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trans-Dichlorobis(piperidine-1-carbonitrile)-platinum(II)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.021
wR factor = 0.029
Data-to-parameter ratio = 20.4

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

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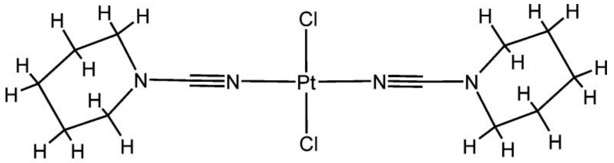
In the title centrosymmetric complex, *trans*-[$PtCl_2(C_6H_{10}N_2)_2$], the Pt^{II} centre is coordinated by two piperidine-1-carbonitrile ligands and two chloro ligands, resulting in a typical square-planar geometry. The C—N distance between the nitrile and piperidine group [1.306 (4) Å] clearly indicates that this bond is not a pure single bond, being closer to a C═N double bond. This points to a noticeable contribution of the bipolar structure [Pt]—N$^-$═C═N$^+$$R_2$ in the resonance hybrid of the push–pull nitrile ligand.

Comment

It has previously been observed that some push–pull nitrile-containing complexes, in particular dialkylcyanamide metal species, display unusual reactivity patterns unknown for conventional *R*CN compounds (Bokach *et al.*, 2003; Cunha *et al.*, 2002; Ferreira *et al.*, 2001; Guedes da Silva *et al.*, 1997; Pombeiro *et al.*, 1989). This difference, in view of our general interest in the reactions of metal-activated nitriles (Kukushkin *et al.*, 2002; Kukushkin *et al.*, 2005; Bokach *et al.*, 2005), prompted us to verify some structural differences between push–pull and conventional nitrile species ligated to a Pt^{II} centre. For this study, we investigated the complex *trans*-[$PtCl_2(NCNC_5H_{10})_2$], (I), containing the push–pull nitrile species piperidine-1-carbonitrile.



(I)

The crystal structure analysis of *trans*-[$PtCl_2(NCNC_5H_{10})_2$] shows that the Pt^{II} atom is located on a centre of symmetry and coordinated by two piperidine-1-carbonitrile ligands (in a mutually *trans* orientation) and by two chloro ligands, resulting in a typical square-planar geometry (Fig. 1). All the bond angles around the Pt^{II} centre are close to 90° (Table 1). The Pt1—N1—C1—N2 arrangement is almost linear [Pt1—N1—C1 = 174.7 (3)° and N1—C1—N2 = 177.1 (4)°] and both piperidine rings have a chair conformation; all C—C,N distances in these rings are typical for C—C,N single bonds, ranging from 1.474 (4) to 1.518 (5) Å. The fragment C1/N2/C2/C6 is almost planar [the maximum deviation is 0.296 (4) Å for atom C6], thus indicating a purely amide character for the CNC_5H_{10} group.

The bond lengths in the [Pt]NCN unit compare well with those observed in the only structurally characterized dialkyl-

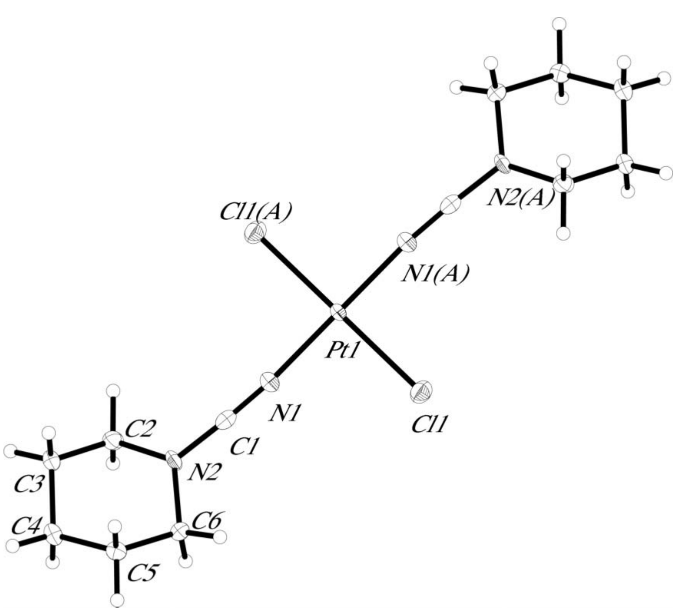


Figure 1

The molecular structure of *trans*-$[PtCl_2(NCNC_5H_{10})_2]$, showing the atom-labeling scheme and displacement ellipsoids drawn at the 50% probability level. Atoms labeled *(A)* refer to symmetry operation $(1 - x, -y, 1 - z)$.

