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Dichloridobis(1,10-phenanthroline-5,6-dione-κ^2N,N')mercury(II)

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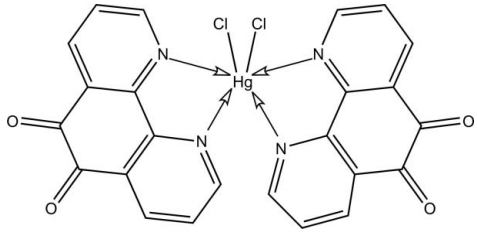
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.012 Å; R factor = 0.037; wR factor = 0.094; data-to-parameter ratio = 15.6.

In the title compound, $[HgCl_2(C_{12}H_6N_2O_2)_2]$, the Hg^{II} atom is located on a twofold rotation axis and exists within a distorted octahedral geometry defined by a *cis*-Cl_2N_4 donor set. Molecules are connected into layers in the *ac* plane *via* extensive C—H···Cl contacts as each Cl atom forms two such interactions. Contacts between the layers are of the type C═O···π [O···centroid distance = 3.110 (8) Å].

Related literature

For related main-group compounds of 1,10-phenanthroline-5,6-dione, see: de Alencastro *et al.* (2005). For the ligand synthesis, see: Yamada *et al.* (1992). For a related structure, see: Ramezanipour *et al.* (2005).



Experimental

Crystal data

$[HgCl_2(C_{12}H_6N_2O_2)_2]$
M_r = 691.87
Orthorhombic, *Fdd*2
a = 8.2261 (2) Å
b = 42.6761 (11) Å
c = 12.6108 (3) Å
V = 4427.12 (19) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 7.24 mm^{-1}
T = 120 K
0.20 × 0.10 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.204, T_{max} = 0.651
10751 measured reflections
2487 independent reflections
2239 reflections with $I > 2\sigma(I)$
R_{int} = 0.075

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.05
2487 reflections
159 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}
Absolute structure: Flack (1983), 1163 Friedel pairs
Flack parameter: −0.012 (13)

Table 1
Selected bond lengths (Å).

Hg—N1	2.439 (7)	Hg—Cl1	2.5270 (19)
Hg—N2	2.512 (6)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl1^{i}	0.95	2.69	3.578 (8)	156
C9—H9···Cl1^{ii}	0.95	2.78	3.701 (8)	164

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

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2254).

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Carlos A. L. Figueiras, João A. S. Bomfim, R. Alan Howie, Edward R. T. Tiekink and James L. Wardell

S1. Comment

In continuation of the previous studies of coordination compounds of 1,10-phenanthroline-5,6-dione (pdon) ligand (de Alencastro *et al.*, 2005), the title compound, $HgCl_2(pdon)_2$, was investigated. The reaction of $HgCl_2$ with pdon (1:1 mol ratio) led to the isolation of a pure 1:1 complex, $HgCl_2(pdon)$. However, as the product was unsuitable for X-ray crystallography, a further recrystallization from $MeNO_2$ solution was attempted, which led to the isolation of the title compound, a 1:2 complex. Of interest was that the 1:1 $HgI_2(pdon)$ complex, prepared similarly to the chloride analogue, was recovered on recrystallization from $MeNO_2$. Unfortunately this set of crystals also proved unsuitable for X-ray crystallography.

In the title compound, the Hg^{II} atom lies on a crystallographic twofold axis and exists within a *cis*-Cl_2N_4 donor set defined by two Cl atoms and four N atoms derived from two chelating pdon ligands (Fig. 1). There is a small disparity in the magnitude of the Hg—N bond distances, with Hg—N1 of 2.439 (7) Å being shorter than Hg—N2 of 2.512 (6) Å. Distortions from an ideal octahedral geometry are related in part to the acute chelate angle of 66.9 (2)°. The pdon ligand is essentially planar with a RMS of 0.226 Å for the N and C atoms, with O1 and O2 atoms lying, respectively, -0.079 (12) and 0.071 (13) Å out of the least-squares plane. The dihedral angle formed between the symmetry related 1,10-phenanthroline planes is 87.13 (11)°. The structural features described herein for the title compound resemble those found for $HgCl_2$(1,10-phenanthroline)$_2$ (Ramezanipour *et al.*, 2005).

