metal-organic compounds

(Benzoylformaldehyde oximato-κ^2N,O)-(benzoylformaldehyde oxime-κN)-chloridoplatinum(II)

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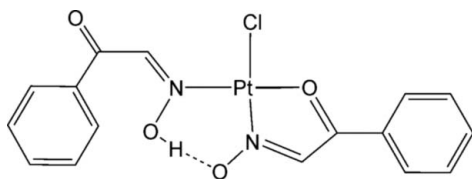Correspondence e-mail: matti.haukka@joensuu.fi

In the title complex, [Pt($C_8H_6NO_2$)Cl($C_8H_7NO_2$)], the Pt^{II} centre is coordinated by a monodentate and an N,O-chelating deprotonated benzoylformaldehyde oxime and a Cl atom. There is an intramolecular $N-O^-\cdots H-O$ hydrogen-bonding system between the oxime OH group and the oximate O atom.

Related literature

For related literature, see: Allen *et al.* (1987); Makarycheva-Mikhailova, Bokach *et al.* (2003); Makarycheva-Mikhailova, Haukka, Bokach *et al.* (2002); Raston *et al.* (1978).

Experimental

Crystal data

[Pt($C_8H_6NO_2$)Cl($C_8H_7NO_2$)]
M_r = 527.82
Monoclinic, $P2_1/c$
a = 7.1236 (2) Å
b = 18.0103 (6) Å
c = 12.5569 (4) Å
β = 97.163 (2)°

V = 1598.45 (9) Å³
Z = 4
Mo $K\alpha$ radiation
μ = 8.97 mm^{-1}
T = 100 (2) K
$0.14 \times 0.05 \times 0.05$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(*XPREP* in *SHELXTL*;
Sheldrick, 2005)
T_{min} = 0.352, T_{max} = 0.636

16177 measured reflections
2855 independent reflections
2439 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.043
S = 1.06
2855 reflections
221 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −1.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H03···O1	0.94 (7)	1.62 (7)	2.550 (4)	170 (6)

Data collection: *COLLECT* (Nonius, 2004); 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: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

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supplementary materials

(Benzoylformaldehyde oximato-κ²N,O)(benzoylformaldehyde oxime-κN)chloridoplatinum(II)

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Comment

In the title complex, (I), a chloride anion is coordinated to the Pt^{II} centre, two sites are occupied by the deprotonated chelate, coordinated *via* the oximato nitrogen and the carbonyl oxygen, with the remaining site occupied by the monodentate oxo(phenyl)acetaldehyde oxime, which is coordinated *via* the oxime nitrogen, located at the *cis*-position to the oximato N atom. The bond lengths obtained for the monodentate ligand (Table 1) are similar to those reported for 1-oxo(phenyl)acetaldehyde oxime (N–O,1.380 (2) Å, N=C, 1.284 (2) Å, C–C,1.491 (3) Å, C=O, 1.224 (2) Å) (Raston *et al.*, 1978) These values are also in concord with the corresponding mean bond lengths values, obtained for N–O, N=C, C–C(unconjugated), C=O bonds: 1.394 (18), 1.281 (13), 1.478 (12), 1.210 (8) Å, respectively (Allen *et al.*, 1987). In contrast, the bond lengths found for the deprotonated N,O-chelated oxime (Table 1) differ from those observed in the monodentate ligand, the free molecule and from the standard bond lengths. We assume that the noticeable decrease in the N=C and C=O and concomitant increase in the N–O and C–C bond lengths in the N,O-chelate are a consequence of the availability of a coplanar conjugated system in the chelated ring, which stabilizes the oximato anion by delocalization of the negative charge. The structure is stabilized also by an intramolecular N—O⁻···H–O hydrogen bond (Table 2).

The N=C–C=O torsion angles differ for the two ligands, being -0.1 (5)° for the chelated ligand and -100.1 (5)° for the monodentate species. The latter results in the phenyl plane being almost perpendicular to the coordination plane.

Experimental

The title compound is formed in small quantities as a by-product of the reaction between *trans*-[PtCl$_4$(EtCN)$_2$] and the oxime leading mostly to *trans*-[PtCl$_4${NH=C(Et)ON=C(H)C(=O)Ph}$_2$], followed by dehydration of the latter (Makarycheva-Mikhailova *et al.*, 2002, 2003).

