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The square-pyramidal Pd^II complex of a cross-bridged tetraazamacrocycle

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Abstract

The preparation and crystal structure of chloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane-κ^4N)-palladium(II) chloride dihydrate, [PdCl(C_{14}H_{30}N_4)]Cl·-2H_2O, are described. The Pd^II ion is coordinated to all four N atoms of the folded macrobicycle and to a single chloride ligand in a square-pyramidal geometry. The bond to the axial N atom is considerably longer than the others [Pd—N_{ax} 2.461 (3) and average Pd—N_{eq} 2.097 (10) Å]. The Pd—Cl distance is 2.3407 (10) Å.

Comment

The coordination geometries of complexes of Pd^II, as of other transition metals, result from a delicate interplay between ligand-field favorability for the metal ion and the steric and topological constraints of the ligand(s) (Huheey *et al.*, 1993; Busch, 1993). As a d^8 ion, Pd^II is overwhelmingly found in four-coordinate square-planar complexes, to maximize occupation of bonding orbitals (Cotton & Wilkinson, 1988). Geometries other than square planar for Pd^II are observed only when the steric or topological demands of the ligand outweigh the loss in stabilization due to the geometric distortion. The title compound, (1), exhibits such a distorted geometry, in this case a five-coordinate square-pyramidal one, because the short ethylene cross-bridge of the macrocyclic ligand 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane, (2), does not allow the macrocycle to occupy the four sites of a square plane. The topological constraint of the two-carbon bridge enforces a fold in the ligand that is conserved on binding to Pd^II.
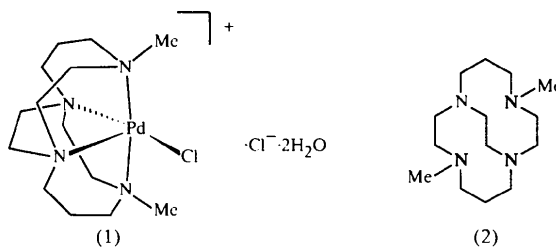
The only non-adjacent nitrogen pair capable of spanning the diagonal of the base of the square pyramid, N4 and N11, do so with an N4—Pd—N11 angle of 171.65 (11)°. The single chloride ligand completes the coordination sphere of Pd^II and allows the complex to retain part of the advantage of a square-based geometry.

The chemically equivalent N atoms, N1 and N8, occupy inequivalent sites on the square pyramid; N1 is on the base, while N8 is at the apex. This inequality is evident in the Pd—N distances; Pd—N1 is 2.112 (3), while Pd—N8 is 2.461 (3) Å. The long Pd—N8 bond demonstrates that ligand topology dictates the coordination geometry in this complex rather than it being determined by the electronic configuration of the Pd^II ion, as in less topologically constrained ligand complexes. The result of the mismatch between ligand constraints
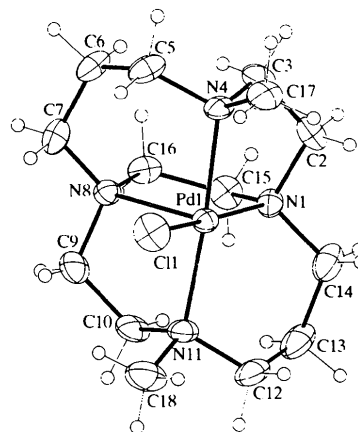

Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

and metal-ion ligand-field effects is a rather unsymmetrical complex where only a chloride and an 'empty' site (of an octahedron) occupy one hemisphere of the palladium ion, while the entire bicyclic ligand is in the other hemisphere.

Experimental

$Pd(MeCN)_2Cl_2$ (0.259 g, 0.001 mol) and 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (0.254 g, 0.001 mol), obtained by literature methods (Weisman et al., 1990), were stirred together in MeCN (20 ml) under nitrogen for 12 h. Removal of a black solid by filtration gave a green solution into which ether was allowed to diffuse. Dark blue X-ray quality crystals of (1) resulted in 55% yield.