In the crystal structure, C—H···Cl interactions are found so that each Cl atom is associated with two H atoms to form supramolecular arrays in the *ac* plane (Table 1 and Fig. 2). The most prominent interactions between the layers are of the type C═O···π. The closest of these involves the carbonyl-O1 group and the centroid (*Cg*) of C4–C7, C11, C12 ring [O1···Cg^i = 3.110 (8) Å with the C5–O1···Cg^i angle being 133.1 (8)°, symmetry code: (i) -1/4+x, 1/4-y, -1/4+z] (Fig. 3).

S2. Experimental

Solutions of $HgCl_2$ (0.272 mg, 1.0 mmol) in EtOH (5 ml) and of 1,10-phenanthroline-5,6-dione (Yamada *et al.*, 1992) (0.212 mg, 1.0 mmol) in EtOH (20 ml) were mixed and stirred at room temperature for 1 h. The precipitate was collected, washed with small portions of EtOH and petroleum ether and dried (yield 0.330 mg). Analysis, calculated for $C_{12}H_6Cl_2HgN_2O_2$ [$HgCl_2(pdon)$]: C 29.9, H 1.3, N 5.8%; found: C 30.2, H 1.5, N 5.2%.

Recrystallization of $HgCl_2(pdon)$ from $MeNO_2$ solution produced crystals of the title compound, $HgCl_2(pdon)_2$.

S3. Refinement

H atoms were geometrically placed with C—H = 0.95 Å, and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The maximum and minimum residual electron density peaks of 2.27 and 0.68 e Å^{-3} were located 0.91 and 0.82 Å from Hg atom, respectively.

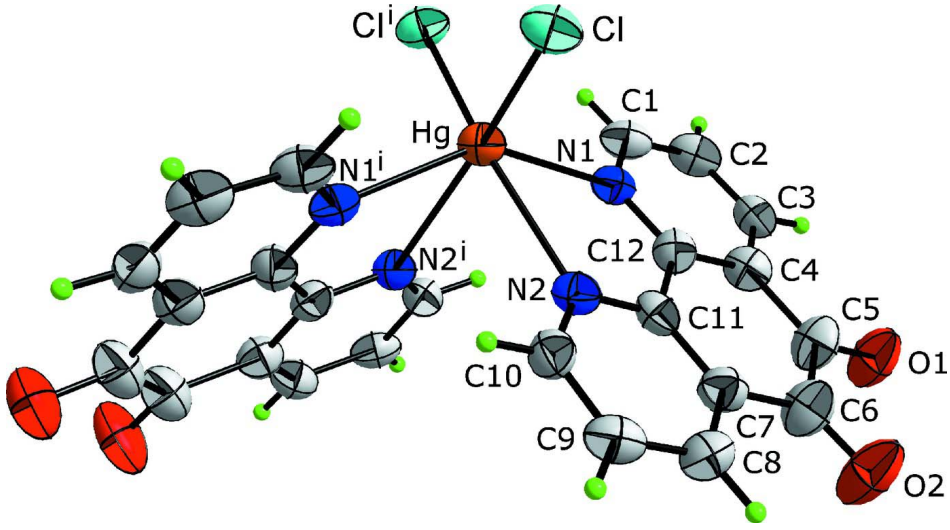

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) -*x*, -*y*, *z*.]

