

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

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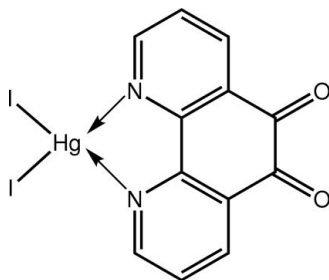
Received 21 September 2011; accepted 21 September 2011

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.022; wR factor = 0.049; data-to-parameter ratio = 18.7.

The Hg^{II} atom in the title complex, [HgI₂(C₁₂H₆N₂O₂)], is tetrahedrally coordinated by the N atoms of the chelating 1,10-phenanthroline-5,6-dione ligand and two I atoms. The range of tetrahedral angles is broad, *viz.* 68.94 (17)° for the chelate angle to a wide 132.627 (15)° for the I—Hg—I angle. The ligand molecule is non-planar with the O atoms lying 0.422 (5) and −0.325 (5) Å out of the plane through the remaining atoms [r.m.s. deviation = 0.068 Å]. Molecules are consolidated in the crystal packing by C—H···O interactions.

Related literature

For the ligand synthesis and the crystal structure of 1,10-phenanthroline-5,6-dione, see: Calderazzo *et al.* (1999). For an evaluation of the different coordinating ability of the two sets of donor atoms in the ligand, see: Fujihara *et al.* (2003). For the structure of the dichlorido analogue with two 1,10-phenanthroline-5,6-dione ligands, see: Figueiras *et al.* (2009). For the crystallization procedure, see: Harrowfield *et al.* (1996).



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Experimental

Crystal data

[HgI₂(C₁₂H₆N₂O₂)]
 $M_r = 664.58$
 Monoclinic, Cc
 $a = 11.7941$ (3) Å
 $b = 8.1725$ (1) Å
 $c = 15.3982$ (3) Å
 $\beta = 108.298$ (2)°

$V = 1409.14$ (5) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 15.30$ mm^{−1}
 $T = 100$ K
 $0.15 \times 0.15 \times 0.15$ mm

Data collection

Agilent SuperNova Dual diffractometer with Atlas detector
 Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2010)
 $T_{\min} = 0.586$, $T_{\max} = 1.000$

15631 measured reflections
 3209 independent reflections
 3155 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.049$
 $S = 1.03$
 3209 reflections
 172 parameters
 2 restraints

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.51$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.79$ e Å^{−3}
 Absolute structure: Flack (1983),
 1579 Friedel pairs
 Flack parameter: −0.005 (3)

Table 1

Selected bond lengths (Å).

Hg1—N1	2.411 (5)	Hg1—I1	2.6637 (4)
Hg1—N2	2.416 (5)	Hg1—I2	2.6739 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1···O2 ⁱ	0.95	2.58	3.077 (8)	113
C12—H12···O1 ⁱⁱ	0.95	2.40	3.248 (7)	148

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

Data collection: CrysAlis PRO (Agilent, 2010); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; 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 DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

We acknowledge financial support of this work by the Islamic Azad University, Saveh Branch, and thank the University of Malaya for support of the crystallographic facility.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5098).

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supplementary materials

Acta Cryst. (2011). E67, m1449-m1450 [doi:10.1107/S1600536811038748]

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

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Comment

1,10-Phenanthroline-5,6-dione (Calderazzo *et al.*, 1999) has attracted our attention due to the presence of two coordinating functionalities within the same molecule, *i.e.* the quinonoid and the diimine residues. Moreover, the presence of two types of basic centres, *i.e.* nitrogen and oxygen, both sp^2 -hybridized, makes this molecule an ideal system to study the different coordinating ability of the two sets of donor atoms (Calderazzo *et al.*, 1999; Fujihara *et al.*, 2003). In connection with a recent structure determination of the related mercury(II)dichlorido structure with two 1,10-phenanthroline-5,6-dione ligands (Figueiras *et al.*, 2009), the structure of the title compound, (I), was determined.

The Hg atom in (I), Fig. 1 and Table 1, is chelated by the 1,10-phenanthroline-5,6-dione ligand and the distorted tetrahedral I_2N_2 donor set is completed by two I atoms. The range of tetrahedral angles is from a narrow 68.94 (17) $^\circ$, for the chelate angle, to a wide 132.627 (15) $^\circ$, for the angle subtended at Hg by the I atoms. The 1,10-phenanthroline-5,6-dione ligand is planar with the r.m.s. deviation for the 14 C and N atoms being 0.068 Å with the maximum deviations from the least-squares plane being 0.146 (6) Å for atom C7 and -0.116 (7) for atom C6; the O1 and O2 atoms lie -0.325 (5) and 0.422 (5) Å out of this plane, respectively.

