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Tetrachloridobis{(*E*)-1-[(*E*)-(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylideneaminooxy]propylideneamine}platinum(IV)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.011 Å
R factor = 0.029
wR factor = 0.088
Data-to-parameter ratio = 20.6

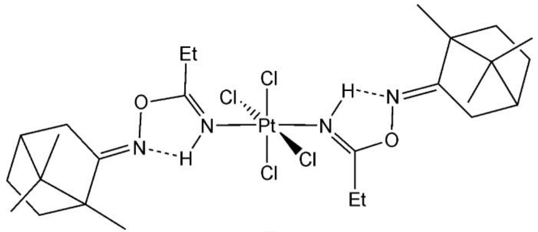
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The metal coordination polyhedron of the title complex, [$PtCl_4(C_{13}H_{22}N_2O)_2$], is a slightly distorted PtN_2Cl_4 octahedron. The *E* configurations of the *trans* imino ligands are stabilized by intramolecular N—H⋯N hydrogen bonds.

Comment

Metal-assisted interactions between coordinated organonitriles and different nucleophilic reagents have great fundamental and synthetic potential (Kukushkin & Pombeiro, 2002). When oximes are used in these reactions, upon addition of the OH group of the oxime to the C≡N group, a species with a new C—O{N=} bond is formed, regardless of the nature of the oxime (Pombeiro & Kukushkin, 2004). Moreover, it has been found that in all the resulting [$PtCl_4${NH=C(*R*)ON=CR_2}$_2$] imino complexes characterized by X-ray crystallography, the imino ligands are in an *E* configuration, stabilized by intramolecular N—H⋯N bonding.

To clarify the role of hydrogen bonding in the selective formation of just one isomer, we report here the structure of one more representative of this class of compounds, the title complex *trans*-[$PtCl_4${NH=C(Et)ON=C(C_9H_{16})}$_2$], (I), formed in the reaction between *trans*-[$PtCl_4(EtCN)_2$] (Luzyanin *et al.*, 2002) and (2*E*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one oxime, (C_9H_{16})C=NOH, in almost quantitative (92%) yield.



(I)

Complex (I) crystallizes in the non-centrosymmetric space group $P2_1$ because of the chirality present in the camphor group of the oxime (atoms C5, C9, C18 and C22 have *R* configurations). The metal coordination polyhedron of the complex (Fig. 1) is a slightly distorted PtN_2Cl_4 octahedron. The Pt—N and Pt—Cl bond distances (Table 1) are normal (Orpen *et al.*, 1989) and their values are in a good agreement with those previously found in the similar anionic (camphoroxime)Pt^{IV} complex [Ph_3PCH_2Ph][$PtCl_5${NH=C(Et)ON=C(C_9H_{16})}] [Pt—Cl = 2.293 (6)–2.322 (7) Å; Pt—N = 1.943 (17) Å; Kuznetsov *et al.*, 2000]. The C=N bond lengths [1.262 (8)–1.276 (10) Å] in (I) correspond to the mean value of such C=N double bonds (1.279 Å; Allen *et al.*, 1987).

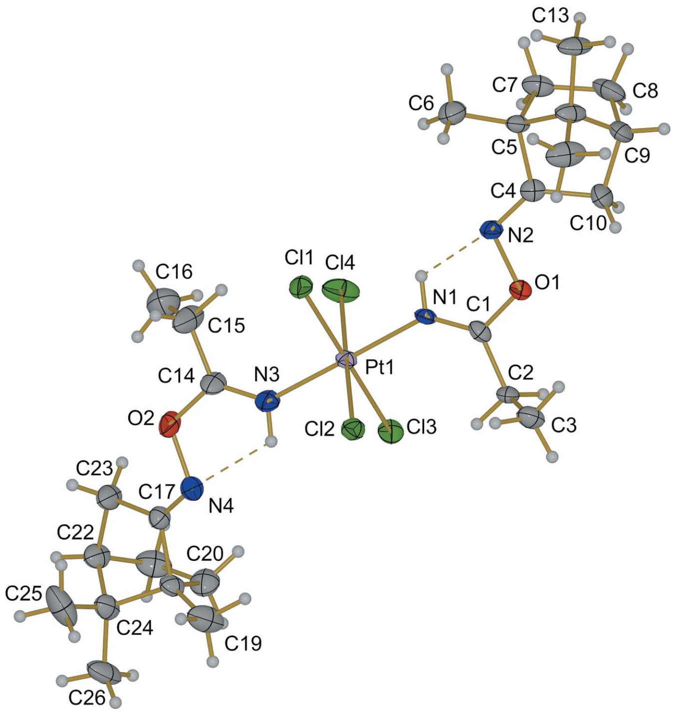


Figure 1
A view of the molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms). Hydrogen bonds are indicated by dashed lines.

In complex (I) the ligands adopt an *E* configuration, which is stabilized by an intramolecular N–H···N hydrogen bond between the imine H atom and oxime N atom (Table 2). Thus, once again there appears to be an explicit tendency toward intramolecular N–H···N bonding, leading to the stabilization of the *E* configuration of imino ligands in this type of complex.

Experimental

A solution of *trans*-[$PtCl_4(EtCN)_2$] (22 g, 0.05 mmol) (Luzyanin *et al.*, 2002) and a racemic mixture of camphoroxime ($(C_9H_{16})C{=}NOH$) (16 mg, 0.10 mmol) in $CHCl_3$ (1 ml) was vigorously stirred at room temperature for 20 min. Complex (I) was purified by column chromatography on SiO_2 (eluant $CHCl_3$). The yield of (I) is 92%. Crystals of (I) suitable for X-ray study were obtained by slow evaporation of a CH_2Cl_2 solution at 298 K in air.

Crystal data

[$PtCl_4(C_{13}H_{22}N_2O)_2$]
M_r = 781.54
Monoclinic, $P2_1$
a = 10.5595 (3) Å
b = 14.5801 (4) Å
c = 11.5436 (4) Å
β = 114.128 (1)°
V = 1621.97 (9) $Å^3$
Z = 2
D_x = 1.600 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 4.68 mm^{-1}
T = 120 (2) K
Block, yellow
0.26 × 0.14 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offset
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.365, T_{max} = 0.718
19090 measured reflections
7036 independent reflections
6279 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.088
S = 1.14
7036 reflections
342 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.87 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.61 e $Å^{-3}$
Absolute structure: Flack (1983), 3165 Friedel pairs
Flack parameter: 0.013 (8)

Table 1
Selected geometric parameters (Å, °).

Pt1—N3	2.009 (6)	Pt1—Cl2	2.3186 (16)
Pt1—N1	2.029 (5)	Pt1—Cl3	2.319 (2)
Pt1—Cl4	2.3114 (18)	Pt1—Cl1	2.325 (2)
N3—Pt1—N1	178.8 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2	0.88	2.09	2.569 (7)	113
N3—H3···N4	0.88	2.11	2.604 (8)	115

The H atoms were positioned geometrically (N—H = 0.88 Å, C—H = 0.98–1.00 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). The deepest difference hole is located 0.88 Å from atom Pt1.

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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