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cis-Diiodido(*N,N,N',N'*-tetramethylethylenediamine- κ^2 *N,N'*)palladium(II)

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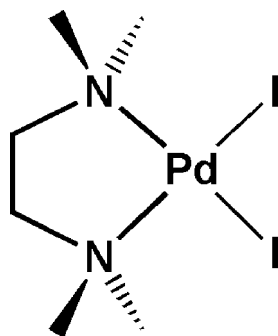
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.023; wR factor = 0.060; data-to-parameter ratio = 25.5.

In the title complex, *cis*-[PdI₂(C₆H₁₆N₂)], the Pd^{II} atom lies on a crystallographic twofold rotation axis and is four-coordinated by the two N atoms of a chelating *N,N,N',N'*-tetramethylethylenediamine ligand [Pd–N = 2.125 (3) Å] and two I atoms [Pd–I = 2.5833 (4) Å], displaying a distorted square-planar geometry (r.m.s. deviation = 0.005 Å), imposed by the small bite of the chelating ligand [N–Pd–N angle = 84.68 (18)°].

Related literature

For related diiodido complexes, see: Jones *et al.* (2007); Wursche *et al.* (1999); Dodd *et al.* (2006); Alsters *et al.* (1993); Bhattacharyya *et al.* (2009); Ha (2009, 2010). For molecular parameters in related dichlorido complexes, see: Boyle *et al.* (2004); Iball *et al.* (1975). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

[PdI ₂ (C ₆ H ₁₆ N ₂)]	$V = 1171.09 (10) \text{ \AA}^3$
$M_r = 476.41$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 7.9266 (4) \text{ \AA}$	$\mu = 6.81 \text{ mm}^{-1}$
$b = 14.6911 (7) \text{ \AA}$	$T = 100 \text{ K}$
$c = 10.5309 (5) \text{ \AA}$	$0.22 \times 0.15 \times 0.03 \text{ mm}$
$\beta = 107.262 (2)^\circ$	

Data collection

Bruker SMART APEX CCD diffractometer	6502 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	1351 independent reflections
$T_{\min} = 0.581$, $T_{\max} = 0.822$	1326 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	53 parameters
$wR(F^2) = 0.060$	H-atom parameters constrained
$S = 1.14$	$\Delta\rho_{\max} = 1.23 \text{ e \AA}^{-3}$
1351 reflections	$\Delta\rho_{\min} = -0.73 \text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LR2073).

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Antonio Abellán-López, María Teresa Chicote-Olalla and Delia Bautista-Cerezo

S1. Comment

A small amount of the title compound (**1**) formed when the complex [PdI(C₆H₄{NHC(Me)=C{C(O)Me}C(C(CO₂Me)C=CHCO₂Me)}-2(tmeda))] was heated in toluene with the aim to isomerize it. The insoluble complex **1** was separated by filtration and, single crystals, obtained by the liquid diffusion method using dichloromethane and diethyl ether, were used for structure determination. The pure compound **1** was prepared as stated in the Experimental section, and crystals grown using the same method and solvents as above were used to confirm the cell dimensions.

Only a few complexes of the type [PdI₂(N^N)] (N^N = chelating nitrogen donor ligand) have been characterized by their *X* ray crystal structures, namely those with N^N = 4,4'-di-*tert*-butyl-2,2'-bipyridine (Jones *et al.* 2007); 2-((4*S*)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)pyridine (Dodd *et al.* 2006); 1,2-bis(1-pyrrolidino)ethane (Wursche *et al.*, 1999); *N*-2-iodobenzyl-*N,N,N'*-trimethylethane-1,2-diamine (Alsters *et al.* 1993); 2,2'-bipyridine (Ha 2009); 1,4-dibenzyl-1,4-diazacyclododec-8-ene-6,10-diyne-N1,N4 (Bhattacharyya *et al.* 2009) and 1,10-phenanthroline (Ha 2010). This contrasts with the nearly five hundred crystal structures of dichloro homologous complexes (CCDC, November 2010).