cyanamide platinum(II) complex $[PtCl_2(NCNMe_2)_2]$ (Bokach *et al.*, 2003), and also with those found in the platinum(II) nitrile compounds $[PtCl_2(NCR)_2]$ [R = Me (Kritzenberger *et al.*, 1994), R = Et (Svensson *et al.*, 1995) and R = Ph (Eysel *et al.*, 1983)]. Thus, the Pt1—N1 distance [1.944 (3) Å] agrees, to within 3σ, with the corresponding value observed in *trans*-$[PtCl_2(NCNMe_2)_2]$ [1.973 (8) Å] and with that in the nitrile complexes *trans*-$[PtCl_2(NCR)_2]$ [1.943 (11) (R = Me; Kritzenberger *et al.*, 1994), 1.96 (2) (R = Et; Svensson *et al.*, 1995) and 1.978 (3) Å (R = Ph; Eysel *et al.*, 1983)]. This distance is also consistent with the average $Pt^{II}—N_{nitrile}$ bond length reported for various nitrile-containing organometallic and coordination compounds [1.980 (19) Å; Orpen *et al.*, 1989]. The N1—C1 distance [1.144 (4) Å] is normal and comparable with that reported for the dialkylcyanamide complex *trans*-$[PtCl_2(NCNMe_2)_2]$ [1.129 (14) Å], and with the distance observed in the nitrile complexes *trans*- $[PtCl_2(NCR)_2]$ [1.154 (18) (R = Me), 1.14 (2) (R = Et) and 1.129 (9) Å (R = Ph)]. It also agrees well with the regular C≡N bond distance in free [1.136 (10) Å; Allen *et al.*, 1987] and in Pt^{II}-bound organonitriles [1.133 (20) Å; Orpen *et al.*, 1989].

The most interesting feature of the complex is the C1—N2 distance [1.306 (4) Å], which is very close to that found in the dialkylcyanamide complex *trans*-$[PtCl_2(NCNMe_2)_2]$ [1.302 (14) Å; Bokach *et al.*, 2003] and to the average C═N double-bond distance (1.31 Å) obtained from the Cambridge Crystal Structural Database (Version 5.27; Allen, 2002). The value of the C1—N2 distance clearly indicates that this bond is not a purely single one, being closer to a C═N double bond, thus pointing out the contribution of the bipolar structure $[Pt]—N^-═C═N^+R_2$ in the resonance hybrid of the push–pull nitrile ligand. We believe that this ground-state difference in the electronic distribution between the push–pull and the conventional nitrile Pt^{II} ligated species may be responsible for the observed difference in reactivity of these compounds.

Experimental

$NCNC_5H_{10}$ (Aldrich; 0.83 ml, 7.2 mmol) was added to $K_2[PtCl_4]$ (0.50 g, 1.2 mmol) in water (5 ml) at room temperature. A yellow powder immediately began to form; it was filtered off after 6 h, washed with three 3 ml portions of water, and dried in air at room temperature (yield 87%). At 293–298 K, the complex is formed as a mixture of *cis* and *trans* isomers in *ca* 1:1 molar ratio, as indicated by ^1H NMR integration. The *trans* isomer was separated by column chromatography on silica gel (Merck 60 F_{254}, eluant $CHCl_3:Et_2O$ = 5:1, first fraction). Yellow crystals of the title compound were obtained by slow evaporation of a chloroform–hexane (1:1) solution. Elemental analyses calculated: C 29.64, H 4.15, N 11.52%; found: C 30.00, H 4.40, N 11.39%. FAB$^+$-MS, m/z: 486 $[M]^+$, 449 $[M - HCl]^+$, 414 $[M - 2Cl]^+$. IR (KBr, selected bands, cm^{-1}): 2292 (*s*) ν (C≡N). ^1H NMR ($CDCl_3$): δ 3.30 (*t*, 5.6 Hz, 2H, α-CH_2), 1.64 (*m*, 2H, β-CH_2), 1.57 (*m*, 2H, γ-CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 114.06 (NCN), 49.59 (α-CH_2), 24.39 (β-CH_2), 2.32 (γ-CH_2).

Crystal data

$[PtCl_2(C_6H_{10}N_2)_2]$
M_r = 486.31
Orthorhombic, *Pccn*
a = 10.1398 (10) Å
b = 11.2092 (10) Å
c = 13.8008 (12) Å
V = 1568.6 (2) Å^3
Z = 4
D_x = 2.059 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4024 reflections
θ = 1.0–27.5°
μ = 9.28 mm^{-1}
T = 120 (2) K
Block, yellow
0.28 × 0.17 × 0.11 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offset
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.151, T_{max} = 0.360
19196 measured reflections
1799 independent reflections

1069 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.029
S = 1.08
1799 reflections
88 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 2.4057P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Pt1—N1	1.944 (3)	N1—C1	1.144 (4)
Pt1—Cl1	2.2882 (9)	N2—C1	1.306 (4)
N1—Pt1—N1^i	180	Cl1—Pt1—Cl1^i	180
N1—Pt1—Cl1	90.83 (9)	C1—N1—Pt1	174.7 (3)
N1^i—Pt1—Cl1	89.17 (9)	N1—C1—N2	177.1 (4)

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

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

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 2005); software used to prepare material for publication: *SHELXL97*.

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