

## Di- $\mu$ -chlorido-bis{[2-(benzylimino-methyl)pyridine- $\kappa^2N,N'$ ]chlorido-mercury(II)} dichloridomercury(II)

Young-Inn Kim,<sup>a</sup> Young-Kwang Song,<sup>a</sup> Seong-Jae Yun,<sup>b</sup>  
In-Chan Kim<sup>b</sup> and Sung Kwon Kang<sup>c\*</sup>

<sup>a</sup>Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan 609-735, Republic of Korea, <sup>b</sup>Department of Chemistry, Pusan National University, Busan 609-735, Republic of Korea, and <sup>c</sup>Department of Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea

Correspondence e-mail: skkang@cnu.ac.kr

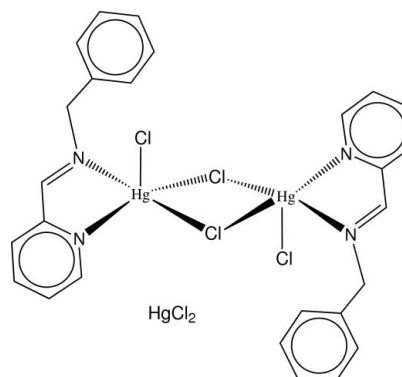
Received 22 November 2010; accepted 3 December 2010

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å;  $R$  factor = 0.025;  $wR$  factor = 0.055; data-to-parameter ratio = 21.9.

The  $\text{Hg}^{\text{II}}$  ion in the title centrosymmetric dinuclear complex,  $[\text{Hg}_2\text{Cl}_4(\text{C}_{13}\text{H}_{12}\text{N}_2)_2] \cdot [\text{HgCl}_2]$ , adopts a distorted square-pyramidal geometry, being coordinated by the bis-chelating  $N$ -heterocyclic ligand, two bridging Cl atoms and one terminal Cl atom. One of the bridging Hg—Cl bonds [2.8428 (11) Å] is significantly longer than the other [2.5327 (10) Å]. In the crystal, there are weak  $\pi$ – $\pi$  interactions [centroid–centroid distance = 3.630 (3) Å] between the aromatic rings of the discrete units. The  $\text{HgCl}_2$  adduct molecule is located on an inversion centre and has an Hg—Cl bond length of 2.2875 (11) Å.

### Related literature

For general background to luminescent mercury compounds, see: Elena *et al.* (2006); Durantaye *et al.* (2006); Fan *et al.* (2009); He *et al.* (2008). For syntheses and structures of Hg(II) complexes, see: Kim & Kang (2010); Kim *et al.* (2010).



### Experimental

#### Crystal data

$[\text{Hg}_2\text{Cl}_4(\text{C}_{13}\text{H}_{12}\text{N}_2)_2] \cdot [\text{HgCl}_2]$   
 $M_r = 1206.96$   
Monoclinic,  $P2_1/n$   
 $a = 10.1329$  (2) Å  
 $b = 8.1141$  (1) Å  
 $c = 19.0591$  (2) Å  
 $\beta = 92.939$  (1)°

$V = 1564.97$  (4) Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 15.22$  mm<sup>-1</sup>  
 $T = 295$  K  
 $0.17 \times 0.13 \times 0.12$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 2002)  
 $T_{\text{min}} = 0.104$ ,  $T_{\text{max}} = 0.158$

16269 measured reflections  
3892 independent reflections  
3279 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$   
 $wR(F^2) = 0.055$   
 $S = 1.04$   
3892 reflections

178 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.18$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Hg1—N8	2.347 (4)	Hg1—Cl1	2.4338 (12)
Hg1—N1	2.373 (3)		
N8—Hg1—N1	70.74 (12)	Cl1—Hg1—Cl2	115.34 (4)
N8—Hg1—Cl1	113.97 (9)	N8—Hg1—Cl2 <sup>i</sup>	142.19 (9)
N1—Hg1—Cl1	106.32 (9)	N1—Hg1—Cl2 <sup>i</sup>	83.87 (8)
N8—Hg1—Cl2	95.92 (9)	Cl1—Hg1—Cl2 <sup>i</sup>	99.58 (4)
N1—Hg1—Cl2	138.01 (8)	Cl2—Hg1—Cl2 <sup>i</sup>	84.37 (3)

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

This work was supported by a National Research Foundation of Korea (NRF) Grant funded by the Ministry of Education, Science and Technology (No. 2010-0017080).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2236).