The molecular structure of complex **1** is shown in Fig. 1. The asymmetric unit comprises a half of the molecule as the Pd atom lies on a crystallographic twofold axis. The coordinated ligand atoms and Pd(II) are coplanar within the limits of experimental errors: I1 and N1 are displaced from the least square plane defined by the five atoms by +0.0050 (15) and +0.0062 (19) Å, respectively. The bite of the chelating tmeda ligand displays a N(1)–C(1)–C(1 A)–N(1 A) torsion angle of -56.37(0.60)°. The planes of the two NMe₂ fragments subtend an angle of 12.10(0.08)°.

The Pd–N bonds in the diiodo complex **1** (2.125 (3) Å) are slightly longer than in the homologous dichloro complex [2.053 (3) and 2.073 (3) Å] reflecting the greater *trans* influence of the iodo ligands. The I(1)–Pd(1)–I(1 A) bond angle in **1** (87.907 (18)°) is narrower than the Cl(1)–Pd–Cl(2) one in [PdCl₂(tmeda)] (Boyle *et al.* 2004) (90.72 (5)°) although the opposite was expected in view of the smaller electronegativity and the bigger size of the iodo ligand compared to chloro. We attribute this fact to the steric hindrance caused on the iodo ligands by the NMe₂ groups in the chelating ligand, imposed by the short Pd–N bonds. This is supported by both, the larger Cl–Pd–Cl angle in [PdCl₂(en)] (Iball *et al.* 1975) (95.3 (3)°) than that in [PdCl₂(tmeda)] (90.72 (5)°) and on a search at the Cambridge Crystallographic Database (version 5.32, November 2010, updated November 2011) for [PdX₂(P^P)] (*X* = Cl, I, P^P = phosphorus donor chelating ligands) showing that the I–Pd–I angles are, as expected, wider than the Cl–Pd–Cl ones in homologous complexes, probably because, in this case, the longer Pd–P bond distances keep the phosphorus substituents away enough from the halogen ligands.

S2. Experimental

Synthesis. The pure compound (**1**) was prepared in 88% yield from [PdCl₂(tmeda)] and NaI (1:5, in acetone, 3 h at room temperature). The complex was extracted into dichloromethane and precipitated with diethyl ether. *M.p.* 194 °C

(decomposition). ^1H NMR (200 MHz, CDCl_3): d 2.68 (s, 2 H, CH_2), 2.96 (s, 6 H, Me). Analysis calcd for $\text{C}_6\text{H}_{16}\text{I}_2\text{N}_2\text{Pd}$: C, 15.13; H, 3.39; N, 5.88. Found: C, 15.62; H, 3.43; N, 6.03.

S3. Refinement

Methyl H atoms were identified in difference syntheses, idealized and refined using rigid groups allowed to rotate but not tip, with C—H 0.98 Å, H—C—H 109.5°. Other H atoms were introduced at the calculated positions and refined using a riding model, with methylene C—H 0.99 Å. The $U_{\text{iso}}(\text{H})$ values were set equal to $mU_{\text{eq}}(\text{C})$ of the parent carbons, with $m = 1.5$ for methyls and 1.2 for all other H.

