Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

trans-Bis[(*E*)-acetone *O*-propanimidoyloxime-κ*N*′]-tetrachloroplatinum(IV)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.008 Å
R factor = 0.031
wR factor = 0.092
Data-to-parameter ratio = 19.7

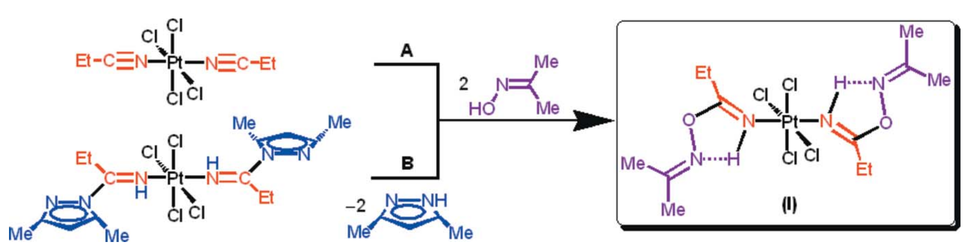
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 24 October 2006
Accepted 9 November 2006

The title complex, [$PtCl_4(C_{12}H_{24}N_4O_2)$] or *trans*-[$PtCl_4${NH═C(Et)ON═$CMe_2$}$_2$], possesses a crystallographically imposed centre of symmetry. The coordination polyhedron of the complex is a slightly distorted octahedron. The two imino ligands are mutually *trans*. This configuration is stabilized by intramolecular N—H···N hydrogen bonding between the imine H atom and the oxime N atom.

Comment

It is now well recognized that the metal-mediated reactions of organonitriles with nucleophilic reagents offer an attractive route for the creation of a great variety of compounds with C—C, C—N, C—O, C—P and C—S bonds (Kukushkin & Pombeiro, 2002; Pombeiro & Kukushkin, 2004; Bokach & Kukushkin, 2005). In particular, the reactivity of metal-activated nitriles toward such HON-nucleophiles as oximes, to give C—O(N) bonds, at substitutionally inert metal centres (for example, platinum group metals) is a relatively unexplored area which has so far attracted only limited interest (Bokach & Kukushkin, 2005). The reactions of oximes with nitriles, coordinated to kinetically labile metal centres (*e.g.* Co^{III}, Ni^{II} and Zn^{II}) have a great synthetic potential, offering attractive routes to the syntheses of important classes of nitrile-derived organic compounds such as amidines, acyl amides, imidoylamidines, phthalocyanines and carboxamides (Kopylovich *et al.*, 2001, 2002, 2003, 2004, 2006; Pombeiro *et al.*, 2001). These findings provide a strong impetus for the further exploration of nitrile reactions with oximes, including the physicochemical characterization of the addition products of HON═CR_2 species across the nitrile C≡N functionality.



Previously, we have reported the crystal structures of *trans*-[$PtCl_4${NH═C(*R*)ON═C*R*′*R*″}$_2$] [*R* = *R*′ = *R*″ = Me (Kukushkin *et al.*, 2000); *R* = Me, *R*′ = Cl, *R*″ = C_6H_4-4-NO_2 (Garnovskii *et al.*, 2000); *R* = Me, *R*′ = Cl, *R*″ = *p*-Tol (Garnovskii *et al.*, 2000); *R* = *R*′ = Me, *R*″ = C(Me)═NOH (Kukushkin *et al.*, 2000); *R* = Et, *R*′ = Ph, *R*″ = OH (Luzyanin *et al.*, 2002); *R* = Et, *R*′ = H, *R*″ = Mes (Bokach *et al.*, 2003); *R* = Et, *R*′ = H, *R*″ = COPh (Makarycheva-Mikhailova *et al.*, 2003); *R* = Et, *R*′ = MeO, *R*″ = Mes (Luzyanin *et al.*, 2004); *R* = Et, *R*′ =

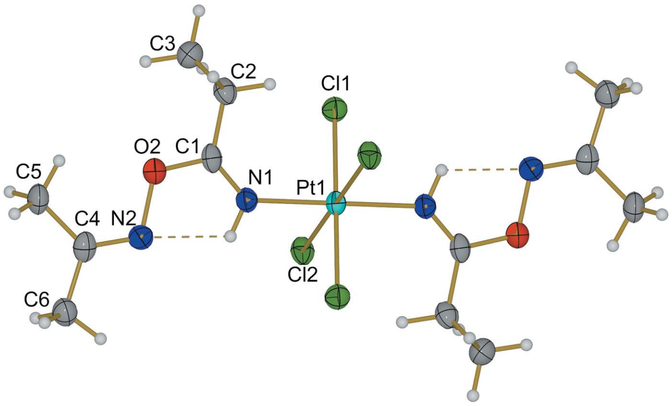


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are indicated by dashed lines.

