metal-organic compounds

Di-μ-chlorido-bis{chlorido[2,3-dimethyl-N-(pyridin-2-ylmethylidene)aniline-κ²N,N′]mercury(II)}

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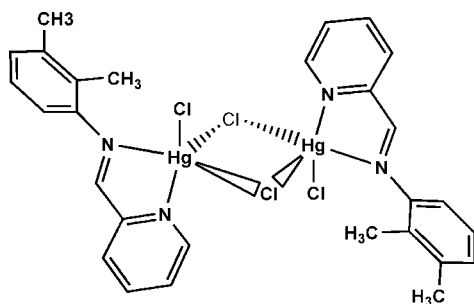Correspondence e-mail: mr_talei@azad.ac.ir

In the centrosymmetric binuclear molecule of the title complex, $[Hg_2Cl_4(C_{14}H_{14}N_2)_2]$, the five-coordinated Hg^{II} ions have a distorted square-pyramidal geometry defined by two N atoms belonging to the chelating iminopyridine ligand and three Cl atoms. The benzene and pyridine rings are oriented at a dihedral angle of 56.7 (6)°. The crystal packing is stabilized by C—H···Cl hydrogen bonds and π–π interactions between the pyridine rings [centroid–centroid distance = 3.796 (6) Å].

Related literature

For background to Schiff base compounds, see: Gibson *et al.* (2007); Gibson & Spitzmesser (2003); Ittel *et al.* (2000). For related structures, see: Baul *et al.* (2004).

Experimental

Crystal data

$[Hg_2Cl_4(C_{14}H_{14}N_2)_2]$	V = 3090.9 (11) Å³
M_r = 963.52	Z = 4
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 7.7989 (16) Å	μ = 10.29 mm⁻¹
b = 26.525 (5) Å	T = 298 K
c = 15.098 (3) Å	0.50 × 0.17 × 0.15 mm
β = 98.26 (3)°	

Data collection

Stoe IPDS-2T diffractometer	12121 measured reflections
Absorption correction: numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 2002)	4164 independent reflections
	3174 reflections with $I > 2\sigma(I)$
T_{min} = 0.126, T_{max} = 0.210	R_{int} = 0.118

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.083	175 parameters
$wR(F^2)$ = 0.206	H-atom parameters constrained
S = 1.11	$\Delta\rho_{max}$ = 3.28 e Å⁻³
4164 reflections	$\Delta\rho_{min}$ = −4.88 e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···Cl2^i	0.93	2.65	3.400 (11)	138
C4—H4···Cl2^ii	0.93	2.67	3.552 (11)	158
C14—H14C···Cl1^iii	0.96	2.76	3.685 (14)	162

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$; (ii) $-x+1, y, -z+\frac{3}{2}$; (iii) $-x+1, -y+1, -z+2$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

Di-**µ**-chlorido-bis{chlorido[2,3-dimethyl-*N*-(pyridin-2-ylmethylidene)aniline-*κ²N,N′*]mercury(II)}

Seyed Jalal Hoseyni, Mohamad Reza Talei Bavil Olyai and Behrouz Notash

S1. Comment

Schiff base metal complexes have been known since the nineteenth century. Investigation on metal-organic complexes represents one of the most active areas of material science and chemical research (Gibson *et al.*, 2007; Gibson & Spitzmesser, 2003; Ittel *et al.*, 2000). Schiff bases form a class of compounds with azomethin group, which are usually synthesized from the condensation of primary amines and active carbonyl groups by the elimination of water molecule. We report herein the crystal structure of the title compound, a new mercury(II) complex. This complex was synthesized by the reaction of HgCl$_2$ with 2-[(2,3-dimethylphenyl)iminomethyl]pyridine in an acetonitril solution.

