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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(C-C)$ = 0.005 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 21.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

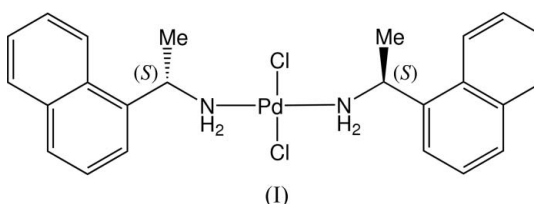
***trans*-Dichlorobis[(*S*)-(-)-1-(1-naphthyl)-ethylamine]palladium(II)**

The title complex, $[PdCl_2(C_{12}H_{13}N_2)_2]$, has two amine ligands coordinated in such a way that the naphthyl and methyl groups are located in the same hemisphere with respect to the $[PdN_2Cl_2]$ coordination plane. This configuration allows for the formation of dimers in the solid state with a metal–metal separation of 3.2499 (4) 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). In this connection, N-containing ligands are generally preferred to their P analogues, since they present a number of advantages such as accessibility and easy recovery. In relation to this field, our interest has recently focused on new chiral Pd^{II} complexes derived from optically pure α -diimines (Martínez-García *et al.*, 2000; Peláez *et al.*, 2004) and, in particular, on the synthesis of new Pd^{II} complexes with optically pure α -diimines derived from pyruvaldehyde and a variety of chiral amines (Vázquez-García *et al.*, 2000). Almost invariably, these syntheses afford by-products, arising from ligand decomposition or rearrangement. The title complex, (I), is one such by-product that we have characterized by X-ray analysis.

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The asymmetric unit (Fig. 1) contains one complex in a general position, with the central Pd^{II} having the expected square planar geometry (Table 1). The amine ligands are *trans* coordinated to a PdCl₂ core, and arranged in a *gauche*

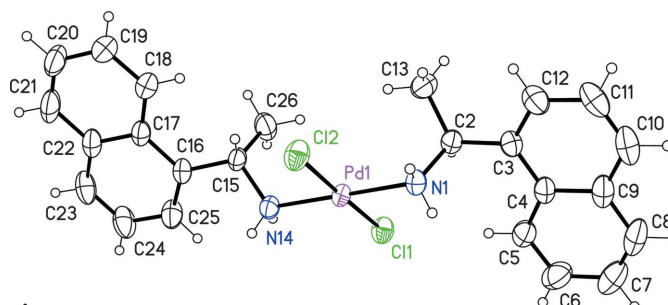


Figure 1
The structure of (I), with displacement ellipsoids at the 50% probability level for non-H atoms.

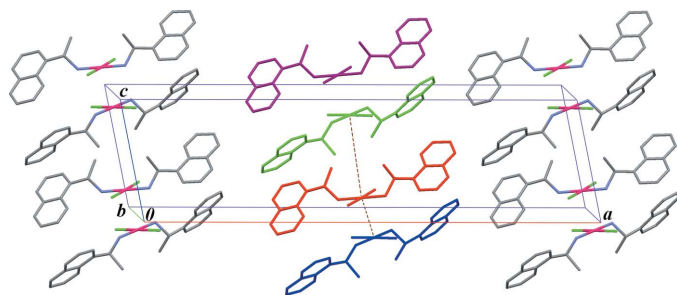


Figure 2

Part of the crystal structure of (I) viewed down the *b* axis, showing Pd...Pd short and long interactions in the central stack (dashed lines). Symmetry codes for this stack: red molecule: asymmetric unit; blue molecule: $1 - x, y, -z$; green molecule: $1 - x, y, 1 - z$; purple molecule: $x, y, 1 + z$. H atoms have been omitted.

conformation, as described by the torsion angle C2–N1–N14–C15 = -57.1 (2)°. The naphthyl and methyl groups are thus both located in the same hemisphere with respect to the coordination plane [PdN₂Cl₂], a situation rarely observed for *trans*-[Pd(amine)₂Cl₂] complexes, which usually crystallize with the metal centre on a special position. However, a configuration similar to that observed in (I) was previously reported in closely related chiral complexes with (*R*)-(+)-bornylamine (Abu-Surrah *et al.*, 2002), (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheylamine (Vázquez *et al.*, 2005) and an L-alanine derivative (Steiner *et al.*, 1988) as the amine ligands.