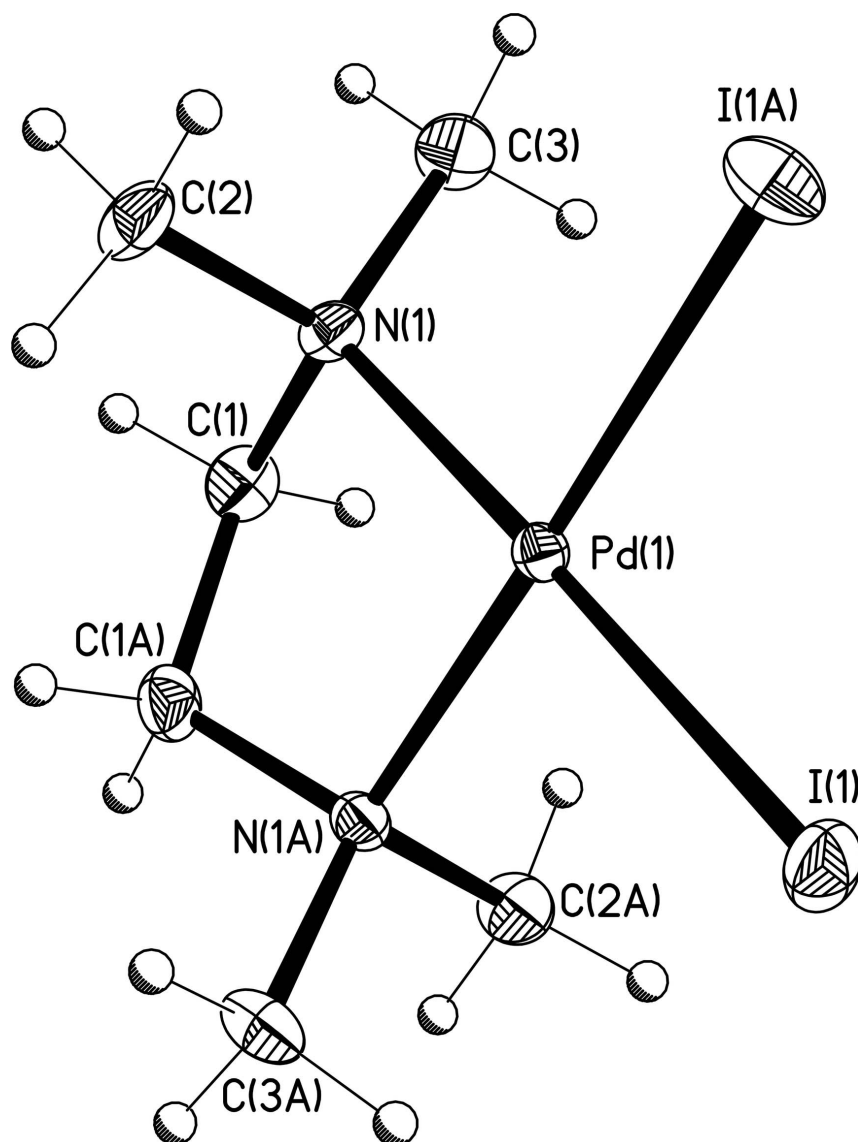


Figure 1

The molecular structure of the title compound. Ellipsoids represent 50% probability levels.

