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trans-Tetrachlorobis[(*E*)-ethyl 2-(1-iminopropoxyimino)propanoate]platinum(IV)

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.020
wR factor = 0.042
Data-to-parameter ratio = 19.0

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

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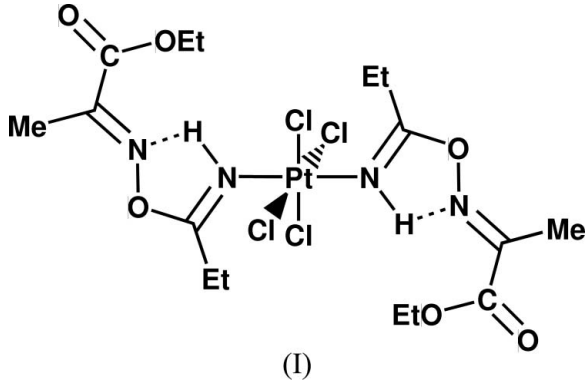
The title Pt^{IV} complex, $[PtCl_4(C_{16}H_{28}N_4O_6)]$ or *trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(Me)C(=O)OEt\}_2]$, possesses a crystallographically imposed centre of symmetry. The coordination environment of the metal centre is a slightly distorted octahedron. An intramolecular N—H···N hydrogen bond between the imine H atom and the oxime N atom stabilizes the *E* configuration of the imine groups.

Comment

In the course of our study of the reactivity of metal-activated nitriles toward nucleophilic addition (Kukushkin & Pombeiro, 2002; Pombeiro & Kukushkin, 2004; Bokach & Kukushkin, 2005), we have observed coupling between nitriles in (*R*CN)[*M*] (*M* = Pt^{IV}, Pt^{II}, Rh^{III} or Re^{IV}) complexes and HON nucleophiles such as 'simple' oximes (Kukushkin *et al.*, 1998; Kuznetsov *et al.*, 2000), *vic*-dioximes (Kukushkin *et al.*, 2000), oximehydrazones (Garnovskii *et al.*, 2004), dialkyl hydroxylamines (Wagner *et al.*, 1999; Luzyanin *et al.*, 2005) and hydroxamic acids (Luzyanin *et al.*, 2002, 2004). The reactions lead to the formation of species with new C—O{N} bonds upon addition of the OH group to the C≡N moiety of metal-activated nitriles, *R*CN.



(I)

Metal-mediated coupling between coordinated propanenitriles in *trans*-$[PtCl_4(EtCN)_2]$ and ethyl 2-(hydroxyimino)propanoate, HON=C(Me)C(=O)OEt, allows the isolation of the title novel imino complex *trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(Me)C(=O)OEt\}_2]$, (I), in almost quantitative (95%) yield. The compound has been characterized by X-ray crystallography, IR, ^1H, $^{13}C\{^1H\}$ and ^{195}Pt NMR spectroscopies, FAB-MS and elemental analyses. It should be noted that the oxime HON=C(Me)C(=O)OEt belongs to the well known class of strong chelating reagents, *viz*. dione monoximes (Abel *et al.*, 1995; Makarycheva-Mikhailova *et al.*, 2002), and the addition of this oxime to the coordinated EtCN

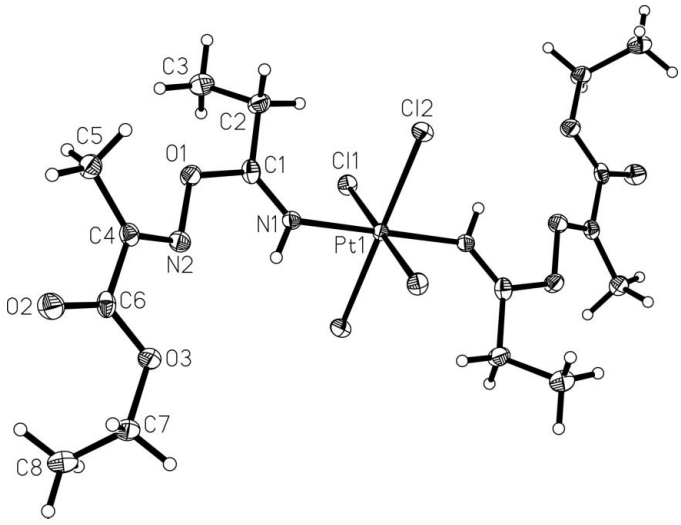


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary size. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, -y, -z)$.

(rather than its substitution) represents an unusual reactivity mode for dione monoxime species.

