

# Conformational change induced by hydration: *trans*-dichlorobis[(1*R*,2*R*,3*R*,5*S*)-(–)-isopinocampheylamine]palladium(II) and *trans*-dichlorobis[(1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheylamine]-palladium(II) hemihydrate

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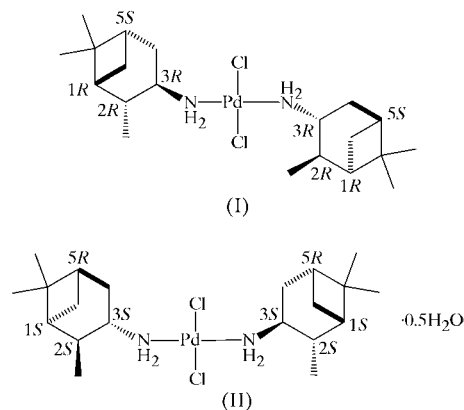
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The title compounds, *trans*-dichlorobis[(1*R*,2*R*,3*R*,5*S*)-(–)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine]palladium(II), [PdCl<sub>2</sub>(C<sub>10</sub>H<sub>19</sub>N)<sub>2</sub>], and *trans*-dichlorobis[(1*S*,2*S*,3*S*,5*R*)-(+)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine]palladium(II) hemihydrate, [PdCl<sub>2</sub>(C<sub>10</sub>H<sub>19</sub>N)<sub>2</sub>]·0.5H<sub>2</sub>O, present different arrangements of the amine ligands coordinated to Pd<sup>II</sup>, *viz.* antiperiplanar in the former case and (–)anticlinal in the latter. The hemihydrate is an inclusion compound, with a Pd coordination complex and disordered water molecules residing on crystallographic twofold axes. The crystal structure for the hemihydrate includes a short Pd···Pd separation of 3.4133 (13) Å.

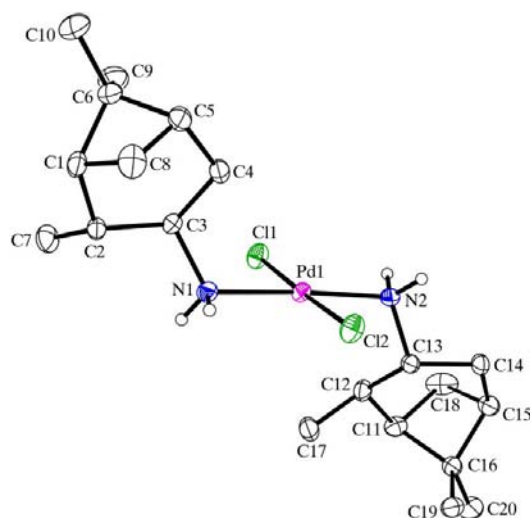
## Comment

The use and applications of chiral complexes of transition metals have experienced an exponential growth in recent years (*e.g.* Maire *et al.*, 2005). The combined use of organometallic and coordination chemistry has allowed the development of a number of new and powerful synthetic methods for important classes of compounds in general and for optically active substances in particular (*e.g.* Gamez *et al.*, 1995). Along this line, N-containing ligands are increasingly used, since they present many advantages (accessibility, easy recovery, *etc.*) over their P analogs (Fache *et al.*, 2000). As such, chiral amines have highlighted the use of such N-donors and are nowadays widely employed. Our interest has recently been focused on new chiral Pd complexes derived from optically pure  $\alpha$ -diimines (Martínez-García *et al.*, 2000; Peláez *et*

*al.*, 2004) and, in this regard, in the synthesis of new Pd<sup>II</sup> complexes with optically pure  $\alpha$ -diimines derived from pyruvaldehyde and a variety of chiral amines (Vázquez-García *et al.*, 2000; Vázquez-García, 2002). However, a limitation observed during this work was a tendency of some  $\alpha$ -diimines to decompose in solution, the only crystallizable products being the coordination compounds including chiral amines as ligands instead of the expected  $\alpha$ -diimines. We have now characterized two complexes of general formula [PdCl<sub>2</sub>L<sub>2</sub>] $\cdot$ *n*H<sub>2</sub>O, where ligand *L* is a commercially available diastereoisomer of isopinocampheylamine; for compound (I), *L* is (–)-isopinocampheylamine and *n* = 0, while for (II), *L* is (+)-isopinocampheylamine and *n* = 0.5.