Me, R'' = C(Ph)═NNH$_2$ (Garnovskii *et al.*, 2004); R = Et, R' = Me, R'' = C(Ph)═NN═CH(C$_6$H$_3$-2-OH-5-NO$_2$) (Garnovskii *et al.*, 2004); R = Et, R' = Me, R'' = COOEt (Luzyanin *et al.*, 2005); R = Me, R' = R'' = C$_5$H$_{10}$ (Kukushkin *et al.*, 1998)]. Here, we report the X-ray structure of one more representative of this class of compounds, the title complex *trans*-[PtCl$_4${NH═C(Et)ON═CMe$_2$}$_2$], (I), formed in the reaction between *trans*-[PtCl$_4$(EtCN)$_2$] (Luzyanin *et al.*, 2002) (route A in the scheme) or *trans*-[PtCl$_4${NH═C(Et)(3,5-Me$_2$pz)}$_2$] (Khripun *et al.*, 2006) (route B in the scheme) and HON═CMe$_2$.

The coordination polyhedron of the centrosymmetric complex (I) (Fig. 1) is a slightly distorted octahedron. The values of all bond distances and angles around the Pt centre (Table 1) are normal and in good agreement with those previously found in the other platinum(IV) complexes *trans*-[PtCl$_4${NH═C(R)ON═CR_2}$_2$]. The C═N bond length in (I) [1.275 (7) Å] corresponds with the mean value for C═N double bonds (1.279 Å; Allen *et al.*, 1987).

In complex (I), the imine H atom is oriented towards the lone pair of the oxime N atom, thus forming an N—H···N hydrogen bond (Table 2), and this bond stabilizes the imino ligands in the E configuration. The values of the van der Waals radii for H and N (1.20 + 1.55 = 2.75 Å; Bondi, 1964) and some reported N···N (2.94–3.15 Å) and H···N (2.20 Å) distances (Wells, 1986) in cases of N—H···N hydrogen bonding also support this conclusion.

Experimental

The title compound was obtained in a typical experiment as follows. A solution of *trans*-[PtCl$_4$(EtCN)$_2$] (16 mg, 0.04 mmol) or *trans*-[PtCl$_4${NH═C(Et)(3,5-Me$_2$pz)}$_2$] (26 mg, 0.04 mmol) and 2-propanone oxime HON═CMe$_2$ (6 mg, 0.08 mmol) in CH$_2$Cl$_2$ (1 ml) was stirred vigorously at room temperature for 10 min or 1 d, respectively. The bright-yellow solution which formed was evaporated to dryness and the residue was washed with three 3 ml portions of Et$_2$O to remove excess oxime. The yield of (I) is 93% and 87%, respectively. Crystals of (I) suitable for X-ray study were obtained by slow evaporation of an acetone solution at 298 K in air.

Crystal data

[PtCl$_4$(C$_{12}$H$_{24}$N$_4$O$_2$)]
M_r = 593.24
Monoclinic, $C2/c$
a = 18.0119 (9) Å
b = 6.8727 (4) Å
c = 16.4295 (6) Å
β = 105.059 (3)°
V = 1963.97 (17) Å^3
Z = 4
D_x = 2.006 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 7.70 mm^{-1}
T = 120 (2) K
Block, yellow
0.27 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offset
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.214, T_{max} = 0.461
13900 measured reflections
2223 independent reflections
1852 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 27.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.092
S = 1.11
2223 reflections
113 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 4.3124P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.19 e Å^{-3}
$\Delta\rho_{min}$ = −1.81 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	2.026 (5)	O2—N2	1.468 (7)
Pt1—Cl2	2.3162 (11)	N1—C1	1.275 (7)
Pt1—Cl1	2.3201 (12)	N2—C4	1.279 (7)
O2—C1	1.345 (6)		
N1—Pt1—Cl2	87.52 (14)	C1—N1—Pt1	134.6 (4)
Cl2—Pt1—Cl1	89.17 (4)	C4—N2—O2	109.9 (4)
C1—O2—N2	112.2 (4)	N1—C1—O2	121.3 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2	0.86 (8)	2.10 (7)	2.577 (7)	114 (6)

The N-bound H atom was located in a difference Fourier map and refined isotropically. Other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.98–0.99 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(C). The highest peak is located 0.98 Å from atom Pt1 and the deepest hole is located 0.81 Å from atom Pt1.

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Russian Fund for Basic Research (grant Nos. 06-03-32065 and 06-03-90901), the Scientific Council of the President of the Russian Federation (grant No. MK-1040.2005.3), the Government of St. Petersburg (grant No. 46/06) and the Academy of Finland (grant No. 110465).

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