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Di-μ-chlorido-bis{[2-(benzyliminomethyl)pyridine-κ^2N,N']chloridomercury(II)} dichloridomercury(II)

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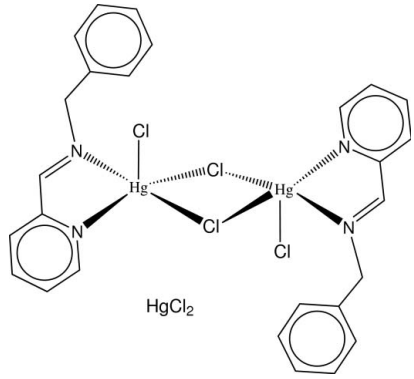
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.008 Å; R factor = 0.025; wR factor = 0.055; data-to-parameter ratio = 21.9.

The Hg^{II} ion in the title centrosymmetric dinuclear complex, $[Hg_2Cl_4(C_{13}H_{12}N_2)_2]\cdot[HgCl_2]$, 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 π–π interactions [centroid–centroid distance = 3.630 (3) Å] between the aromatic rings of the discrete units. The $HgCl_2$ 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

$[Hg_2Cl_4(C_{13}H_{12}N_2)_2]\cdot[HgCl_2]$
M_r = 1206.96
Monoclinic, $P2_1/n$
a = 10.1329 (2) Å
b = 8.1141 (1) Å
c = 19.0591 (2) Å
β = 92.939 (1)°
V = 1564.97 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 15.22 mm^{-1}
T = 295 K
0.17 × 0.13 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
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_{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
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −1.18 e Å^{-3}

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^{i}	142.19 (9)
N1—Hg1—Cl1	106.32 (9)	N1—Hg1—Cl2^{i}	83.87 (8)
N8—Hg1—Cl2	95.92 (9)	Cl1—Hg1—Cl2^{i}	99.58 (4)
N1—Hg1—Cl2	138.01 (8)	Cl2—Hg1—Cl2^{i}	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).

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

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supplementary materials

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Di-μ-chlorido-bis{[2-(benzyliminomethyl)pyridine-κ^2N,N']chloridomercury(II)} dichloridomercury(II)

Y.-I. Kim, Y.-K. Song, S.-J. Yun, I.-C. Kim and S. K. Kang

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)$HgCl_2$, 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, $[(bpma)HgCl_2]_2$ $HgCl_2$.

In (I), Fig. 1, the $Hg1^{II}$ 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 Cl1 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 π-π interactions [centroid-centroid distance = 3.630 (3) Å] between the aromatic rings of the discrete units.

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).

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.

Figures

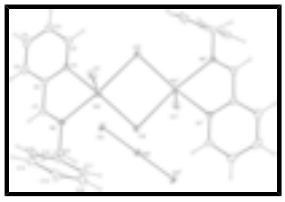


Fig. 1. Molecular structure of (I), showing the atom-numbering scheme and 30% probability ellipsoids [symmetry code: (i) -*x*, -*y* + 1, -*z*; (ii) -*x*, -*y* + 2, -*z*].

Di-μ-chlorido-bis{[2-(benzyliminomethyl)pyridine- κ^2N,N']chloridomercury(II)} dichloridomercury(II)

Crystal data

$[Hg_2Cl_4(C_{13}H_{12}N_2)_2]\cdot[HgCl_2]$	$F(000) = 1100$
$M_r = 1206.96$	$D_x = 2.561$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5840 reflections
$a = 10.1329$ (2) Å	$\theta = 2.2–28.0°$
$b = 8.1141$ (1) Å	$\mu = 15.22$ mm^{-1}
$c = 19.0591$ (2) Å	$T = 295$ K
$\beta = 92.939$ (1)°	Block, yellow
$V = 1564.97$ (4) Å^3	0.17 × 0.13 × 0.12 mm
$Z = 2$	

Data collection

Bruker SMART CCD area-detector diffractometer	3279 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$
$T_{min} = 0.104$, $T_{max} = 0.158$	$h = -13\rightarrow10$
16269 measured reflections	$k = -10\rightarrow10$
3892 independent reflections	$l = -25\rightarrow25$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 1.1429P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 1.21$ e Å^{-3}
3892 reflections	$\Delta\rho_{min} = -1.18$ e Å^{-3}
178 parameters	