In the title compound (Fig. 1), the Hg^{II} atom is five-coordinated in a distorted squar-pyramidal geometry. The Schiff base ligand coordinates to the Hg^{II} atom as a bidentate ligand through the N atoms of the imine group and pyridine ring. Also two bridging and one terminal chloride anions are present in the coordination environment of the Hg^{II} atom (Baul *et al.*, 2004). The benzene and pyridine rings are oriented at a dihedral angle of 56.7 (6)°. Crystal packing is stabilized by intermolecular C—H···Cl hydrogen bonds (Fig. 2, Table 1) and π–π interactions between the pyridine rings [centroid–centroid distance = 3.796 (6) Å].

S2. Experimental

For the preparation of the title compound, a solution of 2-[(2,3-dimethylphenyl)iminomethyl]pyridine (0.210 g, 1.00 mmol) in acetonitril (10 ml) was added slowly to a solution of HgCl$_2$ (0.271 g, 1.00 mmol) in acetonitril (10 ml) and the resulting yellow solution was stirred for 45 min at room temperature. Then the yellow precipitate was filtered and dissolved in acetonitril and left to evaporate slowly at -18°C. After a few days, yellow crystals of the title compound were isolated (yield: 0.272 g, 56.5%; m.p. 489 K).

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (CH) and 0.96 (CH$_3$) Å and with U_{iso}(H) = 1.2(1.5 for methyl)U_{eq}(C). The highest residual electron density was found at 0.85 Å from Hg1 atom and the deepest hole at 0.92 Å from Hg1 atom.
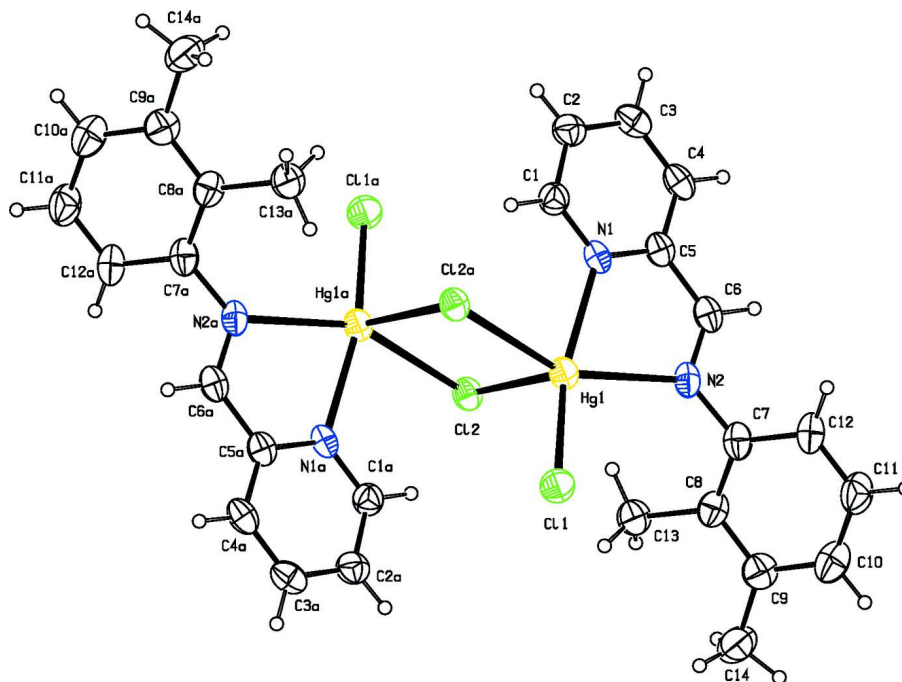
Figure 1