Complex (I) is based on a classical *trans*-[PdN<sub>2</sub>Cl<sub>2</sub>] plane rectangular coordination geometry (Fig. 1 and Table 1). The molecule lies on a general position and the amine ligands, (1*R*,2*R*,3*R*,5*S*)-(–)-isopinocampheylamine, adopt an antiperiplanar arrangement, as described by the C3–N1–N2–C13 torsion angle [–167.2 (2)°]. The complex exhibits approximate C<sub>2</sub> point symmetry, with the symmetry axis within the coordination plane (Cl–Pd–Cl line), minimizing steric hindrance and giving a relatively well packed crystal

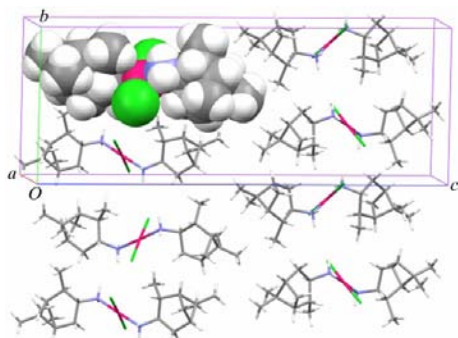


**Figure 1**  
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are shown at the 25% probability level and H atoms bonded to C atoms have been omitted for clarity.

structure in space group  $P2_12_12_1$  (Fig. 2), as reflected by the packing index of 0.666 (Spek, 2003). Metallic centers are well separated in the cell; the shortest Pd $\cdots$ Pd separations are 6.6037 (5) [Pd1 $\cdots$ Pd1(1 + x, y, z)] and 6.7037 (5) Å [Pd1 $\cdots$ Pd1(1 - x, y -  $\frac{1}{2}$ ,  $\frac{1}{2}$  - z)]. No voids are available for solvent molecules in the structure of (I).

Complex (II), based on (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheylamine coordinated to the PdCl<sub>2</sub> central core, presents a different molecular structure (Fig. 3 and Table 2). The metal center resides on a twofold axis and the amine ligands are arranged in a (-)antichiral configuration, as described by the C3-N1-N1<sup>i</sup>-C3<sup>i</sup> torsion angle [-106.0 (9)°; symmetry code: (i) 1 - x, y, 1 - z]. By comparison with (I), one amine ligand is thus rotated around the  $\sigma$  bond Pd1-N1, giving a boat-like conformation for the whole molecule. The [PdCl<sub>2</sub>L<sub>2</sub>] complex in (II) actually belongs to the C<sub>2</sub> point symmetry group, with the molecular axis normal to the [PdN<sub>2</sub>Cl<sub>2</sub>] coordination plane and coincident with the [010] crystallographic twofold axis.

The main difference between (I) and (II) is in the presence of disordered water molecules, lying on a twofold rotation axis along [100], in (II). These water molecules are located in the cavities allowed by the boat geometry of the complex (Fig. 4). Indeed, omitting these water molecules would result in a very low packing index for (II), *viz.* 0.592. Moreover, it should be noted that the reported refinement for (II) probably underestimates water content, as suggested by the SQUEEZE option available in PLATON (Spek, 2003); starting from a water-free model, this option recovered 116 electrons belonging to diffusely diffracting solvent molecules, equally distributed in two voids located close to (0, 0, 0) and (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ), each void having a volume of 156 Å<sup>3</sup>. The actual estimation of the water content was based on the refinement of the site-occupation factors, which converged to 0.125 for both water molecules, and which were fixed in the last least-squares cycles. The *ca* sixfold difference between the refined and SQUEEZE calculated amounts of water (0.5 *versus* 2.9 water molecules per complex) may appear unrealistic. However, it is worth noting that available voids, estimated by SQUEEZE to be 78 Å<sup>3</sup> per asymmetric unit, can accommodate no more than two water molecules, assuming a steric volume of 40 Å<sup>3</sup> for a



**Figure 2**

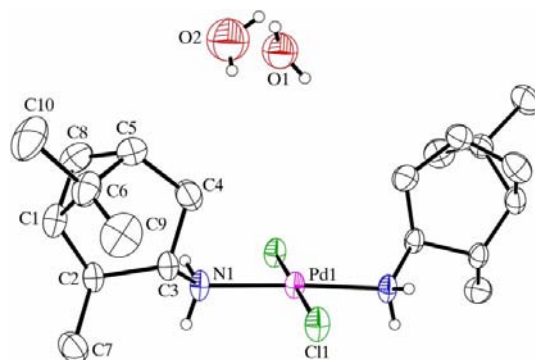
Part of the crystal structure of (I), viewed approximately down the [100] axis. Eight symmetry-related molecules are included.

water molecule. These observations are consistent with the presence of strongly disordered water molecules in the structure of (II), to an extent that cannot be estimated accurately on the basis of the currently available X-ray data. However, (II) may be safely formulated as [PdCl<sub>2</sub>L<sub>2</sub>] $\cdot$ *n*H<sub>2</sub>O, with 0.5 < *n* < 2.0. Thermal studies or related techniques would help for an accurate determination of *n*.