Crystal data

$[PdCl(C_{14}H_{30}N_4)]Cl\cdot2H_2O$	Mo $K\alpha$ radiation
$M_r = 467.75$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 5706
$C2/c$	reflections
$a = 29.7207\,(13)$ Å	$\theta = 3\text{--}20°$
$b = 7.7934\,(3)$ Å	$\mu = 1.248$ mm^{-1}
$c = 17.2154\,(7)$ Å	$T = 188\,(2)$ K
$\beta = 102.3920\,(10)°$	Block
$V = 3894.6\,(3)$ Å^3	$0.40 \times 0.20 \times 0.15$ mm
$Z = 8$	Dark blue
$D_x = 1.593$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART diffractometer with Cryostream cooler (Cosier & Glazer, 1986)	11 454 measured reflections
	4583 independent reflections
	3177 reflections with
ω scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.044$
multi-scan (SADABS;	$\theta_{max} = 28.58°$
Sheldrick, 1996)	$h = -36 \rightarrow 38$
$T_{min} = 0.67$, $T_{max} = 0.81$	$k = -10 \rightarrow 10$
	$l = -17 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0420P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{max} = 0.027$
$S = 1.058$	$\Delta\rho_{max} = 0.902$ e Å^{-3}
4583 reflections	$\Delta\rho_{min} = -1.159$ e Å^{-3}
209 parameters	Extinction correction: none
H-atom parameters	Scattering factors from
constrained	International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd1	0.149785 (9)	0.76690 (3)	0.074625 (15)	0.02182 (9)
Cl1	0.22391 (4)	0.88515 (13)	0.10093 (6)	0.0419 (3)
Cl2	0.07181 (4)	0.17421 (12)	0.19694 (6)	0.0401 (3)
O3	0	0.9380 (4)	1/4	0.0363 (9)
O4	0	0.4105 (5)	1/4	0.0530 (12)
O5	0.04677 (10)	0.6742 (4)	0.34822 (16)	0.0507 (8)
N1	0.08064 (10)	0.6920 (4)	0.06635 (17)	0.0253 (7)
C2	0.07598 (14)	0.7027 (5)	0.1516 (2)	0.0344 (9)
C3	0.11567 (13)	0.6118 (5)	0.2039 (2)	0.0326 (9)
N4	0.15940 (11)	0.6903 (4)	0.19263 (17)	0.0265 (7)
C5	0.19811 (14)	0.5646 (5)	0.2152 (2)	0.0371 (10)
C6	0.19290 (14)	0.3896 (5)	0.1748 (2)	0.0361 (10)
C7	0.19395 (14)	0.3808 (5)	0.0871 (2)	0.0364 (10)
N8	0.15439 (10)	0.4652 (4)	0.03486 (17)	0.0258 (7)
C9	0.16265 (15)	0.4978 (5)	-0.0449 (2)	0.0376 (10)
C10	0.13058 (15)	0.6347 (5)	-0.0890 (2)	0.0361 (10)
N11	0.13749 (11)	0.8070 (4)	-0.04880 (17)	0.0288 (7)
C12	0.09649 (15)	0.9184 (5)	-0.0771 (2)	0.0417 (11)
C13	0.05087 (16)	0.8498 (6)	-0.0637 (2)	0.0468 (12)
C14	0.04746 (15)	0.8209 (5)	0.0222 (2)	0.0406 (10)
C15	0.06985 (13)	0.5147 (4)	0.0338 (2)	0.0316 (9)
C16	0.10970 (13)	0.3886 (4)	0.0361 (2)	0.0296 (9)
C17	0.17008 (15)	0.8418 (5)	0.2463 (2)	0.0373 (10)
C18	0.17671 (16)	0.8951 (5)	-0.0750 (3)	0.0486 (12)

Table 2. Selected geometric parameters (Å, °)

Pd1—N4	2.078 (3)	Pd1—Cl1	2.3407 (10)
Pd1—N11	2.101 (3)	Pd1—N8	2.461 (3)
Pd1—N1	2.112 (3)		
N4—Pd1—N11	171.65 (11)	N1—Pd1—Cl1	169.68 (8)
N4—Pd1—N1	85.07 (11)	N4—Pd1—N8	89.61 (10)
N11—Pd1—N1	91.00 (12)	N11—Pd1—N8	82.45 (10)
N4—Pd1—Cl1	89.87 (9)	N1—Pd1—N8	80.12 (10)
N11—Pd1—Cl1	95.12 (9)	Cl1—Pd1—N8	108.89 (7)

Three lattice water molecules were located, two on special positions; their H atoms were not included. They presumably derive from incompletely dried solvents. Other H atoms were added at calculated positions and refined using a riding model (including free rotation about C—C bonds for methyl groups). H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl-H atoms) times U_{eq} of the carrier atom.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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cis-Bis(cyanomethyl)bis(triphenylphosphine)platinum(II)–dichloromethane (1/0.6)

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Abstract

The cyanomethyl ligands of the title complex, cis-[Pt(CH$_2$CN)$_2$(PPh$_3$)$_2$]·0.6CH$_2$Cl$_2$, adopt a syn geometry. The Pt—C bond lengths have an average value of 2.121 (17) Å, and the C—Pt—C bond angle is 85.3 (3)°.