Refinement

The OH hydrogen atom was located from the difference Fourier map and refined isotropically. Other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95 Å, and U_{iso}(H) = 1.2 U_{eq}(parent atom). The highest peak is located 1.04Å from atom H16 and the deepest hole is located 0.86Å from atom Pt1.
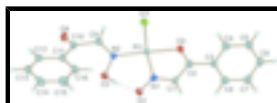
Figures

Fig. 1. A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen is indicated by dashed line.

supplementary materials

(Benzoylformaldehyde oximato-κ²*N,O*)(benzoylformaldehyde oxime-κ*N*)chloridoplatinum(II)

Crystal data

[Pt(C$_8$H$_6$NO$_2$)Cl(C$_8$H$_7$NO$_2$)]	$F_{000} = 1000$
$M_r = 527.82$	$D_x = 2.193$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 16177 reflections
$a = 7.1236$ (2) Å	$\theta = 2.3–25.2°$
$b = 18.0103$ (6) Å	$\mu = 8.97$ mm^{-1}
$c = 12.5569$ (4) Å	$T = 100$ (2) K
$\beta = 97.163$ (2)°	Needle, orange red
$V = 1598.45$ (9) Å^3	$0.14 \times 0.05 \times 0.05$ mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2855 independent reflections
Radiation source: fine-focus sealed tube	2439 reflections with $I > 2\sigma(I)$
Monochromator: horizontally mounted graphite crystal	$R_{int} = 0.051$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 25.2°$
$T = 100(2)$ K	$\theta_{min} = 2.3°$
φ scans and ω scans with κ offset	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (XPREP in SHELXTL; Sheldrick, 2005)	$k = -21 \rightarrow 21$
$T_{min} = 0.352$, $T_{max} = 0.636$	$l = -15 \rightarrow 15$
16177 measured reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 1.3333P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.043$	$\Delta\rho_{max} = 1.21$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -1.17$ e Å^{-3}
2855 reflections	Extinction correction: none
221 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: mixed	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
C1	0.1876 (5)	0.4606 (2)	−0.0671 (3)	0.0183 (9)
H1	0.1727	0.4803	−0.1379	0.022*
C2	0.2619 (5)	0.5028 (2)	0.0253 (3)	0.0181 (9)
C3	0.3210 (5)	0.5805 (2)	0.0197 (3)	0.0175 (9)
C4	0.3804 (6)	0.6181 (2)	0.1148 (4)	0.0239 (10)
H4	0.3826	0.5932	0.1816	0.029*
C5	0.4363 (6)	0.6916 (2)	0.1125 (4)	0.0281 (11)
H5	0.4765	0.7171	0.1775	0.034*
C6	0.4335 (6)	0.7279 (2)	0.0145 (4)	0.0278 (11)
H6	0.4711	0.7784	0.0129	0.033*
C7	0.3765 (6)	0.6910 (2)	−0.0801 (4)	0.0265 (10)
H7	0.3759	0.7161	−0.1467	0.032*
C8	0.3200 (5)	0.6175 (2)	−0.0786 (4)	0.0220 (10)
H8	0.2807	0.5922	−0.1439	0.026*
C9	0.0374 (5)	0.2189 (2)	0.1658 (3)	0.0210 (9)
H9	0.0588	0.2361	0.2378	0.025*
C10	−0.0491 (6)	0.1426 (2)	0.1463 (3)	0.0201 (9)
C11	0.0789 (5)	0.0790 (2)	0.1372 (3)	0.0197 (9)
C12	0.0063 (6)	0.0068 (2)	0.1389 (3)	0.0212 (10)
H12	−0.1236	−0.0008	0.1458	0.025*
C13	0.1232 (6)	−0.0531 (2)	0.1304 (3)	0.0247 (10)
H13	0.0743	−0.1021	0.1322	0.030*
C14	0.3121 (6)	−0.0421 (3)	0.1192 (4)	0.0296 (11)
H14	0.3919	−0.0837	0.1124	0.036*
C15	0.3855 (6)	0.0293 (3)	0.1179 (4)	0.0325 (11)
H15	0.5155	0.0364	0.1108	0.039*
C16	0.2703 (6)	0.0897 (3)	0.1270 (3)	0.0264 (10)
H16	0.3207	0.1385	0.1263	0.032*
N1	0.1419 (4)	0.39174 (18)	−0.0447 (3)	0.0193 (8)
N2	0.0835 (4)	0.26159 (18)	0.0929 (3)	0.0177 (7)
O1	0.0805 (4)	0.34699 (16)	−0.1200 (2)	0.0263 (7)
O2	0.2757 (4)	0.47114 (15)	0.1162 (2)	0.0186 (6)
O3	0.0550 (5)	0.23008 (18)	−0.0082 (3)	0.0316 (8)