The molecules of (I) are consolidated in the crystal packing *via* weak C—H \cdots O interactions involving both O atoms, Table 2 and Fig. 2.

Experimental

The title complex was obtained by the branched tube method (Harrowfield *et al.*, 1996). 1,10-Phenanthroline-5,6-dione (0.136 g, 0.648 mmol) and HgI_2 (0.294 g, 0.648 mmol) were placed at the bottom of main arm of a branched tube. Methanol was carefully added to fill both arms. The tube was sealed and the main arm immersed in a bath at 333 K while the other was kept at ambient temperature. After five days, red crystals were deposited in the cooler arm. These were filtered off, washed with acetone and ether, and air dried; Yield: 60%; *M.pt.* 524–526 K. Anal. Calc for $C_{12}H_6HgI_2N_2O_2$; C, 21.7, H, 0.60, N, 4.2%; Found: C, 21.89, H, 0.69, N: 4.24%. Selected FT—IR data, $\nu(\text{cm}^{-1})$: 1687 (C=O). $^1\text{H NMR}$ (δ): 7.85–7.89 (dd, 2H, H3,8), 8.53–8.56 (dd, 2H, H2,9), 9.01–9.03 (dd, 2H, H4,7) p.p.m..

Refinement

The H-atoms were placed in calculated positions (C—H 0.95 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{equiv}}(\text{C})$. A number of reflections, *i.e.* 4 0 -10, 1 3 -10, 6 0 -10, 0 0 $\bar{8}$, 2 4 -11, 6 0 $\bar{8}$, 5 3 -14 and 3 3 -12, were omitted from the final refinement owing to poor agreement.

Figures

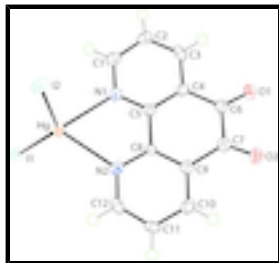


Fig. 1. The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

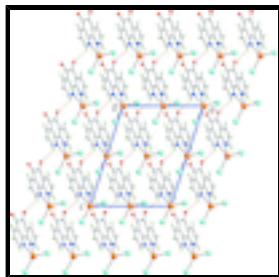


Fig. 2. A view in projection down the *b* axis of the unit-cell contents of (I). The C—H...O interactions are shown as orange dashed lines.

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M_r = 664.58

Monoclinic, *Cc*

Hall symbol: C -2yc

a = 11.7941 (3) Å

b = 8.1725 (1) Å

c = 15.3982 (3) Å

β = 108.298 (2)°

V = 1409.14 (5) Å³

Z = 4

F(000) = 1176

D_x = 3.133 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 11298 reflections

θ = 2.8–29.3°

μ = 15.30 mm⁻¹

T = 100 K

Block, red

0.15 × 0.15 × 0.15 mm

Data collection

Agilent SuperNova Dual
diffractometer with Atlas detector

Radiation source: SuperNova (Mo) X-ray Source

Mirror

Detector resolution: 10.4041 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2010)

T_{min} = 0.586, *T_{max}* = 1.000

15631 measured reflections

3209 independent reflections

3155 reflections with *I* > 2σ(*I*)

R_{int} = 0.041

θ_{\max} = 27.5°, θ_{\min} = 2.8°

h = -15→15

k = -10→10

l = -19→19

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H-atom parameters constrained
$wR(F^2) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
3209 reflections	$(\Delta/\sigma)_{\max} = 0.001$
172 parameters	$\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$
2 restraints	$\Delta\rho_{\min} = -0.79 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1579 Friedel pairs Flack parameter: $-0.005 (3)$