## References

- Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Durantaye, L. D. L., McCormick, T., Liu, X.-Y. & Wang, S. (2006). *Dalton Trans.* pp. 5675–5682.
- Elena, L.-T., Antoina, M. & Ceser, J. P. (2006). *Polyhedron*, **25**, 1464–1470.
- Fan, R., Yang, Y., Yin, Y., Hasi, W. & Mu, Y. (2009). *Inorg. Chem.* **48**, 6034–6943.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- He, G., Zhao, Y., He, C., Liu, Y. & Duan, C. (2008). *Inorg. Chem.* **47**, 5169–5176.
- Kim, Y.-I. & Kang, S. K. (2010). *Acta Cryst.* **E66**, m1251.
- Kim, Y.-I., Seo, H.-J., Kim, J.-H., Lee, Y.-S. & Kang, S. K. (2010). *Acta Cryst.* **E66**, m124.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

## supporting information

*Acta Cryst.* (2011). E67, m52–m53 [https://doi.org/10.1107/S1600536810050725]

## Di- $\mu$ -chlorido-bis{[2-(benzyliminomethyl)pyridine- $\kappa^2$ N,N']}chloridomercury(II)} dichloridomercury(II)

Young-Inn Kim, Young-Kwang Song, Seong-Jae Yun, In-Chan Kim and Sung Kwon Kang

### S1. Comment

Much attention has been paid to the design and synthesis of luminescent mercury compounds for the detection and extraction of the mercury (Elena *et al.*, 2006; Durantaye *et al.*, 2006), among which, Hg(II) complexes with pyridine-containing ligands are of importance for their high luminescent efficiency (Fan *et al.*, 2009). In a previous report (Kim & Kang, 2010), we presented a structure of white Hg(II) complex with benzyl(2-pyridylmethylene)amine(bpma), (bpma)HgCl<sub>2</sub>, concerning its luminescence behavior (Kim *et al.*, 2010; He *et al.*, 2008). The reported white crystals were obtained after recrystallization from methanol solution in a day. However, we could find another yellow crystals in 3–4 days in the same solution. Herein, we report the structure of separated yellow crystals, [(bpma)HgCl<sub>2</sub>]<sub>2</sub> HgCl<sub>2</sub>.

In (I), Fig. 1, the Hg1<sup>II</sup> ion is coordinated by two N atoms of heterocyclic ligand, two bridging Cl atoms and one terminal Cl atom. The angles around Hg1 atoms are in the range of 70.74 (12) – 142.19 (9)°, suggesting the coordination geometry around the Hg1 atom is described as a distorted square pyrdmid with an apical position of Cl11 atom. One of the bridging Hg1—Cl bonds (2.843 (1) Å) is significantly longer than the other (2.533 (1) Å). The phenyl ring on the bpma ligand is twisted out of the pyridine plane, and form a dihedral angel of 81.21 (11)°. In the crystal structure, there are weak  $\pi$ - $\pi$  interactions [centroid-centroid distance = 3.630 (3) Å] between the aromatic rings of the discrete units.

### S2. Experimental

Benzyl(2-pyridylmethylene)amine (bpma) was synthesized from the reaction of 2-pyridinecarboxylaldehyde and benzylamine. And bpma reacted with mercury dichloride in methanol to yield the titled complex. The yellow crystals were separated from white crystals in 3–4 days from methanol solution. The detailed synthetic method was previously reported (Kim & Kang, 2010).

### S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 - 0.97 Å, and with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The maximum and minimum residual electron density peaks were located at 0.79 and 0.63 Å, respectively, from the Hg1 atom.