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

[Symmetry code: (a) 1/2-x, 3/2-y, 2-z.]
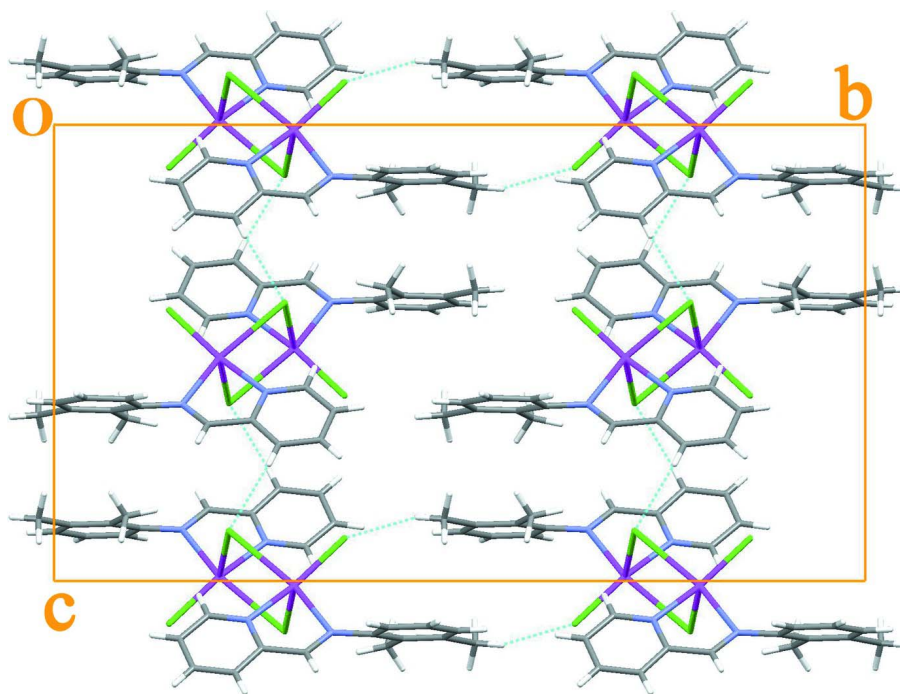
Figure 2

Packing diagram of the title compound. Hydrogen bonds are shown as blue dashed lines.

Di-*µ*-chlorido-bis{chlorido[2,3-dimethyl-*N*-(pyridin-2- ylmethylidene)aniline-*κ²N*,*N*′]mercury(II)}

Crystal data

$[Hg_2Cl_4(C_{14}H_{14}N_2)_2]$	$F(000) = 1808.0$
$M_r = 963.52$	$D_x = 2.071$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 4164 reflections
$a = 7.7989$ (16) Å	$\theta = 2.1–29.2°$
$b = 26.525$ (5) Å	$\mu = 10.29$ mm^{-1}
$c = 15.098$ (3) Å	$T = 298$ K
$\beta = 98.26$ (3)°	Column, yellow
$V = 3090.9$ (11) Å^3	$0.50 \times 0.17 \times 0.15$ mm
$Z = 4$	

Data collection

Stoe IPDS-2T diffractometer	12121 measured reflections
Radiation source: fine-focus sealed tube	4164 independent reflections
Graphite monochromator	3174 reflections with $I > 2\sigma(I)$
Detector resolution: 0.15 mm pixels mm^{-1}	$R_{int} = 0.118$
ω scans	$\theta_{max} = 29.2°$, $\theta_{min} = 2.1°$
Absorption correction: numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 2002)	$h = -10\rightarrow10$
	$k = -36\rightarrow35$
	$l = -20\rightarrow16$
$T_{min} = 0.126$, $T_{max} = 0.210$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.083$	$w = 1/[\sigma^2(F_o^2) + (0.1219P)^2]$
$wR(F^2) = 0.206$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
4164 reflections	$\Delta\rho_{max} = 3.28$ e Å^{-3}
175 parameters	$\Delta\rho_{min} = -4.88$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0012 (2)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Hg1	0.43296 (5)	0.703848 (14)	0.98975 (3)	0.0525 (2)
Cl2	0.1308 (3)	0.71572 (10)	0.88978 (17)	0.0524 (5)