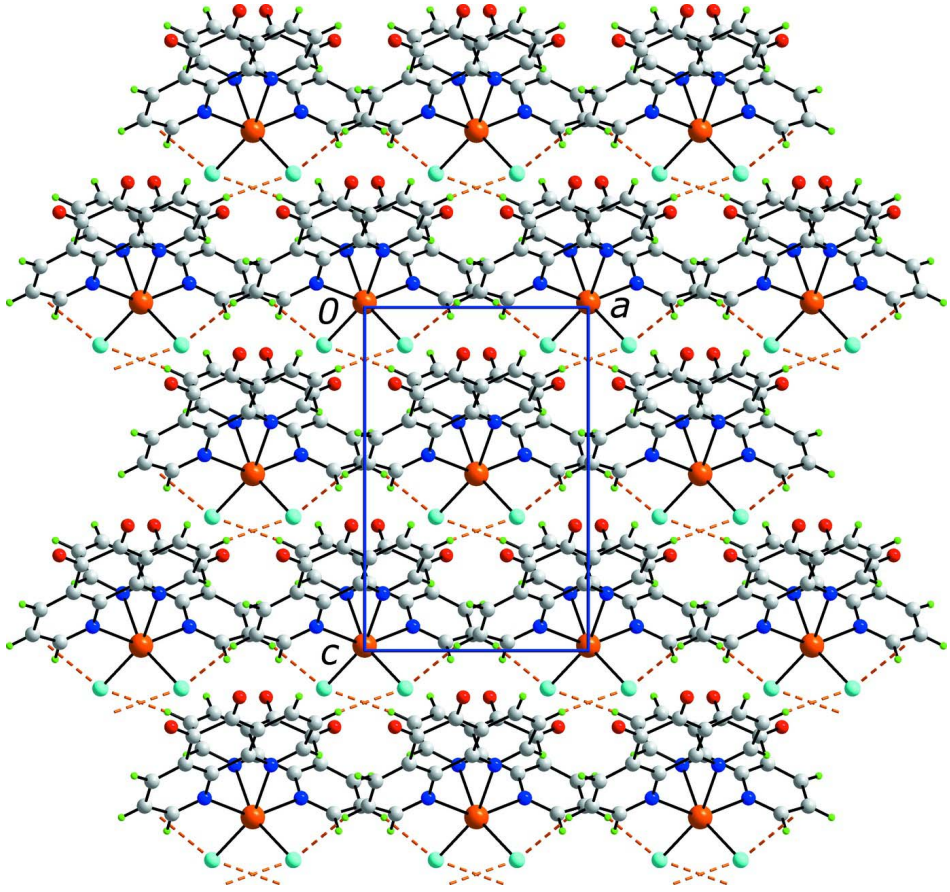

Figure 2

Supramolecular array in the *ac* plane mediated by C—H···Cl contacts (orange dashed lines). [Colour codes: Hg orange; Cl cyan; O red; N blue; C grey; H green.]

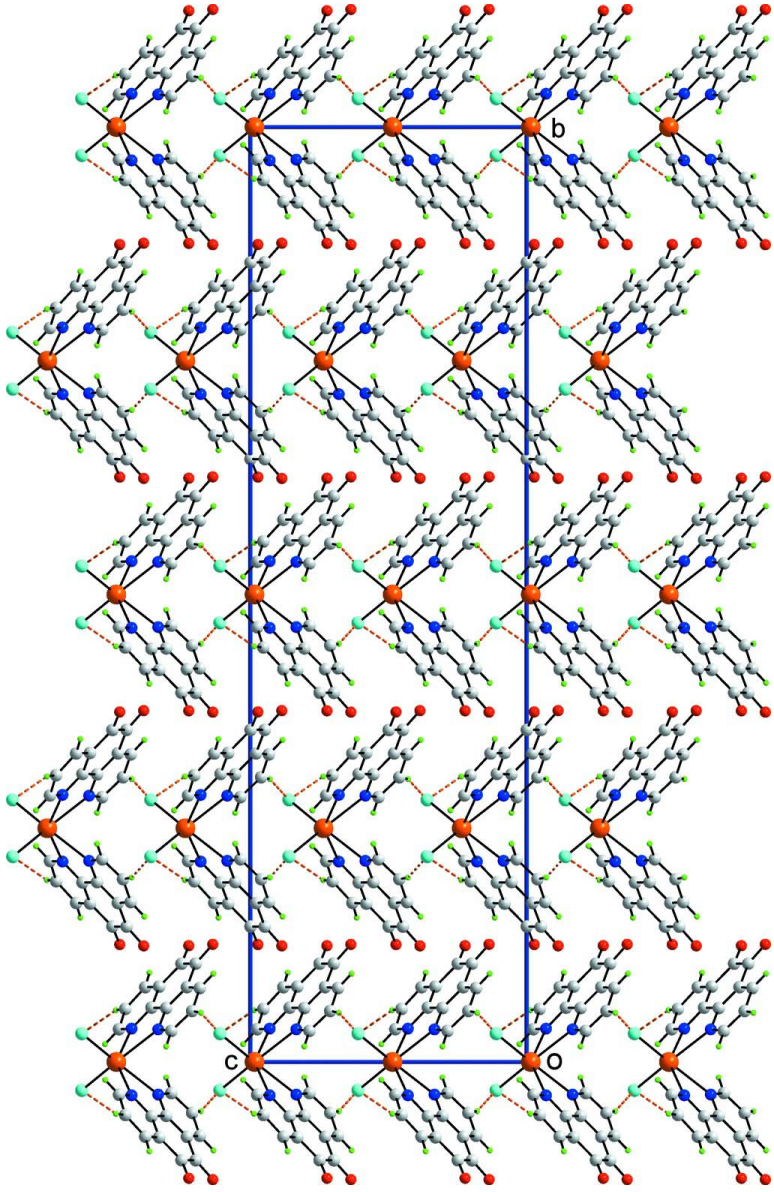

Figure 3

Unit-cell contents viewed in projection down the *a* axis. The C—H···Cl contacts are shown as orange dashed lines. [Colour codes: Hg orange; Cl cyan; O red; N blue; C grey; H green.]