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.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.499993 (19)	0.48034 (2)	0.500006 (16)	0.01421 (6)
I1	0.46538 (3)	0.38365 (4)	0.65496 (2)	0.01434 (9)
I2	0.66399 (3)	0.67286 (5)	0.46534 (3)	0.01911 (10)
O1	0.0663 (4)	0.5129 (5)	0.0820 (3)	0.0211 (10)
O2	0.2083 (4)	0.2572 (5)	0.0607 (3)	0.0174 (9)
N1	0.3288 (4)	0.5884 (6)	0.3831 (3)	0.0132 (10)
N2	0.4235 (4)	0.2848 (6)	0.3779 (3)	0.0120 (10)
C1	0.2862 (5)	0.7383 (7)	0.3878 (4)	0.0154 (12)
H1	0.3175	0.7988	0.4428	0.018*
C2	0.1973 (6)	0.8101 (7)	0.3152 (4)	0.0160 (12)
H2	0.1679	0.9164	0.3208	0.019*
C3	0.1537 (5)	0.7221 (8)	0.2351 (4)	0.0156 (12)
H3	0.0938	0.7673	0.1842	0.019*
C4	0.1990 (6)	0.5657 (7)	0.2299 (4)	0.0132 (11)
C5	0.2882 (6)	0.5030 (6)	0.3057 (4)	0.0111 (11)
C6	0.1530 (6)	0.4715 (7)	0.1439 (4)	0.0142 (12)
C7	0.2238 (5)	0.3175 (7)	0.1356 (4)	0.0115 (11)

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C8	0.3413 (5)	0.3392 (7)	0.3019 (4)	0.0100 (11)
C9	0.3084 (5)	0.2485 (7)	0.2209 (4)	0.0130 (12)
C10	0.3582 (5)	0.0953 (7)	0.2196 (4)	0.0156 (12)
H10	0.3378	0.0324	0.1650	0.019*
C11	0.4383 (6)	0.0363 (7)	0.2996 (4)	0.0147 (12)
H11	0.4713	-0.0702	0.3019	0.018*
C12	0.4696 (6)	0.1365 (8)	0.3764 (4)	0.0155 (12)
H12	0.5267	0.0971	0.4307	0.019*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hg1	0.01526 (11)	0.01650 (11)	0.01011 (10)	-0.00067 (10)	0.00290 (7)	-0.00105 (10)
I1	0.01624 (19)	0.01475 (19)	0.01394 (18)	-0.00041 (15)	0.00747 (15)	-0.00073 (14)
I2	0.0206 (2)	0.01604 (19)	0.0225 (2)	-0.00531 (16)	0.00937 (17)	-0.00433 (16)
O1	0.023 (3)	0.019 (2)	0.015 (2)	-0.0015 (18)	-0.0049 (19)	0.0022 (17)
O2	0.021 (2)	0.018 (2)	0.012 (2)	-0.0045 (18)	0.0053 (17)	-0.0010 (18)
N1	0.012 (2)	0.013 (2)	0.015 (2)	-0.001 (2)	0.007 (2)	-0.001 (2)
N2	0.014 (2)	0.012 (2)	0.012 (2)	-0.0029 (19)	0.0064 (19)	-0.0014 (19)
C1	0.017 (3)	0.015 (3)	0.016 (3)	0.000 (2)	0.009 (3)	-0.002 (2)
C2	0.017 (3)	0.011 (3)	0.021 (3)	-0.003 (2)	0.009 (3)	-0.002 (2)
C3	0.013 (3)	0.021 (3)	0.012 (3)	0.000 (2)	0.004 (2)	0.006 (2)
C4	0.015 (3)	0.012 (3)	0.013 (3)	-0.005 (2)	0.005 (2)	-0.001 (2)
C5	0.013 (3)	0.011 (3)	0.011 (3)	-0.004 (2)	0.006 (2)	0.001 (2)
C6	0.018 (3)	0.014 (3)	0.011 (3)	-0.005 (2)	0.005 (3)	0.001 (2)
C7	0.009 (3)	0.013 (3)	0.014 (3)	-0.004 (2)	0.005 (2)	0.002 (2)
C8	0.010 (3)	0.008 (2)	0.012 (3)	0.000 (2)	0.003 (2)	0.001 (2)
C9	0.015 (3)	0.013 (3)	0.012 (3)	-0.005 (2)	0.006 (2)	0.002 (2)
C10	0.018 (3)	0.014 (3)	0.015 (3)	-0.007 (2)	0.005 (2)	-0.001 (2)
C11	0.014 (3)	0.009 (3)	0.021 (3)	-0.001 (2)	0.006 (3)	0.005 (2)
C12	0.014 (3)	0.019 (3)	0.012 (3)	-0.001 (2)	0.004 (2)	0.006 (2)

Geometric parameters (\AA , $^\circ$)

