—H14 | 118.9      | C2—N1—C6    | 118.1 (11)  |
| C16—C15—C14 | 117.9 (13) | C2—N1—Cu1   | 128.5 (8)   |
| C16—C15—H15 | 121.1      | C6—N1—Cu1   | 113.4 (8)   |
| C14—C15—H15 | 121.1      | C11—N12—C7  | 120.2 (10)  |
| C17—C16—C15 | 121.6 (13) | C11—N12—Cu1 | 124.2 (9)   |
| C17—C16—H16 | 119.2      | C7—N12—Cu1  | 115.1 (7)   |
| C15—C16—H16 | 119.2      | C14—N13—C18 | 119.1 (11)  |
| C16—C17—C18 | 117.4 (12) | C14—N13—Cu1 | 125.1 (9)   |
| C16—C17—H17 | 121.3      | C18—N13—Cu1 | 115.7 (8)   |

|             |            |             |            |
|-------------|------------|-------------|------------|
| C18—C17—H17 | 121.3      | C23—N24—C19 | 119.2 (11) |
| N13—C18—C17 | 121.6 (12) | C23—N24—Cu1 | 127.4 (9)  |
| N13—C18—C19 | 115.0 (10) | C19—N24—Cu1 | 113.0 (8)  |
| C17—C18—C19 | 123.3 (11) |             |            |

Fig. 1