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Crystal data

$[HgCl_2(C_{12}H_6N_2O_2)_2]$
$M_r = 691.87$
Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d
$a = 8.2261\ (2)$ Å
$b = 42.6761\ (11)$ Å
$c = 12.6108\ (3)$ Å
$V = 4427.12\ (19)$ Å^3
$Z = 8$
$F(000) = 2640$
$D_x = 2.076$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 18660 reflections
$\theta = 2.9$–$27.5°$
$\mu = 7.24$ mm^{-1}
$T = 120$ K
Block, yellow
0.20 × 0.10 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: Enraf Nonius FR591 rotating anode
10 cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.204, T_{max} = 0.651
10751 measured reflections
2487 independent reflections
2239 reflections with $I > 2\sigma(I)$
R_{int} = 0.075
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −10→8
k = −55→55
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.05
2487 reflections
159 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 3.1352P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}
Absolute structure: Flack (1983), 1163 Friedel pairs
Absolute structure parameter: −0.012 (13)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Hg	0.0000	0.0000	0.48512 (8)	0.04052 (12)
Cl1	0.1811 (2)	0.03035 (5)	0.61020 (15)	0.0486 (4)
O1	−0.3649 (8)	0.12440 (15)	0.2228 (6)	0.072 (2)
O2	−0.0592 (10)	0.12581 (18)	0.1361 (7)	0.081 (2)
N1	−0.2157 (8)	0.03565 (16)	0.4299 (5)	0.0406 (14)
N2	0.0815 (7)	0.03486 (14)	0.3337 (4)	0.0399 (13)
C1	−0.3618 (9)	0.03505 (19)	0.4754 (6)	0.0472 (16)
H1	−0.3840	0.0191	0.5258	0.057*
C2	−0.4837 (9)	0.0567 (2)	0.4528 (7)	0.050 (2)
H2	−0.5869	0.0554	0.4864	0.060*
C3	−0.4507 (11)	0.07993 (18)	0.3806 (6)	0.0459 (17)
H3	−0.5300	0.0955	0.3653	0.055*
C4	−0.3014 (10)	0.08061 (18)	0.3300 (6)	0.0435 (16)
C5	−0.2664 (10)	0.1051 (2)	0.2493 (14)	0.057 (3)
C6	−0.0923 (11)	0.1052 (2)	0.1979 (8)	0.059 (2)
C7	0.0217 (9)	0.0800 (2)	0.2297 (7)	0.0450 (17)
C8	0.1742 (11)	0.0790 (2)	0.1830 (6)	0.0482 (18)
H8	0.2071	0.0945	0.1335	0.058*
C9	0.2777 (9)	0.0545 (2)	0.2110 (6)	0.0453 (18)
H9	0.3818	0.0526	0.1792	0.054*
C10	0.2257 (10)	0.03325 (19)	0.2861 (7)	0.0437 (17)
H10	0.2965	0.0166	0.3047	0.052*
C11	−0.0196 (9)	0.05763 (18)	0.3047 (6)	0.0409 (16)