H03	0.061 (8)	0.270 (4)	−0.056 (5)	0.08 (2)*
O4	−0.2187 (4)	0.13761 (15)	0.1456 (2)	0.0251 (7)
Cl1	0.26457 (14)	0.34896 (6)	0.28994 (8)	0.0236 (2)
Pt1	0.18476 (2)	0.365032 (8)	0.108499 (12)	0.01658 (6)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.020 (2)	0.016 (2)	0.019 (2)	−0.0014 (17)	0.0037 (17)	0.0049 (18)
C2	0.009 (2)	0.018 (2)	0.028 (3)	0.0041 (16)	0.0037 (17)	0.0009 (19)
C3	0.015 (2)	0.016 (2)	0.021 (2)	0.0045 (16)	0.0032 (16)	0.0001 (18)
C4	0.022 (2)	0.023 (3)	0.027 (3)	−0.0002 (18)	0.0050 (18)	−0.0026 (19)
C5	0.029 (3)	0.023 (2)	0.032 (3)	−0.0059 (19)	0.005 (2)	−0.006 (2)
C6	0.023 (2)	0.018 (2)	0.043 (3)	0.0000 (18)	0.010 (2)	0.000 (2)
C7	0.021 (2)	0.025 (3)	0.034 (3)	0.0015 (19)	0.0084 (19)	0.010 (2)
C8	0.018 (2)	0.023 (2)	0.025 (3)	0.0024 (17)	0.0027 (18)	0.0009 (18)
C9	0.024 (2)	0.019 (2)	0.020 (2)	0.0011 (18)	0.0023 (18)	−0.0009 (19)
C10	0.029 (2)	0.016 (2)	0.015 (2)	−0.0036 (19)	0.0007 (17)	0.0043 (18)
C11	0.024 (2)	0.018 (2)	0.017 (2)	−0.0021 (18)	0.0010 (17)	0.0004 (18)
C12	0.022 (2)	0.023 (2)	0.018 (2)	−0.0027 (18)	0.0011 (17)	0.0003 (19)
C13	0.033 (3)	0.019 (2)	0.021 (3)	−0.0042 (19)	−0.0024 (19)	0.0018 (19)
C14	0.031 (3)	0.024 (3)	0.032 (3)	0.007 (2)	−0.003 (2)	−0.005 (2)
C15	0.020 (2)	0.038 (3)	0.039 (3)	0.001 (2)	0.002 (2)	−0.006 (2)
C16	0.026 (2)	0.024 (3)	0.028 (3)	−0.009 (2)	0.0015 (18)	−0.003 (2)
N1	0.0146 (17)	0.0199 (19)	0.024 (2)	−0.0008 (14)	0.0054 (14)	−0.0022 (16)
N2	0.0205 (18)	0.0172 (18)	0.0158 (19)	−0.0001 (15)	0.0036 (14)	−0.0017 (15)
O1	0.0374 (18)	0.0210 (17)	0.0201 (17)	−0.0086 (13)	0.0016 (13)	−0.0041 (13)
O2	0.0179 (14)	0.0163 (15)	0.0213 (17)	0.0022 (12)	0.0011 (11)	0.0006 (13)
O3	0.053 (2)	0.0237 (18)	0.0195 (18)	−0.0125 (15)	0.0093 (15)	−0.0039 (15)
O4	0.0198 (16)	0.0215 (16)	0.0342 (19)	−0.0010 (13)	0.0031 (13)	0.0031 (14)
Cl1	0.0298 (6)	0.0211 (6)	0.0192 (6)	−0.0015 (4)	−0.0001 (4)	0.0008 (4)
Pt1	0.01681 (9)	0.01454 (9)	0.01845 (10)	0.00001 (7)	0.00242 (6)	−0.00053 (8)