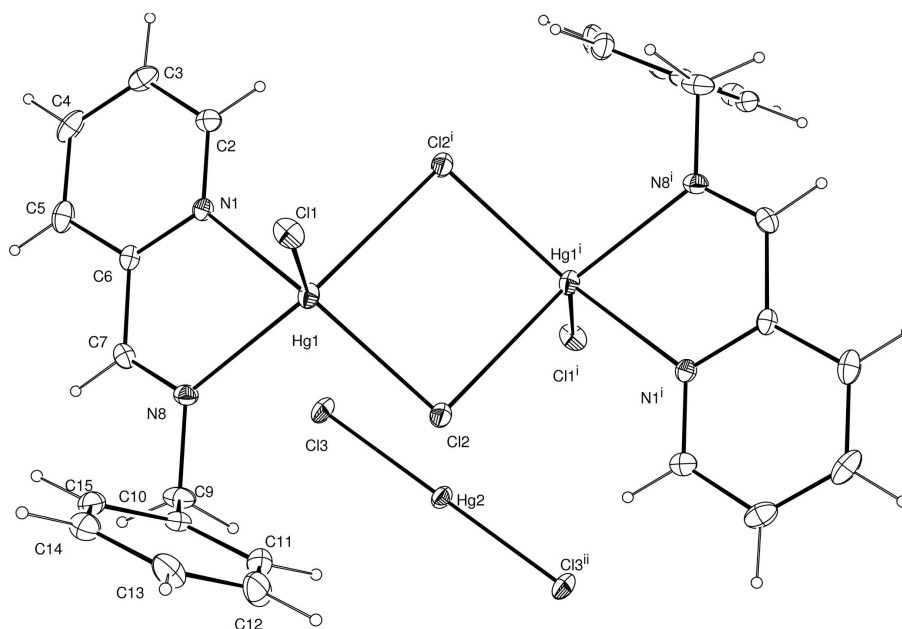


Figure 1

Molecular structure of (I), showing the atom-numbering scheme and 30% probability ellipsoids [symmetry code: (i)  $-x, -y + 1, -z$ ; (ii)  $-x, -y + 2, -z$ ].

### Di- $\mu$ -chlorido-bis[[2-(benzyliminomethyl)pyridine- $\kappa^2N,N'$ ]chloridomercury(II)] dichloridomercury(II)

#### Crystal data

$[\text{Hg}_2\text{Cl}_4(\text{C}_{13}\text{H}_{12}\text{N}_2)_2] \cdot [\text{HgCl}_2]$

$M_r = 1206.96$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 10.1329\ (2)\ \text{\AA}$

$b = 8.1141\ (1)\ \text{\AA}$

$c = 19.0591\ (2)\ \text{\AA}$

$\beta = 92.939\ (1)^\circ$

$V = 1564.97\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 1100$

$D_x = 2.561\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5840 reflections

$\theta = 2.2\text{--}28.0^\circ$

$\mu = 15.22\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Block, yellow

$0.17 \times 0.13 \times 0.12\ \text{mm}$

#### Data collection

Bruker SMART CCD area-detector  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2002)

$T_{\min} = 0.104$ ,  $T_{\max} = 0.158$

16269 measured reflections

3892 independent reflections

3279 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 2.1^\circ$

$h = -13 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -25 \rightarrow 25$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.055$

$S = 1.04$

3892 reflections

178 parameters

0 restraints

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 1.1429P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 1.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.18 \text{ e } \text{\AA}^{-3}$$