C12	−0.1850 (9)	0.05809 (16)	0.3578 (7)	0.0413 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg	0.03662 (19)	0.04817 (18)	0.03677 (16)	0.00021 (19)	0.000	0.000
Cl1	0.0400 (9)	0.0635 (11)	0.0424 (9)	−0.0042 (8)	−0.0003 (8)	−0.0077 (8)
O1	0.062 (4)	0.064 (4)	0.091 (5)	0.015 (3)	0.005 (4)	0.029 (4)
O2	0.055 (4)	0.082 (5)	0.106 (6)	0.016 (4)	0.016 (4)	0.049 (4)
N1	0.042 (3)	0.046 (3)	0.034 (3)	−0.003 (3)	0.004 (2)	−0.003 (3)
N2	0.035 (3)	0.049 (3)	0.036 (3)	0.003 (3)	0.000 (2)	−0.001 (2)
C1	0.039 (4)	0.064 (4)	0.039 (3)	−0.007 (3)	−0.002 (3)	−0.005 (4)
C2	0.033 (4)	0.069 (5)	0.047 (4)	−0.006 (3)	0.001 (3)	−0.010 (3)
C3	0.044 (4)	0.047 (4)	0.047 (4)	0.006 (3)	−0.004 (3)	−0.011 (3)
C4	0.032 (3)	0.053 (4)	0.045 (4)	0.001 (3)	−0.006 (3)	−0.004 (3)
C5	0.048 (5)	0.055 (4)	0.067 (10)	0.002 (4)	−0.011 (5)	0.012 (5)
C6	0.052 (5)	0.059 (5)	0.067 (5)	0.000 (4)	−0.008 (4)	0.012 (4)
C7	0.044 (4)	0.048 (4)	0.043 (4)	−0.003 (3)	0.004 (3)	−0.001 (3)
C8	0.050 (5)	0.052 (4)	0.043 (4)	−0.004 (3)	−0.001 (3)	0.007 (3)
C9	0.037 (4)	0.062 (5)	0.038 (4)	−0.011 (3)	0.001 (3)	−0.007 (3)
C10	0.047 (5)	0.042 (4)	0.042 (4)	0.005 (3)	−0.007 (3)	−0.001 (3)
C11	0.043 (4)	0.042 (4)	0.038 (3)	0.000 (3)	−0.002 (3)	−0.009 (3)
C12	0.039 (4)	0.040 (3)	0.045 (3)	0.000 (3)	−0.009 (3)	−0.002 (3)

Geometric parameters (Å, º)

Hg—N1	2.439 (7)	C3—H3	0.9500
Hg—N2	2.512 (6)	C4—C12	1.401 (11)
Hg—Cl1	2.5270 (19)	C4—C5	1.487 (15)
O1—C5	1.203 (11)	C5—C6	1.572 (14)
O2—C6	1.206 (11)	C6—C7	1.483 (12)
N1—C1	1.332 (10)	C7—C11	1.386 (12)
N1—C12	1.344 (10)	C7—C8	1.387 (12)
N2—C11	1.330 (10)	C8—C9	1.392 (12)
N2—C10	1.331 (10)	C8—H8	0.9500
C1—C2	1.393 (12)	C9—C10	1.380 (11)
C1—H1	0.9500	C9—H9	0.9500
C2—C3	1.374 (13)	C10—H10	0.9500
C2—H2	0.9500	C11—C12	1.516 (11)
C3—C4	1.384 (11)		
N1—Hg—N1^{i}	146.8 (3)	C4—C3—H3	120.1
N1—Hg—N2^{i}	87.6 (2)	C3—C4—C12	118.4 (8)
N1^{i}—Hg—N2^{i}	66.9 (2)	C3—C4—C5	120.1 (7)
N1—Hg—N2	66.9 (2)	C12—C4—C5	121.4 (7)
N1^{i}—Hg—N2	87.6 (2)	O1—C5—C4	122.8 (9)
N2^{i}—Hg—N2	81.0 (3)	O1—C5—C6	119.8 (11)
N1—Hg—Cl1	106.71 (16)	C4—C5—C6	117.4 (8)

N1^{i}—Hg—Cl1	93.95 (16)	O2—C6—C7	124.1 (9)
N2^{i}—Hg—Cl1	159.31 (13)	O2—C6—C5	118.3 (9)
N2—Hg—Cl1	90.78 (14)	C7—C6—C5	117.5 (8)
N1—Hg—Cl1^{i}	93.95 (16)	C11—C7—C8	119.4 (8)
N1^{i}—Hg—Cl1^{i}	106.71 (16)	C11—C7—C6	122.0 (7)
N2^{i}—Hg—Cl1^{i}	90.78 (14)	C8—C7—C6	118.6 (8)
N2—Hg—Cl1^{i}	159.31 (13)	C7—C8—C9	117.9 (8)
Cl1—Hg—Cl1^{i}	102.75 (10)	C7—C8—H8	121.0
C1—N1—C12	118.3 (7)	C9—C8—H8	121.0
C1—N1—Hg	121.4 (5)	C10—C9—C8	118.6 (7)
C12—N1—Hg	120.0 (5)	C10—C9—H9	120.7
C11—N2—C10	118.1 (7)	C8—C9—H9	120.7
C11—N2—Hg	118.3 (5)	N2—C10—C9	123.5 (7)
C10—N2—Hg	123.4 (5)	N2—C10—H10	118.3
N1—C1—C2	123.3 (8)	C9—C10—H10	118.3
N1—C1—H1	118.4	N2—C11—C7	122.5 (7)
C2—C1—H1	118.4	N2—C11—C12	116.7 (7)
C3—C2—C1	118.2 (7)	C7—C11—C12	120.8 (7)
C3—C2—H2	120.9	N1—C12—C4	122.0 (8)
C1—C2—H2	120.9	N1—C12—C11	117.3 (7)
C2—C3—C4	119.8 (7)	C4—C12—C11	120.7 (7)
C2—C3—H3	120.1		