Hg1—N1	2.411 (5)	C3—C4	1.398 (9)
Hg1—N2	2.416 (5)	C3—H3	0.9500
Hg1—I1	2.6637 (4)	C4—C5	1.400 (9)
Hg1—I2	2.6739 (4)	C4—C6	1.479 (8)
O1—C6	1.207 (8)	C5—C8	1.487 (8)
O2—C7	1.215 (7)	C6—C7	1.538 (8)
N1—C5	1.333 (8)	C7—C9	1.488 (8)
N1—C1	1.335 (8)	C8—C9	1.396 (8)
N2—C8	1.341 (7)	C9—C10	1.386 (9)
N2—C12	1.331 (8)	C10—C11	1.382 (9)
C1—C2	1.399 (9)	C10—H10	0.9500
C1—H1	0.9500	C11—C12	1.390 (9)
C2—C3	1.380 (9)	C11—H11	0.9500
C2—H2	0.9500	C12—H12	0.9500

N2—Hg1—N1	68.94 (17)	N1—C5—C4	121.3 (5)
N2—Hg1—I1	112.07 (11)	N1—C5—C8	118.0 (5)
N1—Hg1—I1	116.72 (11)	C4—C5—C8	120.7 (5)
N2—Hg1—I2	110.55 (11)	O1—C6—C4	122.9 (6)
N1—Hg1—I2	97.13 (12)	O1—C6—C7	120.7 (5)
I1—Hg1—I2	132.627 (15)	C4—C6—C7	116.4 (5)
C5—N1—C1	119.5 (5)	O2—C7—C9	123.0 (5)
C5—N1—Hg1	117.2 (4)	O2—C7—C6	119.2 (5)
C1—N1—Hg1	122.5 (4)	C9—C7—C6	117.9 (5)
C8—N2—C12	118.3 (5)	N2—C8—C9	121.7 (5)
C8—N2—Hg1	116.8 (4)	N2—C8—C5	117.5 (5)
C12—N2—Hg1	124.1 (4)	C9—C8—C5	120.7 (5)
N1—C1—C2	122.8 (6)	C10—C9—C8	119.5 (6)
N1—C1—H1	118.6	C10—C9—C7	120.0 (5)
C2—C1—H1	118.6	C8—C9—C7	120.5 (5)
C3—C2—C1	118.1 (6)	C9—C10—C11	118.5 (6)
C3—C2—H2	120.9	C9—C10—H10	120.8
C1—C2—H2	120.9	C11—C10—H10	120.8
C2—C3—C4	119.1 (6)	C10—C11—C12	118.5 (6)
C2—C3—H3	120.5	C10—C11—H11	120.8
C4—C3—H3	120.5	C12—C11—H11	120.8
C5—C4—C3	119.1 (6)	N2—C12—C11	123.4 (6)
C5—C4—C6	121.6 (5)	N2—C12—H12	118.3
C3—C4—C6	119.2 (6)	C11—C12—H12	118.3
N2—Hg1—N1—C5	-9.4 (4)	C5—C4—C6—C7	-11.3 (8)
I1—Hg1—N1—C5	-114.3 (4)	C3—C4—C6—C7	167.7 (5)
I2—Hg1—N1—C5	99.9 (4)	O1—C6—C7—O2	15.4 (8)
N2—Hg1—N1—C1	-179.3 (5)	C4—C6—C7—O2	-163.1 (5)
I1—Hg1—N1—C1	75.8 (5)	O1—C6—C7—C9	-164.2 (6)
I2—Hg1—N1—C1	-69.9 (4)	C4—C6—C7—C9	17.3 (7)
N1—Hg1—N2—C8	10.8 (4)	C12—N2—C8—C9	-3.4 (8)
I1—Hg1—N2—C8	122.1 (4)	Hg1—N2—C8—C9	167.0 (4)
I2—Hg1—N2—C8	-79.1 (4)	C12—N2—C8—C5	178.2 (5)
N1—Hg1—N2—C12	-179.4 (5)	Hg1—N2—C8—C5	-11.3 (6)
I1—Hg1—N2—C12	-68.1 (5)	N1—C5—C8—N2	2.7 (8)
I2—Hg1—N2—C12	90.8 (5)	C4—C5—C8—N2	-177.9 (5)
C5—N1—C1—C2	1.7 (9)	N1—C5—C8—C9	-175.7 (5)
Hg1—N1—C1—C2	171.3 (4)	C4—C5—C8—C9	3.8 (8)
N1—C1—C2—C3	-0.9 (9)	N2—C8—C9—C10	2.5 (8)
C1—C2—C3—C4	0.4 (9)	C5—C8—C9—C10	-179.2 (5)
C2—C3—C4—C5	-0.6 (9)	N2—C8—C9—C7	-175.3 (5)
C2—C3—C4—C6	-179.6 (5)	C5—C8—C9—C7	3.0 (8)
C1—N1—C5—C4	-1.8 (8)	O2—C7—C9—C10	-10.9 (8)
Hg1—N1—C5—C4	-172.0 (4)	C6—C7—C9—C10	168.7 (5)
C1—N1—C5—C8	177.6 (5)	O2—C7—C9—C8	166.9 (5)
Hg1—N1—C5—C8	7.4 (6)	C6—C7—C9—C8	-13.6 (8)
C3—C4—C5—N1	1.3 (9)	C8—C9—C10—C11	0.9 (9)
C6—C4—C5—N1	-179.7 (5)	C7—C9—C10—C11	178.6 (5)
C3—C4—C5—C8	-178.1 (5)	C9—C10—C11—C12	-3.0 (9)