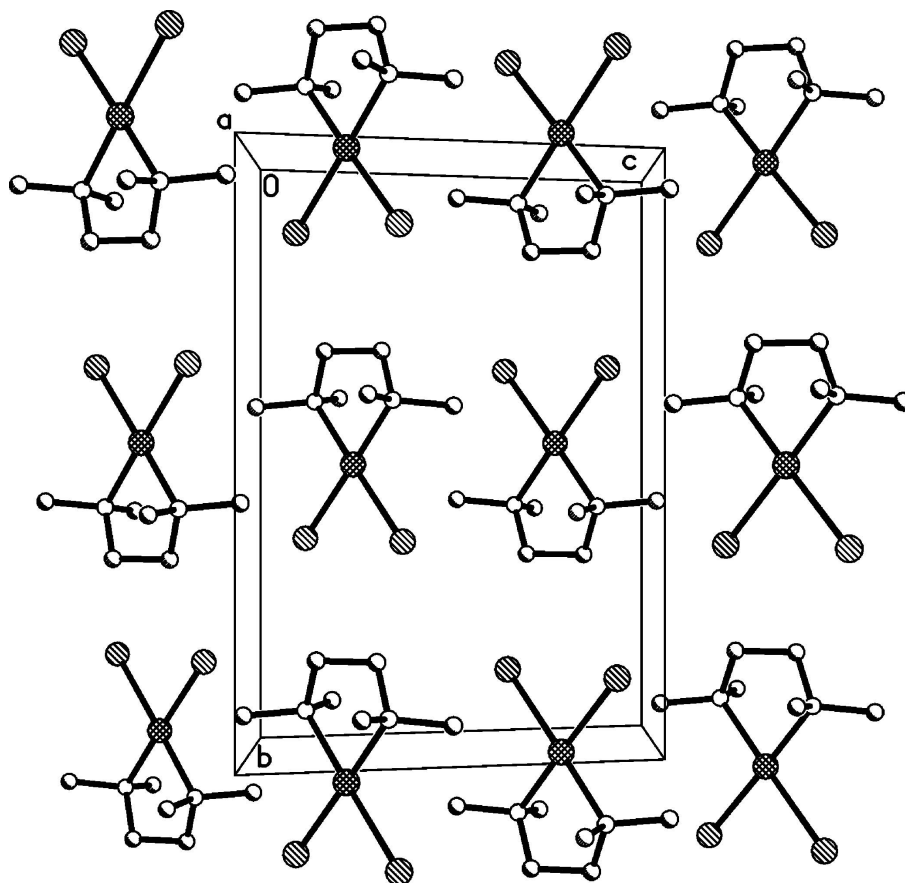


Figure 2

Packing diagram of the title compound view down *b* axis Hydrogen atoms are omitted.

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Crystal data

[PdI₂(C₆H₁₆N₂)]

M_r = 476.41

Monoclinic, *C2/c*

Hall symbol: -C 2yc

a = 7.9266 (4) Å

b = 14.6911 (7) Å

c = 10.5309 (5) Å

β = 107.262 (2)°

V = 1171.09 (10) Å³

Z = 4

F(000) = 872

D_x = 2.702 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 4971 reflections

θ = 2.8–28.1°

μ = 6.81 mm⁻¹

T = 100 K

Needle, red

0.22 × 0.15 × 0.03 mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.26 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(*SADABS*; Bruker, 2003)

T_{min} = 0.581, *T_{max}* = 0.822

6502 measured reflections

1351 independent reflections

1326 reflections with *I* > 2 σ (*I*)

R_{int} = 0.020

$\theta_{\max} = 28.1^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -10 \rightarrow 10$

$k = -18 \rightarrow 18$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 1.14$
 1351 reflections
 53 parameters
 0 restraints
 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
 $w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 10.9315P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.73 \text{ e } \text{\AA}^{-3}$

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.

Least-squares planes (x, y, z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$-0.3294 (0.0368) x + 14.6093 (0.0042) y + 1.1036 (0.0293) z = 6.0620 (0.0112)$

* 0.0000 (0.0000) N1 * 0.0000 (0.0000) C2 * 0.0000 (0.0000) C3

Rms deviation of fitted atoms = 0.0000

$0.3294 (0.0369) x + 14.6093 (0.0042) y - 1.1036 (0.0293) z = 5.8396 (0.0312)$

Angle to previous plane (with approximate e.s.d.) = 12.10 (0.08)

* 0.0000 (0.0000) N1_\$1 * 0.0000 (0.0000) C2_\$1 * 0.0000 (0.0000) C3_\$1

Rms deviation of fitted atoms = 0.0000

$5.5219 (0.0048) x - 0.0000 (0.0000) y - 9.3919 (0.0040) z = 0.4130 (0.0034)$

Angle to previous plane (with approximate e.s.d.) = 84.35 (0.22)

* 0.0000 (0.0000) Pd1 * 0.0062 (0.0019) N1 * 0.0050 (0.0015) I1 * -0.0062 (0.0019) N1_\$1 * -0.0050 (0.0015) I1_\$1

Rms deviation of fitted atoms = 0.0050

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.5000	0.51798 (3)	0.2500	0.01073 (10)
I1	0.71154 (4)	0.644568 (18)	0.37384 (3)	0.02349 (10)
N1	0.3317 (4)	0.4111 (2)	0.1504 (3)	0.0136 (6)
C1	0.4427 (5)	0.3275 (3)	0.1794 (4)	0.0191 (8)
H1A	0.5175	0.3246	0.1192	0.023*
H1B	0.3656	0.2731	0.1632	0.023*
C2	0.1807 (5)	0.4035 (3)	0.2057 (4)	0.0209 (8)
H2A	0.1129	0.4603	0.1896	0.031*
H2B	0.2251	0.3922	0.3016	0.031*
H2C	0.1045	0.3529	0.1625	0.031*
C3	0.2605 (6)	0.4205 (3)	0.0038 (4)	0.0216 (8)
H3A	0.1947	0.3654	-0.0336	0.032*
H3B	0.3584	0.4291	-0.0341	0.032*