Geometric parameters (Å, °)

C1—N1	1.322 (5)	C10—C11	1.477 (6)
C1—C2	1.432 (6)	C11—C16	1.398 (6)
C1—H1	0.9500	C11—C12	1.401 (6)
C2—O2	1.270 (5)	C12—C13	1.375 (6)
C2—C3	1.465 (5)	C12—H12	0.9500
C3—C4	1.392 (6)	C13—C14	1.384 (6)
C3—C8	1.402 (6)	C13—H13	0.9500
C4—C5	1.383 (6)	C14—C15	1.389 (6)
C4—H4	0.9500	C14—H14	0.9500
C5—C6	1.391 (6)	C15—C16	1.377 (6)
C5—H5	0.9500	C15—H15	0.9500
C6—C7	1.378 (6)	C16—H16	0.9500
C6—H6	0.9500	N1—O1	1.278 (4)
C7—C8	1.384 (6)	N1—Pt1	1.970 (3)

C7—H7	0.9500	N2—O3	1.383 (4)
C8—H8	0.9500	N2—Pt1	1.999 (3)
C9—N2	1.269 (5)	O2—Pt1	2.016 (3)
C9—C10	1.514 (6)	O3—H03	0.94 (7)
C9—H9	0.9500	Cl1—Pt1	2.2967 (10)
C10—O4	1.211 (5)		
N1—C1—C2	113.7 (4)	C16—C11—C10	121.3 (4)
N1—C1—H1	123.2	C12—C11—C10	119.1 (4)
C2—C1—H1	123.2	C13—C12—C11	119.9 (4)
O2—C2—C1	118.0 (3)	C13—C12—H12	120.0
O2—C2—C3	118.8 (4)	C11—C12—H12	120.0
C1—C2—C3	123.2 (4)	C12—C13—C14	120.1 (4)
C4—C3—C8	119.4 (4)	C12—C13—H13	119.9
C4—C3—C2	118.9 (4)	C14—C13—H13	119.9
C8—C3—C2	121.7 (4)	C13—C14—C15	120.3 (4)
C5—C4—C3	120.4 (4)	C13—C14—H14	119.8
C5—C4—H4	119.8	C15—C14—H14	119.8
C3—C4—H4	119.8	C16—C15—C14	120.1 (4)
C4—C5—C6	119.7 (4)	C16—C15—H15	119.9
C4—C5—H5	120.2	C14—C15—H15	119.9
C6—C5—H5	120.2	C15—C16—C11	119.8 (4)
C7—C6—C5	120.5 (4)	C15—C16—H16	120.1
C7—C6—H6	119.8	C11—C16—H16	120.1
C5—C6—H6	119.8	O1—N1—C1	120.3 (4)
C6—C7—C8	120.2 (4)	O1—N1—Pt1	124.5 (3)
C6—C7—H7	119.9	C1—N1—Pt1	115.1 (3)
C8—C7—H7	119.9	C9—N2—O3	113.1 (3)
C7—C8—C3	119.8 (4)	C9—N2—Pt1	128.1 (3)
C7—C8—H8	120.1	O3—N2—Pt1	118.8 (2)
C3—C8—H8	120.1	C2—O2—Pt1	113.2 (2)
N2—C9—C10	124.7 (4)	N2—O3—H03	105 (4)
N2—C9—H9	117.6	N1—Pt1—N2	97.01 (14)
C10—C9—H9	117.6	N1—Pt1—O2	79.94 (12)
O4—C10—C11	124.5 (4)	N2—Pt1—O2	176.47 (12)
O4—C10—C9	117.0 (4)	N1—Pt1—Cl1	171.42 (10)
C11—C10—C9	118.3 (3)	N2—Pt1—Cl1	91.22 (10)
C16—C11—C12	119.7 (4)	O2—Pt1—Cl1	91.91 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H03···O1	0.94 (7)	1.62 (7)	2.550 (4)	170 (6)

Fig. 1