Cl1	0.3754 (4)	0.64201 (11)	1.0936 (2)	0.0663 (7)
N1	0.5738 (9)	0.7612 (3)	0.9145 (5)	0.0452 (16)
N2	0.6082 (10)	0.6579 (3)	0.8873 (6)	0.0528 (19)
C5	0.6666 (12)	0.7441 (4)	0.8523 (6)	0.050 (2)
C6	0.6903 (13)	0.6896 (4)	0.8436 (7)	0.052 (2)
H6	0.7656	0.6776	0.8060	0.062*
C8	0.5112 (14)	0.5709 (4)	0.8740 (7)	0.057 (2)
C7	0.6450 (14)	0.6053 (4)	0.8836 (7)	0.058 (2)
C1	0.5528 (15)	0.8102 (4)	0.9243 (7)	0.055 (2)
H1	0.4887	0.8214	0.9678	0.066*
C13	0.3227 (15)	0.5888 (5)	0.8577 (9)	0.065 (3)
H13A	0.2696	0.5828	0.9102	0.098*
H13B	0.2608	0.5706	0.8081	0.098*
H13C	0.3194	0.6242	0.8445	0.098*
C12	0.8192 (15)	0.5889 (5)	0.8986 (8)	0.065 (3)
H12	0.9093	0.6122	0.9065	0.078*
C9	0.5443 (17)	0.5190 (5)	0.8768 (9)	0.068 (3)
C2	0.6211 (14)	0.8450 (4)	0.8733 (8)	0.060 (2)
H2	0.6030	0.8792	0.8814	0.072*
C4	0.7403 (13)	0.7770 (5)	0.7992 (7)	0.056 (2)
H4	0.8051	0.7649	0.7566	0.068*
C3	0.7178 (14)	0.8285 (5)	0.8093 (8)	0.062 (3)
H3	0.7669	0.8515	0.7736	0.074*
C14	0.406 (2)	0.4806 (5)	0.8639 (13)	0.092 (5)
H14A	0.3288	0.4876	0.8098	0.138*
H14B	0.3418	0.4814	0.9138	0.138*
H14C	0.4561	0.4478	0.8599	0.138*
C11	0.8530 (17)	0.5385 (5)	0.9014 (10)	0.080 (4)
H11	0.9672	0.5273	0.9101	0.096*
C10	0.7187 (19)	0.5035 (6)	0.8912 (10)	0.082 (4)
H10	0.7446	0.4693	0.8940	0.098*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.0468 (3)	0.0595 (3)	0.0521 (3)	0.00288 (15)	0.00989 (16)	0.00296 (15)
Cl2	0.0445 (11)	0.0637 (13)	0.0479 (11)	0.0022 (10)	0.0026 (9)	0.0021 (10)
Cl1	0.0688 (17)	0.0655 (14)	0.0649 (16)	0.0064 (12)	0.0102 (13)	0.0160 (12)
N1	0.034 (3)	0.064 (4)	0.037 (3)	−0.003 (3)	0.006 (3)	−0.009 (3)
N2	0.041 (4)	0.063 (5)	0.055 (4)	0.007 (4)	0.008 (3)	−0.013 (4)
C5	0.039 (4)	0.067 (6)	0.043 (4)	0.002 (4)	−0.002 (4)	0.000 (4)
C6	0.039 (4)	0.075 (6)	0.041 (4)	0.002 (4)	0.002 (4)	−0.006 (4)
C8	0.055 (5)	0.062 (5)	0.051 (5)	0.009 (5)	−0.003 (4)	−0.004 (4)
C7	0.047 (5)	0.073 (6)	0.053 (5)	0.009 (5)	0.003 (4)	−0.009 (5)
C1	0.056 (6)	0.058 (5)	0.053 (5)	0.004 (4)	0.012 (5)	0.003 (4)
C13	0.054 (6)	0.070 (6)	0.068 (7)	0.001 (5)	−0.002 (5)	0.001 (5)
C12	0.052 (6)	0.079 (7)	0.063 (6)	0.020 (5)	0.006 (5)	−0.010 (5)
C9	0.066 (7)	0.071 (7)	0.065 (7)	0.001 (6)	0.002 (5)	0.001 (5)