As expected, inclusion of water in (II) results in lower density for the crystal compared with (I), *viz.* 1.295 and 1.417 Mg m<sup>-3</sup>, respectively. Weak hydrogen bonds involving Cl<sup>-</sup> ions and water molecules are observed in the crystal structure (Table 3). Another consequence of the conformational change observed in (II) is the occurrence of a short metal-metal separation [Pd1 $\cdots$ Pd1<sup>iii</sup> = 3.4133 (13) Å; symmetry code: (iii) -x + 1, -y + 2, z] close to the sum of the van der Waals radii (3.26 Å; Bondi, 1964).

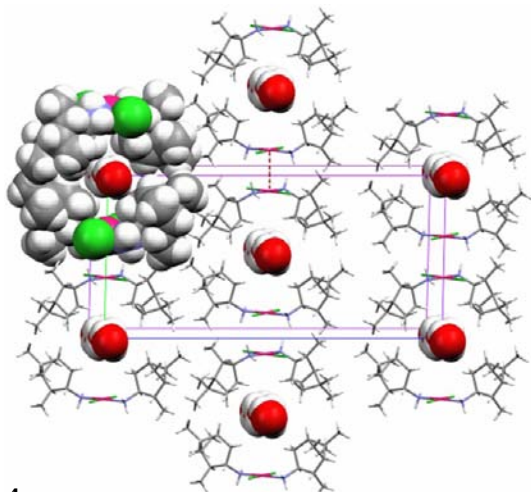
It is worth noting that (I) crystallizes in the most common space group for chiral molecules,  $P2_12_12_1$ , while (II) crystallizes in  $I222$ , a space group poorly represented in the Cambridge Structural Database (CSD; Version 5.26, update of May 2005; Allen, 2002), with 91 entries to date. An examination of these hits shows that 45% are flagged as disordered structures, a frequency more than twice that observed for the entire database (18%). Moreover, 33% of the structures reported in space group  $I222$  are solvates, including hydrates. These observations suggest that symmetry  $I222$  fits crystal structures featuring disorder, hindered conformations or solvation, as in the case of (II).

Defining the complex [PdCl<sub>2</sub>L<sub>2</sub>] as a templating host molecule, (II) may be considered as an inclusion compound with water as guest (Fig. 4). On the other hand, we assume that two crystals of [PdCl<sub>2</sub>L<sub>2</sub>] prepared with both enantiomers of *L* should crystallize as isostructural species (*e.g.* Leung *et al.*, 1999), as two enantiomeric compounds do, unless a true polymorphism occurs. Therefore, regardless of the handedness of the chiral amines *L* used in the present work, the variety of conformations observed for complex [PdCl<sub>2</sub>L<sub>2</sub>] probably depends on the presence or absence of water molecules in the crystal structure.



**Figure 3**

The structure of (II), showing the atom-numbering scheme for the asymmetric unit. Displacement ellipsoids for non-H atoms are shown at the 25% probability level and H atoms bonded to C atoms have been omitted for clarity.



**Figure 4**  
Part of the crystal structure of (II), viewed approximately down the [100] axis. 14 symmetry-related coordination complexes and 28 disordered water molecules are represented in order to emphasize the host character of the coordination complex. The short Pd...Pd contact is indicated by a dashed line.

### Experimental

A solution of bis[(1*R*,2*R*,3*R*,5*S*)-isopinocampheyl]-1,2-propanediimine (0.120 g, 0.35 mmol) in benzene (20 ml) was treated with dichloro(1,5-cyclooctadiene)palladium(II) (0.100 g, 0.35 mmol) with stirring at 298 K for 10 min. A yellow precipitate was collected and yellow crystals of (I) were grown from the filtered solution by slow evaporation (9% yield). The same procedure was repeated with bis[(1*S*,2*S*,3*S*,5*R*)-isopinocampheyl]-1,2-propandiimine and afforded (II), in a low yield of *ca* 5%, by slow evaporation in a non-controlled atmosphere.

### Compound (I)

#### Crystal data

[PdCl<sub>2</sub>(C<sub>10</sub>H<sub>19</sub>N)<sub>2</sub>]

*M<sub>r</sub>* = 483.82

Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>

*a* = 6.6037 (5) Å

*b* = 11.3935 (10) Å

*c* = 30.143 (2) Å

*V* = 2267.9 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.417 Mg m<sup>-3</sup>

Mo *K*α radiation

Cell parameters from 76

reflections

*θ* = 4.8–13.9°

*μ* = 1.06 mm<sup>-1</sup>

*T* = 296 (2) K

Plate, yellow

0.60 × 0.42 × 0.12 mm

#### Data collection

Bruker *P4* diffractometer

*ω* scans

Absorption correction: *ψ* scan

(*XSCANS*; Siemens, 1996)

*T<sub>min</sub>* = 0.703, *T<sub>max</sub>* = 0.879

7901 measured reflections

6612 independent reflections

5860 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.020

*θ<sub>max</sub>* = 30.0°

*h* = -9 → 9

*k* = -16 → 1

*l* = -1 → 42

3 standard reflections

every 97 reflections

intensity decay: 1.5%

#### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036

*wR*(*F*<sup>2</sup>) = 0.087

*S* = 1.02

6612 reflections

232 parameters

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0431*P*)<sup>2</sup>

+ 0.6075*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 1.08 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.80 e Å<sup>-3</sup>

Absolute structure: Flack (1983),

2839 Friedel pairs

Flack parameter: -0.03 (3)

**Table 1**

Selected geometric parameters (Å, °) for (I).