In spite of the *C*₁ symmetry, molecules of (I) are well packed in the solid state, without inclusion of solvent. The conformation described above for the amine ligands allows for the formation of a short Pd1...Pd1ⁱ contact of 3.2499 (4) Å [symmetry code: (i) $1 - x, y, -z$], virtually equal to the sum of the van der Waals radii, 3.26 Å (Bondi, 1964). The dimers are separated by a long Pd1...Pd1^{iv} distance, 6.4931 (5) Å [symmetry code: (iv) $1 - x, y, 1 - z$]. The short–long separations alternate, forming a stack along the [001] axis (Fig. 2). No significant π – π interactions are observed between symmetry-related naphthyl rings. For instance, the dihedral angle between ring systems C3–C12 and C16–C25 belonging to two molecules within a dimer is 59.02 (6)°. The shortest C–H... π contact within this dimer is C6–H6A...Cg1ⁱ, with a separation H6A...Cg1ⁱ of 2.78 Å (Cg1 is the centroid of ring C16/C17/C22–C25). Finally, weak N–H...Cl hydrogen bonds involving all Cl and amine H atoms (Table 2), link the molecules into chains along the short cell axis [010].

Experimental

A solution of *N,N'*-bis[(*S*)-(-)-1-(1-ethylnaphthyl)]propanediimine (0.13 g, 0.35 mmol) in benzene (20 ml) was treated with (COD)PdCl₂ (0.1 g, 0.35 mmol) with stirring at 298 K for 2 h. The yellow precipitate was filtered and the resulting solution was slowly evaporated. After a few days, orange crystals of (I) were collected. Yield 15%; m.p. 501–503 K. Analysis: $[\alpha]_{\text{D}}^{25} = -27.5$ (c 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃, p.p.m.): δ 1.50 (*d*, 3H, Me), 1.60 (broad s, 2H, NH₂), 4.88 (*c*, 1H, methine), 7.40–8.10 (*m*, 7H, naphthyl); ¹³C NMR (100.6 MHz, CDCl₃, p.p.m.): δ 24.27 (1C, Me), 46.27 (1C, methine), 120.98–142.92 (10C, naphthyl).

Crystal data

[PdCl₂(C₁₂H₁₃N₂)₂]
M_r = 519.77
 Monoclinic, *C*₂
a = 35.310 (3) Å
b = 6.7996 (7) Å
c = 9.7193 (7) Å
 β = 102.893 (4)°
V = 2274.7 (3) Å³
Z = 4

D_x = 1.518 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 94 reflections
 θ = 4.7–13.6°
 μ = 1.06 mm⁻¹
T = 296 (1) K
 Plate, orange
 0.50 × 0.20 × 0.08 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (*XSCANS*; Siemens, 1996)
 $T_{\text{min}} = 0.566$, $T_{\text{max}} = 0.920$
 6025 measured reflections
 5769 independent reflections
 5658 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.021
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -49 \rightarrow 1$
 $k = -9 \rightarrow 6$
 $l = -13 \rightarrow 13$
 2 standard reflections
 every 48 reflections
 intensity decay: 1%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.08$
 5769 reflections
 274 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.3281P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -1.02 \text{ e } \text{Å}^{-3}$
 Absolute structure: Flack (1983),
 2217 Friedel pairs
 Flack parameter: -0.01 (2)

Table 1

Selected geometric parameters (Å, °).

Pd1–N1	2.061 (2)	Pd1–Cl1	2.3099 (8)
Pd1–N14	2.071 (2)	Pd1...Pd1 ⁱ	3.2499 (4)
Pd1–Cl2	2.2947 (8)		
N1–Pd1–N14	179.70 (14)	N1–Pd1–Cl1	90.78 (9)
N1–Pd1–Cl2	88.64 (7)	N14–Pd1–Cl1	89.50 (8)
N14–Pd1–Cl2	91.08 (9)	Cl2–Pd1–Cl1	178.81 (4)

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

Table 2

Hydrogen-bond geometry (Å, °).

<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 ⁱⁱ	0.87 (2)	2.89 (3)	3.700 (3)	156 (4)
N1–H1B...Cl2 ⁱ	0.83 (2)	2.83 (3)	3.339 (2)	121 (3)
N14–H14A...Cl1 ⁱ	0.85 (2)	2.60 (3)	3.330 (2)	145 (3)
N14–H14B...Cl2 ⁱⁱⁱ	0.86 (2)	2.86 (2)	3.702 (3)	168 (4)

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

H atoms bonded to C atoms were placed in idealized positions and refined with a riding model approximation [C–H = 0.93 Å for aromatic CH, 0.96 Å for methyl CH₃ and 0.98 Å for methine CH; *U*_{iso}(H) = 1.2*U*_{eq}(carrier C atom) for aromatic and methine CH; *U*_{iso}(H) = 1.5*U*_{eq}(carrier C atom) for methyl CH₃]. H atoms bonded to N atoms were found in a difference map and their positions refined with an N–H distance restrained to 0.85 (2) Å and *U*_{iso} = 1.5 *U*_{eq}(carrier N atom). The deepest hole is located 0.59 Å from atom Pd1.

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: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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