C2	0.050 (5)	0.062 (6)	0.064 (6)	−0.004 (5)	−0.001 (5)	0.004 (5)
C4	0.041 (5)	0.084 (7)	0.043 (5)	−0.006 (5)	0.004 (4)	−0.002 (5)
C3	0.052 (6)	0.079 (7)	0.053 (5)	−0.013 (5)	0.003 (5)	0.009 (5)
C14	0.089 (10)	0.059 (7)	0.125 (14)	0.008 (6)	0.001 (9)	0.001 (8)
C11	0.057 (7)	0.083 (8)	0.096 (10)	0.019 (6)	−0.005 (7)	−0.004 (7)
C10	0.083 (9)	0.074 (8)	0.084 (9)	0.022 (7)	−0.003 (7)	−0.005 (7)

Geometric parameters (Å, º)

Hg1—N1	2.273 (8)	C13—H13A	0.9600
Hg1—Cl1	2.356 (3)	C13—H13B	0.9600
Hg1—N2	2.521 (8)	C13—H13C	0.9600
Hg1—Cl2	2.628 (3)	C12—C11	1.363 (18)
Hg1—Cl2^i	2.893 (3)	C12—H12	0.9300
N1—C1	1.322 (14)	C9—C10	1.407 (18)
N1—C5	1.345 (13)	C9—C14	1.479 (19)
N2—C6	1.295 (14)	C2—C3	1.379 (17)
N2—C7	1.426 (14)	C2—H2	0.9300
C5—C4	1.365 (16)	C4—C3	1.390 (18)
C5—C6	1.466 (15)	C4—H4	0.9300
C6—H6	0.9300	C3—H3	0.9300
C8—C7	1.379 (16)	C14—H14A	0.9600
C8—C9	1.400 (17)	C14—H14B	0.9600
C8—C13	1.531 (15)	C14—H14C	0.9600
C7—C12	1.413 (14)	C11—C10	1.39 (2)
C1—C2	1.358 (16)	C11—H11	0.9300
C1—H1	0.9300	C10—H10	0.9300
N1—Hg1—Cl1	161.8 (2)	C8—C13—H13B	109.5
N1—Hg1—N2	70.9 (3)	H13A—C13—H13B	109.5
Cl1—Hg1—N2	104.1 (2)	C8—C13—H13C	109.5
N1—Hg1—Cl2	95.2 (2)	H13A—C13—H13C	109.5
Cl1—Hg1—Cl2	102.99 (10)	H13B—C13—H13C	109.5
N2—Hg1—Cl2	103.1 (2)	C11—C12—C7	119.0 (13)
N1—Hg1—Cl2^i	87.7 (2)	C11—C12—H12	120.5
Cl1—Hg1—Cl2^i	91.64 (10)	C7—C12—H12	120.5
N2—Hg1—Cl2^i	154.2 (2)	C8—C9—C10	117.5 (12)
Cl2—Hg1—Cl2^i	92.97 (7)	C8—C9—C14	123.0 (11)
Hg1—Cl2—Hg1^i	87.03 (7)	C10—C9—C14	119.4 (13)
C1—N1—C5	119.7 (9)	C1—C2—C3	118.8 (11)
C1—N1—Hg1	121.8 (7)	C1—C2—H2	120.6
C5—N1—Hg1	118.2 (7)	C3—C2—H2	120.6
C6—N2—C7	119.9 (9)	C5—C4—C3	119.6 (10)
C6—N2—Hg1	110.4 (7)	C5—C4—H4	120.2
C7—N2—Hg1	128.9 (7)	C3—C4—H4	120.2
N1—C5—C4	120.7 (10)	C2—C3—C4	118.5 (10)
N1—C5—C6	118.7 (9)	C2—C3—H3	120.7
C4—C5—C6	120.6 (10)	C4—C3—H3	120.7

N2—C6—C5	121.2 (9)	C9—C14—H14A	109.5
N2—C6—H6	119.4	C9—C14—H14B	109.5
C5—C6—H6	119.4	H14A—C14—H14B	109.5
C7—C8—C9	121.0 (11)	C9—C14—H14C	109.5
C7—C8—C13	120.4 (10)	H14A—C14—H14C	109.5
C9—C8—C13	118.6 (11)	H14B—C14—H14C	109.5
C8—C7—C12	120.6 (11)	C12—C11—C10	120.8 (12)
C8—C7—N2	119.9 (9)	C12—C11—H11	119.6
C12—C7—N2	119.3 (10)	C10—C11—H11	119.6
N1—C1—C2	122.7 (11)	C11—C10—C9	121.2 (12)
N1—C1—H1	118.6	C11—C10—H10	119.4
C2—C1—H1	118.6	C9—C10—H10	119.4
C8—C13—H13A	109.5		