*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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.092853 (16)	0.45122 (2)	0.092463 (9)	0.04770 (6)
Cl1	0.02059 (13)	0.19456 (15)	0.14429 (6)	0.0625 (3)
Cl2	-0.09059 (10)	0.64548 (14)	0.05096 (6)	0.0503 (3)
N1	0.3257 (3)	0.4310 (4)	0.08642 (17)	0.0395 (7)
C2	0.3903 (5)	0.3289 (6)	0.0459 (2)	0.0515 (11)
H2	0.3421	0.2636	0.0137	0.062*
C3	0.5252 (5)	0.3161 (7)	0.0498 (3)	0.0637 (14)
H3	0.5671	0.2431	0.0206	0.076*
C4	0.5977 (5)	0.4107 (8)	0.0965 (3)	0.0700 (17)
H4	0.6895	0.4035	0.0997	0.084*
C5	0.5319 (5)	0.5178 (7)	0.1392 (3)	0.0623 (14)
H5	0.5789	0.5839	0.1716	0.075*
C6	0.3952 (4)	0.5253 (5)	0.1331 (2)	0.0422 (9)
C7	0.3196 (4)	0.6329 (5)	0.1779 (2)	0.0457 (10)
H7	0.3644	0.7015	0.2101	0.055*
N8	0.1950 (4)	0.6345 (4)	0.17363 (18)	0.0451 (8)
C9	0.1223 (6)	0.7461 (6)	0.2188 (3)	0.0658 (14)
H9A	0.0734	0.8259	0.1899	0.079*
H9B	0.1844	0.8057	0.2498	0.079*
C10	0.0277 (4)	0.6506 (6)	0.2621 (2)	0.0495 (10)
C11	-0.1060 (5)	0.6560 (8)	0.2474 (3)	0.0740 (16)
H11	-0.1404	0.7177	0.2096	0.089*
C12	-0.1907 (5)	0.5681 (11)	0.2896 (3)	0.090 (2)
H12	-0.2816	0.5723	0.28	0.108*
C13	-0.1409 (6)	0.4767 (8)	0.3446 (3)	0.0747 (17)
H13	-0.1975	0.4182	0.3724	0.09*
C14	-0.0083 (6)	0.4711 (6)	0.3589 (3)	0.0625 (13)
H14	0.0259	0.4081	0.3963	0.075*
C15	0.0756 (5)	0.5576 (5)	0.3184 (3)	0.0531 (11)
H15	0.1662	0.5537	0.329	0.064*
Hg2	0	1	0	0.04776 (7)
Cl3	0.21296 (11)	0.91503 (18)	0.02343 (7)	0.0664 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Hg1	0.03772 (9)	0.05296 (12)	0.05168 (11)	-0.00140 (7)	-0.00498 (7)	0.00188 (7)
C11	0.0824 (8)	0.0537 (7)	0.0518 (6)	-0.0145 (6)	0.0082 (6)	0.0031 (5)
C12	0.0455 (6)	0.0592 (7)	0.0456 (6)	0.0081 (5)	-0.0034 (4)	0.0008 (5)
N1	0.0362 (17)	0.0416 (19)	0.0408 (18)	-0.0014 (14)	0.0015 (14)	0.0033 (15)
C2	0.058 (3)	0.047 (3)	0.050 (3)	0.005 (2)	0.009 (2)	0.001 (2)
C3	0.063 (3)	0.062 (3)	0.068 (3)	0.018 (3)	0.024 (3)	0.020 (3)
C4	0.037 (2)	0.083 (4)	0.091 (4)	0.011 (3)	0.014 (3)	0.040 (3)
C5	0.046 (3)	0.069 (3)	0.071 (3)	-0.014 (2)	-0.012 (2)	0.021 (3)
C6	0.037 (2)	0.044 (2)	0.045 (2)	-0.0056 (16)	-0.0036 (17)	0.0101 (18)
C7	0.057 (3)	0.041 (2)	0.039 (2)	-0.0116 (19)	-0.0028 (18)	0.0030 (17)
N8	0.058 (2)	0.0355 (19)	0.0425 (19)	0.0052 (15)	0.0057 (16)	-0.0015 (14)
C9	0.094 (4)	0.043 (3)	0.063 (3)	0.011 (3)	0.020 (3)	-0.008 (2)
C10	0.056 (3)	0.045 (2)	0.048 (2)	0.010 (2)	0.007 (2)	-0.0124 (19)
C11	0.065 (3)	0.101 (4)	0.054 (3)	0.025 (3)	-0.008 (3)	-0.008 (3)
C12	0.043 (3)	0.154 (7)	0.071 (4)	-0.004 (3)	0.000 (3)	-0.034 (4)
C13	0.073 (4)	0.096 (5)	0.056 (3)	-0.025 (3)	0.013 (3)	-0.019 (3)
C14	0.073 (4)	0.055 (3)	0.060 (3)	-0.001 (2)	0.006 (3)	-0.006 (2)
C15	0.049 (3)	0.048 (3)	0.063 (3)	0.005 (2)	0.002 (2)	-0.009 (2)
Hg2	0.03219 (11)	0.05415 (15)	0.05669 (15)	0.00592 (9)	-0.00021 (10)	0.00053 (11)
C13	0.0374 (6)	0.0813 (9)	0.0799 (9)	0.0158 (6)	-0.0035 (5)	0.0004 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Hg1—N8	2.347 (4)	C7—H7	0.93
Hg1—N1	2.373 (3)	N8—C9	1.473 (5)
Hg1—C11	2.4338 (12)	C9—C10	1.510 (7)
Hg1—C12	2.5327 (10)	C9—H9A	0.97
Hg1—C12 <sup>i</sup>	2.8428 (11)	C9—H9B	0.97
C12—Hg1 <sup>i</sup>	2.8428 (11)	C10—C11	1.370 (7)
N1—C2	1.328 (5)	C10—C15	1.379 (6)
N1—C6	1.345 (5)	C11—C12	1.402 (9)
C2—C3	1.369 (6)	C11—H11	0.93
C2—H2	0.93	C12—C13	1.360 (10)
C3—C4	1.363 (8)	C12—H12	0.93
C3—H3	0.93	C13—C14	1.359 (8)
C4—C5	1.385 (8)	C13—H13	0.93
C4—H4	0.93	C14—C15	1.371 (7)
C5—C6	1.385 (6)	C14—H14	0.93
C5—H5	0.93	C15—H15	0.93
C6—C7	1.465 (6)	Hg2—C13 <sup>ii</sup>	2.2875 (11)
C7—N8	1.262 (5)	Hg2—C13	2.2875 (11)
N8—Hg1—N1	70.74 (12)	N8—C7—H7	119.3
N8—Hg1—C11	113.97 (9)	C6—C7—H7	119.3
N1—Hg1—C11	106.32 (9)	C7—N8—C9	119.8 (4)