In complex (I) (Fig. 1), the coordination polyhedron of the central Pt atom is a slightly distorted octahedron, and the bond lengths and angles (Table 1) are normal (Orpen *et al.*, 1989). The closely similar values of the Pt—Cl bonds [2.3206 (6)–2.3252 (6) Å] indicate that the ground-state *trans* influence is similar for the imine and chloride species. The two C═N bonds from the imine fragment are 1.271 (3) Å, within the typical range for C═N double bonds (1.26–1.29 Å; Allen *et al.*, 1987).

An intermolecular N—H···N hydrogen bond between the imine H atom and the oxime N atom (Table 2) stabilizes the *E* configuration of the imine ligands. This hydrogen bonding has also been observed in related complexes, *viz.* *trans*-$[PtCl_4\{NH{=}C(Me)ON{=}CR_2\}_2]$ (Kukushkin *et al.*, 1998) and *trans*-$[PtCl_4\{NH{=}C(Et)ON{=}C(OMe)(2,4,6\text{-}Me_3C_6H_2)\}_2]$ (Luzyanin *et al.*, 2004).

Experimental

The title compound was prepared in accordance with the previously published procedure (Kukushkin *et al.*, 1998), using *trans*-$[PtCl_4(EtCN)_2]$ and HON═C(Me)C(═O)OEt (Norman, 1968) as starting materials. Suitable crystals of (I) for X-ray study were obtained by slow evaporation of an acetone solution at 298 K in air. Analysis calculated for $C_{16}H_{28}N_4Cl_4O_6Pt$: C 27.09, H 3.98, N 7.90%; found: C 26.56, H 3.94, N 7.54%; FAB-MS, *m*/*z*: 673 $[M-Cl]^+$, 638 $[M-2Cl]^+$; IR (selected bands, ν, cm^{-1}): 3220 (*mw*, N—H), 1666 (*s*, C═N), 1638 (*s*, C═N); ^1H NMR ($CDCl_3$, δ, p.p.m.): 1.37 (*t*, J = 7.5 Hz, 3H, CH_2Me), 1.40 (*t*, J = 7.5 Hz, 3H, OCH_2Me), 2.34 (*s*, 3H, Me), 3.14 (*q*, J = 7.5 Hz, 2H, CCH_2), 4.39 (*q*, J = 7.5 Hz, 2H, OCH_2), 8.88 (*s*, *br*, 1H, NH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, p.p.m.): 10.6 (CH_3) and 25.3 (CH_2)(Et), 13.5 (CH_3), 13.9 (CH_3) and 62.8 (OCH_2)(Et), 153.7 (C═N), 157.5 (C═O), 176.4 (HN═C); ^{195}Pt NMR ($CDCl_3$, δ, p.p.m.): −200 (1120 Hz).

Crystal data

$[PtCl_4(C_{16}H_{28}N_4O_6)]$	D_x = 1.960 Mg m^{-3}
M_r = 709.31	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 11553 reflections
a = 8.5514 (3) Å	θ = 2.5–27.5°
b = 8.3410 (3) Å	μ = 6.32 mm^{-1}
c = 17.6134 (7) Å	T = 100 (2) K
β = 106.939 (2)°	Block, yellow
V = 1201.81 (8) Å^3	0.17 × 0.16 × 0.15 mm
Z = 2	

Data collection

Nonius KappaCCD area-detector diffractometer	2748 independent reflections
φ scans, and ω scans with κ offset	2274 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Sheldrick, 2003)	R_{int} = 0.033
T_{min} = 0.270, T_{max} = 0.388	θ_{max} = 27.5°
11553 measured reflections	$h = -11 \rightarrow 10$
	$k = -10 \rightarrow 9$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 0.4361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.020	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.042	$\Delta\rho_{max}$ = 0.78 e Å^{-3}
S = 1.09	$\Delta\rho_{min}$ = −1.40 e Å^{-3}
2748 reflections	
145 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pt1—N1	2.020 (2)	O3—C6	1.312 (3)
Pt1—Cl1	2.3206 (6)	O3—C7	1.472 (3)
Pt1—Cl2	2.3252 (6)	N1—C1	1.272 (3)
O1—C1	1.351 (3)	C1—C2	1.498 (4)
O1—N2	1.437 (3)	C2—C3	1.527 (4)
O2—C6	1.195 (3)	C7—C8	1.527 (4)
N1—Pt1—Cl1	93.49 (6)	Cl1—Pt1—Cl2	91.21 (2)
N1—Pt1—Cl2	93.60 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2	0.88	2.15	2.607 (3)	112

H atoms were positioned geometrically and allowed to ride on their parent atoms, with N—H = 0.88 Å and C—H = 0.98–0.99 Å, and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2003); software used to prepare material for publication: *SHELXL97*.

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