H3C	0.1816	0.4733	-0.0176	0.032*
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Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01163 (18)	0.01133 (18)	0.00958 (18)	0.000	0.00366 (13)	0.000
I1	0.02803 (17)	0.02164 (16)	0.01984 (16)	-0.01018 (10)	0.00561 (11)	-0.00239 (10)
N1	0.0124 (14)	0.0169 (15)	0.0119 (14)	-0.0017 (12)	0.0040 (11)	-0.0028 (12)
C1	0.0214 (19)	0.0140 (17)	0.022 (2)	-0.0004 (15)	0.0073 (16)	-0.0038 (15)
C2	0.0145 (18)	0.029 (2)	0.022 (2)	-0.0052 (15)	0.0090 (15)	-0.0034 (17)
C3	0.024 (2)	0.025 (2)	0.0134 (18)	-0.0046 (16)	0.0033 (15)	-0.0043 (16)

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

Pd1—N1	2.125 (3)	C1—H1A	0.9900
Pd1—N1 ⁱ	2.125 (3)	C1—H1B	0.9900
Pd1—I1	2.5833 (4)	C2—H2A	0.9800
Pd1—I1 ⁱ	2.5833 (4)	C2—H2B	0.9800
N1—C2	1.483 (5)	C2—H2C	0.9800
N1—C3	1.484 (5)	C3—H3A	0.9800
N1—C1	1.488 (5)	C3—H3B	0.9800
C1—C1 ⁱ	1.494 (8)	C3—H3C	0.9800
N1—Pd1—N1 ⁱ	84.68 (18)	N1—C1—H1B	109.5
N1—Pd1—I1	178.36 (9)	C1 ⁱ —C1—H1B	109.5
N1 ⁱ —Pd1—I1	93.71 (9)	H1A—C1—H1B	108.1
N1—Pd1—I1 ⁱ	93.71 (9)	N1—C2—H2A	109.5
N1 ⁱ —Pd1—I1 ⁱ	178.36 (9)	N1—C2—H2B	109.5
I1—Pd1—I1 ⁱ	87.906 (18)	H2A—C2—H2B	109.5
C2—N1—C3	108.3 (3)	N1—C2—H2C	109.5
C2—N1—C1	110.7 (3)	H2A—C2—H2C	109.5
C3—N1—C1	108.1 (3)	H2B—C2—H2C	109.5
C2—N1—Pd1	108.9 (2)	N1—C3—H3A	109.5
C3—N1—Pd1	115.7 (2)	N1—C3—H3B	109.5
C1—N1—Pd1	105.2 (2)	H3A—C3—H3B	109.5
N1—C1—C1 ⁱ	110.6 (3)	N1—C3—H3C	109.5
N1—C1—H1A	109.5	H3A—C3—H3C	109.5
C1 ⁱ —C1—H1A	109.5	H3B—C3—H3C	109.5
N1 ⁱ —Pd1—N1—C2	104.9 (3)	I1 ⁱ —Pd1—N1—C1	166.5 (2)
I1 ⁱ —Pd1—N1—C2	-74.8 (2)	C2—N1—C1—C1 ⁱ	-77.3 (4)
N1 ⁱ —Pd1—N1—C3	-133.0 (3)	C3—N1—C1—C1 ⁱ	164.2 (4)
I1 ⁱ —Pd1—N1—C3	47.3 (3)	Pd1—N1—C1—C1 ⁱ	40.1 (4)
N1 ⁱ —Pd1—N1—C1	-13.83 (18)	N1—C1—C1 ⁱ —N1 ⁱ	-56.4 (6)

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