N8—Hg1—C12	95.92 (9)	C7—N8—Hg1	116.2 (3)
N1—Hg1—C12	138.01 (8)	C9—N8—Hg1	123.9 (3)
C11—Hg1—C12	115.34 (4)	N8—C9—C10	110.8 (4)
N8—Hg1—C12 <sup>i</sup>	142.19 (9)	N8—C9—H9A	109.5
N1—Hg1—C12 <sup>i</sup>	83.87 (8)	C10—C9—H9A	109.5
C11—Hg1—C12 <sup>i</sup>	99.58 (4)	N8—C9—H9B	109.5
C12—Hg1—C12 <sup>i</sup>	84.37 (3)	C10—C9—H9B	109.5
Hg1—C12—Hg1 <sup>i</sup>	95.63 (3)	H9A—C9—H9B	108.1
C2—N1—C6	118.8 (4)	C11—C10—C15	118.8 (5)
C2—N1—Hg1	126.3 (3)	C11—C10—C9	121.4 (5)
C6—N1—Hg1	114.7 (3)	C15—C10—C9	119.8 (4)
N1—C2—C3	122.5 (5)	C10—C11—C12	119.6 (5)
N1—C2—H2	118.8	C10—C11—H11	120.2
C3—C2—H2	118.8	C12—C11—H11	120.2
C4—C3—C2	119.8 (5)	C13—C12—C11	120.4 (5)
C4—C3—H3	120.1	C13—C12—H12	119.8
C2—C3—H3	120.1	C11—C12—H12	119.8
C3—C4—C5	118.5 (5)	C14—C13—C12	119.8 (6)
C3—C4—H4	120.7	C14—C13—H13	120.1
C5—C4—H4	120.7	C12—C13—H13	120.1
C4—C5—C6	119.2 (5)	C13—C14—C15	120.4 (5)
C4—C5—H5	120.4	C13—C14—H14	119.8
C6—C5—H5	120.4	C15—C14—H14	119.8
N1—C6—C5	121.2 (4)	C14—C15—C10	120.9 (5)
N1—C6—C7	116.9 (4)	C14—C15—H15	119.5
C5—C6—C7	121.8 (4)	C10—C15—H15	119.5
N8—C7—C6	121.4 (4)	C13 <sup>ii</sup> —Hg2—C13	180

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