supplementary materials

C6—C4—C5—C8	0.8 (9)	C8—N2—C12—C11	1.1 (9)
C5—C4—C6—O1	170.3 (6)	Hg1—N2—C12—C11	-168.6 (4)
C3—C4—C6—O1	-10.8 (9)	C10—C11—C12—N2	2.1 (9)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1 \cdots O2 ⁱ	0.95	2.58	3.077 (8)	113
C12—H12 \cdots O1 ⁱⁱ	0.95	2.40	3.248 (7)	148

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

Fig. 1

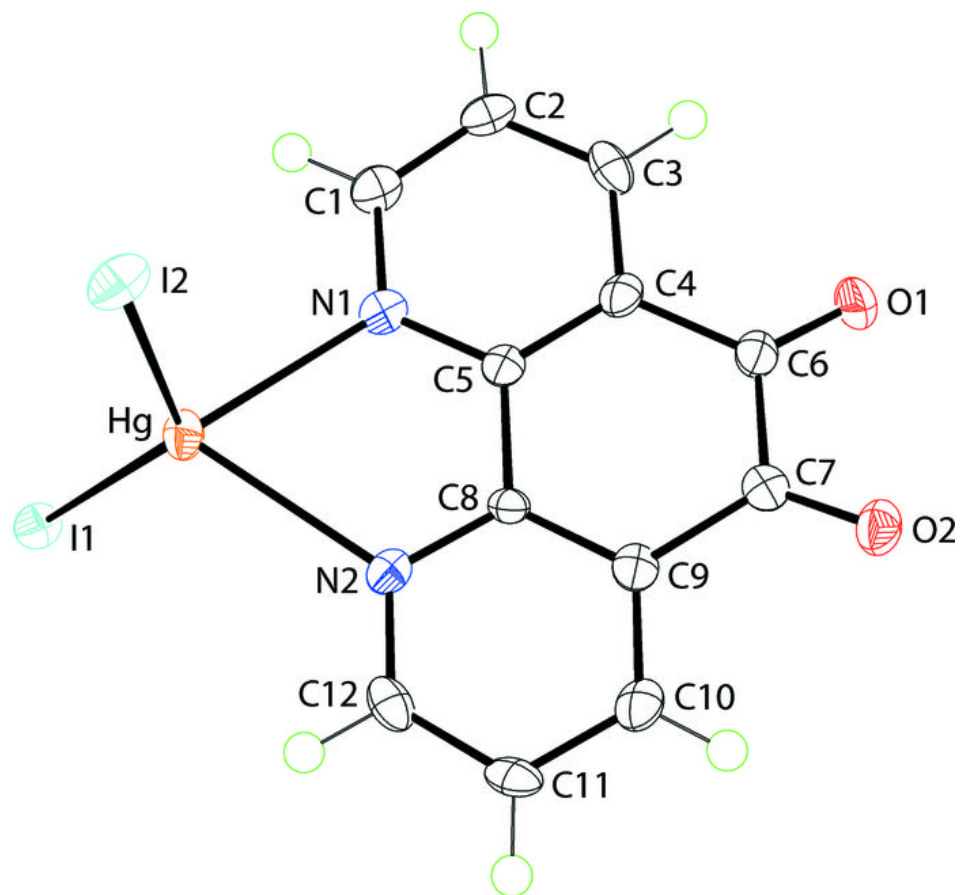


Fig. 2