Pd1—N2	2.044 (2)	Pd1—Cl2	2.3201 (8)
Pd1—N1	2.052 (3)	N1—C3	1.502 (4)
Pd1—Cl1	2.3177 (8)	N2—C13	1.499 (4)
N2—Pd1—N1	177.28 (10)	N1—Pd1—Cl2	90.00 (8)
N2—Pd1—Cl1	90.09 (7)	Cl1—Pd1—Cl2	177.86 (3)
N1—Pd1—Cl1	90.51 (8)	C3—N1—Pd1	116.39 (19)
N2—Pd1—Cl2	89.50 (8)	C13—N2—Pd1	114.28 (17)

### Compound (II)

#### Crystal data

[PdCl<sub>2</sub>(C<sub>10</sub>H<sub>19</sub>N)<sub>2</sub>].0.5H<sub>2</sub>O

*M<sub>r</sub>* = 492.83

Orthorhombic, *I*222

*a* = 6.6873 (8) Å

*b* = 13.427 (2) Å

*c* = 28.159 (4) Å

*V* = 2528.4 (6) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.295 Mg m<sup>-3</sup>

Mo *K*α radiation

Cell parameters from 68

reflections

*θ* = 4.2–12.5°

*μ* = 0.95 mm<sup>-1</sup>

*T* = 296 (2) K

Needle, yellow

0.60 × 0.18 × 0.18 mm

#### Data collection

Bruker *P4* diffractometer

*ω* scans

Absorption correction: *ψ* scan

(*XSCANS*; Siemens, 1996)

*T<sub>min</sub>* = 0.735, *T<sub>max</sub>* = 0.842

2145 measured reflections

2029 independent reflections

1750 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.029

*θ<sub>max</sub>* = 27.5°

*h* = -8 → 1

*k* = -1 → 17

*l* = -1 → 36

3 standard reflections

every 97 reflections

intensity decay: 1%

#### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.040

*wR*(*F*<sup>2</sup>) = 0.114

*S* = 1.11

2029 reflections

121 parameters

H-atom parameters constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0664*P*)<sup>2</sup>

+ 1.4484*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.88 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.67 e Å<sup>-3</sup>

Absolute structure: Flack (1983),

349 Friedel pairs

Flack parameter: 0.00 (7)

**Table 2**

Selected geometric parameters (Å, °) for (II).

Pd1—N1	2.059 (4)	N1—C3	1.514 (7)
Pd1—Cl1	2.3041 (12)		
N1 <sup>i</sup> —Pd1—N1	177.5 (5)	Cl1—Pd1—Cl1 <sup>i</sup>	179.04 (16)
N1 <sup>i</sup> —Pd1—Cl1	86.66 (12)	C3—N1—Pd1	119.7 (4)
N1—Pd1—Cl1	93.32 (13)		

Symmetry code: (i) -*x* + 1, *y*, -*z* + 1.

**Table 3**

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...Cl1 <sup>ii</sup>	0.90	2.74	3.514 (5)	144
N1—H1B...Cl1 <sup>iii</sup>	0.90	2.54	3.382 (7)	157

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

In the case of (I), the highest residual peak found in the final difference map is located in the vicinity of atom Cl2. Attempts to

refine this residual as a water molecule with a partial occupation factor were unsuccessful. In the case of (II), site-occupation factors for the two water molecules were fixed at 0.125. Corresponding O atoms were refined isotropically, otherwise they converged to non-positive definite displacement ellipsoids. Water H atoms were found in difference maps and their positions were refined with a restrained geometry [O—H = 0.85 (1) Å]. In the final cycles, water H atoms were constrained to ride on their carrier O atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{carrier O atom})$ . For both compounds, H atoms bonded to C and N atoms were placed in idealized positions and refined using a riding-model approximation, with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$ : methine C—H = 0.98 Å and  $x = 1.2$ ; methylene C—H = 0.97 Å and  $x = 1.2$ ; methyl C—H = 0.96 Å and  $x = 1.5$ ; amine N—H = 0.90 Å and  $x = 1.5$ . The methyl groups were allowed to rotate about their C—C bonds in order to obtain the correct torsion angles for these groups.

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics and publication material: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ1007). Services for accessing these data are described at the back of the journal.

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