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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)

Cl1	0.0824 (8)	0.0537 (7)	0.0518 (6)	−0.0145 (6)	0.0082 (6)	0.0031 (5)
Cl2	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)
Cl3	0.0374 (6)	0.0813 (9)	0.0799 (9)	0.0158 (6)	−0.0035 (5)	0.0004 (7)

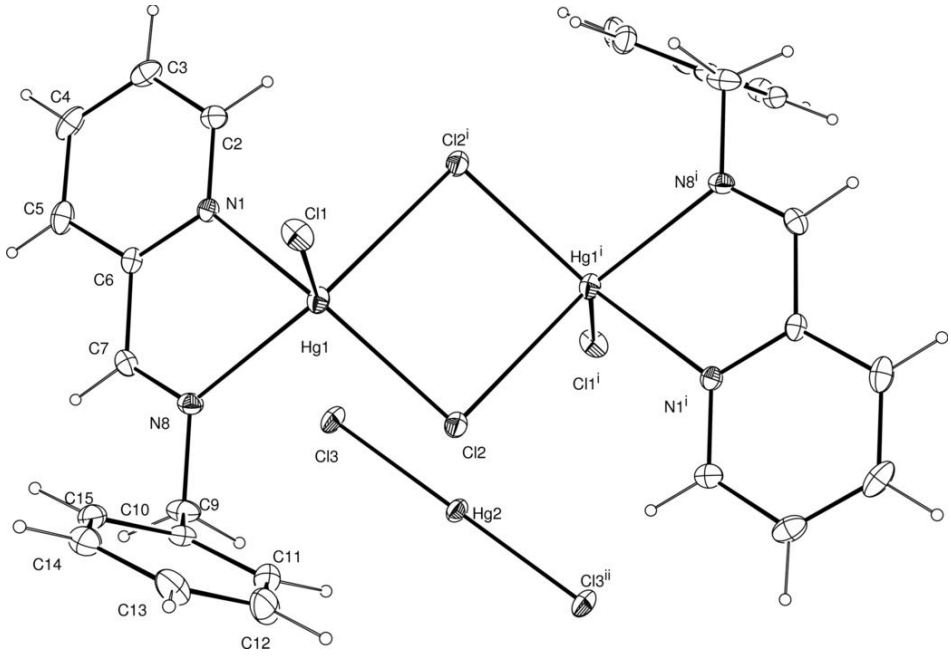
Geometric parameters (Å, °)

Hg1—N8	2.347 (4)	C7—H7	0.93
Hg1—N1	2.373 (3)	N8—C9	1.473 (5)
Hg1—Cl1	2.4338 (12)	C9—C10	1.510 (7)
Hg1—Cl2	2.5327 (10)	C9—H9A	0.97
Hg1—Cl2^{i}	2.8428 (11)	C9—H9B	0.97
Cl2—Hg1^{i}	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—Cl3^{ii}	2.2875 (11)
C7—N8	1.262 (5)	Hg2—Cl3	2.2875 (11)
N8—Hg1—N1	70.74 (12)	N8—C7—H7	119.3
N8—Hg1—Cl1	113.97 (9)	C6—C7—H7	119.3
N1—Hg1—Cl1	106.32 (9)	C7—N8—C9	119.8 (4)
N8—Hg1—Cl2	95.92 (9)	C7—N8—Hg1	116.2 (3)
N1—Hg1—Cl2	138.01 (8)	C9—N8—Hg1	123.9 (3)
Cl1—Hg1—Cl2	115.34 (4)	N8—C9—C10	110.8 (4)
N8—Hg1—Cl2^{i}	142.19 (9)	N8—C9—H9A	109.5
N1—Hg1—Cl2^{i}	83.87 (8)	C10—C9—H9A	109.5

Cl1—Hg1—Cl2^{i}	99.58 (4)	N8—C9—H9B	109.5
Cl2—Hg1—Cl2^{i}	84.37 (3)	C10—C9—H9B	109.5
Hg1—Cl2—Hg1^{i}	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)	Cl3^{ii}—Hg2—Cl3	180

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

Fig. 1


C3
C4
C2
Cl2i
N8i
C5
N1
Cl1
Hg1i
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Hg1
C7
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Cl2
C15
C10
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C12