N1—Hg1—Cl2—Hg1^i	−88.0 (2)	C4—C5—C6—N2	−173.4 (9)
Cl1—Hg1—Cl2—Hg1^i	92.38 (10)	C9—C8—C7—C12	−1.6 (18)
N2—Hg1—Cl2—Hg1^i	−159.6 (2)	C13—C8—C7—C12	−180.0 (11)
Cl2^i—Hg1—Cl2—Hg1^i	0.0	C9—C8—C7—N2	−175.2 (11)
Cl1—Hg1—N1—C1	−105.9 (9)	C13—C8—C7—N2	6.4 (16)
N2—Hg1—N1—C1	177.2 (8)	C6—N2—C7—C8	−137.2 (11)
Cl2—Hg1—N1—C1	75.2 (7)	Hg1—N2—C7—C8	54.0 (13)
Cl2^i—Hg1—N1—C1	−17.6 (7)	C6—N2—C7—C12	49.1 (15)
Cl1—Hg1—N1—C5	80.8 (9)	Hg1—N2—C7—C12	−119.7 (10)
N2—Hg1—N1—C5	3.9 (6)	C5—N1—C1—C2	0.3 (15)
Cl2—Hg1—N1—C5	−98.1 (6)	Hg1—N1—C1—C2	−172.9 (8)
Cl2^i—Hg1—N1—C5	169.1 (6)	C8—C7—C12—C11	1.6 (19)
N1—Hg1—N2—C6	0.1 (6)	N2—C7—C12—C11	175.3 (12)
Cl1—Hg1—N2—C6	−161.6 (6)	C7—C8—C9—C10	1.1 (18)
Cl2—Hg1—N2—C6	91.2 (6)	C13—C8—C9—C10	179.5 (11)
Cl2^i—Hg1—N2—C6	−35.8 (10)	C7—C8—C9—C14	−177.9 (13)
N1—Hg1—N2—C7	169.7 (9)	C13—C8—C9—C14	0.5 (19)
Cl1—Hg1—N2—C7	8.0 (8)	N1—C1—C2—C3	−0.7 (17)
Cl2—Hg1—N2—C7	−99.2 (8)	N1—C5—C4—C3	−0.5 (14)
Cl2^i—Hg1—N2—C7	133.8 (7)	C6—C5—C4—C3	−179.3 (8)
C1—N1—C5—C4	0.3 (14)	C1—C2—C3—C4	0.5 (16)
Hg1—N1—C5—C4	173.8 (7)	C5—C4—C3—C2	0.1 (15)
C1—N1—C5—C6	179.1 (8)	C7—C12—C11—C10	−1 (2)
Hg1—N1—C5—C6	−7.5 (11)	C12—C11—C10—C9	1 (2)
C7—N2—C6—C5	−174.6 (8)	C8—C9—C10—C11	−1 (2)
Hg1—N2—C6—C5	−3.9 (11)	C14—C9—C10—C11	178.3 (15)
N1—C5—C6—N2	7.8 (13)		

Symmetry code: (i) −x+1/2, −y+3/2, −z+2.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1⋯Cl2^i	0.93	2.65	3.400 (11)	138

C4—H4···Cl2ⁱⁱ	0.93	2.67	3.552 (11)	158
C14—H14*C*···Cl1ⁱⁱⁱ	0.96	2.76	3.685 (14)	162

Symmetry codes: (i) −*x*+1/2, −*y*+3/2, −*z*+2; (ii) −*x*+1, *y*, −*z*+3/2; (iii) −*x*+1, −*y*+1, −*z*+2.