Comment

Silver(I) oxide promotes the synthesis of a wide range of novel metallacycles (Henderson et al., 1994; Dinger & Henderson, 1998). While attempting to synthesize metallalactone complexes using cyanoacetic acid and cis-[PtCl$_2$(PPh$_3$)$_2$], we observed instead a novel decarboxylation reaction giving the title compound, (I).

Ph$_3$P	CH$_2$—C≡N
   \ /
    Pt	·0.6CH$_2$Cl$_2$
   / \
Ph$_3$P	CH$_2$—C≡N

(I)
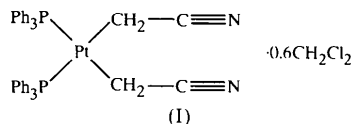
The structure of only one other bis(cyanomethyl) complex, [Ir(CH$_2$CN)$_2$(CO)$_2$][(Ph$_3$P)$_2$N], has been reported (Porta et al., 1990). Reactions of platinum(II) hydroxo complexes with CH$_3$CN, some in the presence of silver(I) oxide, gave cis-[Pt(CH$_2$CN)(X)L$_2$] complexes [X = cyclohexene, OH, Cl or CH$_3$, and L$_2$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe); Arnold & Bennett, 1980;

Cairns et al., 1977]. The facile synthesis of the complex [Pd(CH$_2$CN)$_2$(PPh$_3$)$_2$] from [PdCl$_2$(PPh$_3$)$_2$] and LiCH$_2$CN provides access to a range of aggregation and degradation products, including a ligand-free [Pd(CH$_2$CN)$_2$] complex (Pracejus et al., 1976). One anomalous result was observed in a study into the formation of platinum dicarboxylate complexes. The reaction of [Pt(CO$_3$)(PPh$_3$)$_2$] with PhC≡CCO$_2$H was found to produce the bis(phenylalkynyl) complex cis-[Pt(C≡CPh)$_2$(PPh$_3$)$_2$] by loss of CO$_2$ from both the carbonate and carboxylate groups (Burrows et al., 1997).

The platinum centre of (I) shows the expected four-coordinate square-planar environment, with the phosphine ligands in a cis arrangement. The P1—Pt—P2 bond angle is slightly more obtuse [98.09 (6)°] than perfect square-planar coordination, while the C2—Pt—C4 and C4—Pt—P2 bond angles have closed up [85.3 (3) and 85.6 (2)°, respectively]. The remaining bond angle (C2—Pt—P1) is near ideal at 90.9 (2)°. Steric considerations clearly give rise to these distortions from regular geometry. The Pt—C bond lengths [2.104 (7) and 2.138 (7) Å for Pt—C2 and Pt—C4, respectively] are comparable with, if fractionally longer than, those in the related [Pt(CH$_2$Cl)$_2$L$_2$] complexes [L$_2$ = bis(diphenylphosphino)methane (dppm) or (2S,4S)-Ph$_2$CHMeCH$_2$CHMePPh$_2$ (S,S-skewphos)] [2.069 (8)–2.109 (10) Å; Alcock et al., 1990; Bergamini et al., 1993].

The interesting feature of complex (I) is the orientation of the cyanomethyl ligands. The ligands have
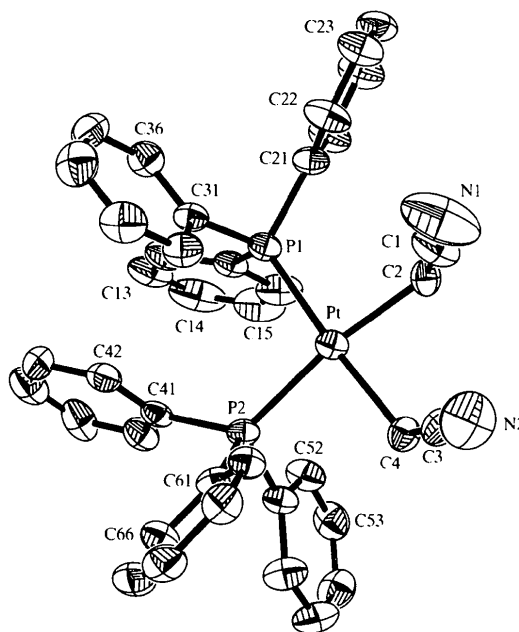

Fig. 1. The molecular structure of complex (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.