N1^{i}—Hg—N1—C1	135.2 (6)	C4—C5—C6—C7	2.9 (16)
N2^{i}—Hg—N1—C1	96.6 (6)	O2—C6—C7—C11	177.0 (10)
N2—Hg—N1—C1	177.8 (6)	C5—C6—C7—C11	−2.3 (14)
Cl1—Hg—N1—C1	−98.6 (6)	O2—C6—C7—C8	−2.6 (15)
Cl1^{i}—Hg—N1—C1	5.9 (6)	C5—C6—C7—C8	178.0 (9)
N1^{i}—Hg—N1—C12	−50.0 (5)	C11—C7—C8—C9	2.5 (12)
N2^{i}—Hg—N1—C12	−88.6 (6)	C6—C7—C8—C9	−177.8 (8)
N2—Hg—N1—C12	−7.4 (5)	C7—C8—C9—C10	−2.2 (12)
Cl1—Hg—N1—C12	76.2 (6)	C11—N2—C10—C9	2.3 (12)
Cl1^{i}—Hg—N1—C12	−179.2 (5)	Hg—N2—C10—C9	−172.5 (6)
N1—Hg—N2—C11	7.4 (5)	C8—C9—C10—N2	−0.2 (12)
N1^{i}—Hg—N2—C11	165.7 (5)	C10—N2—C11—C7	−1.9 (11)
N2^{i}—Hg—N2—C11	98.7 (5)	Hg—N2—C11—C7	173.2 (6)
Cl1—Hg—N2—C11	−100.4 (5)	C10—N2—C11—C12	177.9 (7)
Cl1^{i}—Hg—N2—C11	30.9 (8)	Hg—N2—C11—C12	−7.0 (8)
N1—Hg—N2—C10	−177.7 (6)	C8—C7—C11—N2	−0.5 (12)
N1^{i}—Hg—N2—C10	−19.5 (6)	C6—C7—C11—N2	179.8 (8)
N2^{i}—Hg—N2—C10	−86.5 (6)	C8—C7—C11—C12	179.7 (7)
Cl1—Hg—N2—C10	74.4 (6)	C6—C7—C11—C12	0.0 (12)
Cl1^{i}—Hg—N2—C10	−154.2 (5)	C1—N1—C12—C4	0.1 (11)
C12—N1—C1—C2	−0.6 (12)	Hg—N1—C12—C4	−174.9 (5)
Hg—N1—C1—C2	174.3 (6)	C1—N1—C12—C11	−178.1 (6)
N1—C1—C2—C3	−0.5 (12)	Hg—N1—C12—C11	6.9 (9)
C1—C2—C3—C4	2.2 (12)	C3—C4—C12—N1	1.6 (11)
C2—C3—C4—C12	−2.7 (11)	C5—C4—C12—N1	−179.4 (9)

C2—C3—C4—C5	178.2 (9)	C3—C4—C12—C11	179.8 (7)
C3—C4—C5—O1	−2.1 (18)	C5—C4—C12—C11	−1.2 (13)
C12—C4—C5—O1	178.8 (11)	N2—C11—C12—N1	0.3 (10)
C3—C4—C5—C6	177.9 (9)	C7—C11—C12—N1	−179.9 (7)
C12—C4—C5—C6	−1.1 (16)	N2—C11—C12—C4	−178.0 (7)
O1—C5—C6—O2	3.5 (19)	C7—C11—C12—C4	1.9 (11)
C4—C5—C6—O2	−176.5 (10)	O1—C5—C6—O2	3.5 (19)
O1—C5—C6—C7	−177.1 (11)		

Symmetry code: (i) −*x*, −*y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Cl1^{ii}	0.95	2.69	3.578 (8)	156
C9—H9···Cl1^{iii}	0.95	2.78	3.701 (8)	164

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