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Crystal and Molecular Structure of *cis*-dichloro-(η-ethylene)(2,6-dimethylpiperidine)platinum(II)

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In the course of a structural study of complexes of the type *trans*[$PtCl_2$(η-ethylene)L] (L = substituted pyridine), we stated that an interaction could take place between the metal orbitals and the antibonding molecular orbitals of the heteroaromatic system [1, 2].

We have since extended our study to complexes of the same type in which L is a substituted piperidine. In this way any strengthening (and then a possible shortening) of the Pt–N bond, which could be ascribed to metal to ligand back bonding, would be avoided.

In the attempt to prepare the *trans* isomer, the complex *cis*[$PtCl_2$(η-C_2H_4)(2,6-dimethylpiperidine)] was obtained. In the present note we report its structural results.

Experimental

The complex was prepared by treating an aqueous solution of Zeise's salt [3] with one equivalent of 2,6-dimethylpiperidine. This procedure, when pyridines are used, yields the *trans* isomers [4]. The precipitate was then recrystallized from a sym-dichloroethane solution, kept at –25 °C, giving a yellow crystalline product.

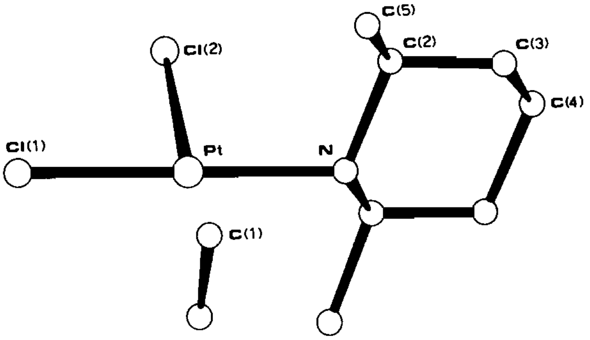

Fig. 1. Perspective view of the molecule of *cis*[$PtCl_2$(η-ethylene)(2,6-dimethylpiperidine)]. The mirror plane passes through Pt, Cl(1), Cl(2), N and C(5) bisecting the ethylene and the piperidine molecules.

The crystals of *cis*[$PtCl_2$(η-ethylene)(2,6-dimethylpiperidine)], $C_9H_{19}Cl_2NPt$, are orthorhombic, space group *Pnma*, with a = 13.201(5), b = 9.575(4), c = 9.805(4) Å, $Z = 4, d_c = 2.183, d_m > 2.0$ g cm^{-3}.

The structure was solved by the heavy atom method and refined by full-matrix least-squares to a final R value of 0.047 for 987 independent reflections having $I > 3\sigma(I)$. The fixed contribution of the hydrogen atoms, geometrically positioned [5], was included in the last cycles of refinement, during which the non-hydrogen atoms were allowed to vibrate anisotropically. The final coordinates of the non-hydrogen atoms of the asymmetric unit (half molecule) are reported in Table I.

Results and discussion

The molecule of *cis*[$PtCl_2$(η-C_2H_4)(NC_7H_{15})] has a crystallographically imposed σ symmetry; its structure is shown in Fig. 1. Interatomic bond lengths and angles are given in Table II.

TABLE I. Final Atomic Coordinates. Standard deviations are given in parentheses.

	x	*y*	*z*
Pt	0.0256(1)	0.2500	–0.1470(1)
Cl(1)	–0.0704(5)	0.2500	0.0468(6)
Cl(2)	–0.1217(4)	0.2500	–0.2792(7)
N	0.1146(13)	0.2500	–0.3260(17)
C(1)	0.1522(12)	0.3207(22)	–0.0269(15)
C(2)	0.0981(10)	0.3829(13)	–0.4101(15)
C(3)	0.1635(13)	0.3793(16)	–0.5366(17)
C(4)	0.1471(20)	0.2500	–0.6232(18)
C(5)	0.1204(15)	0.5097(17)	–0.3248(19)

TABLE II. Bond Lengths and Angles. Estimated standard deviations are given in parentheses[a].

Pt–Cl(1)	2.285(6) A	Cl(1)–Pt–Cl(2)	90.0(2)°
Pt–Cl(2)	2.337(6)	Cl(1)–Pt–N	180.0(6)
Pt–N	2.111(17)	Cl(1)–Pt–M	88.6
Pt–M	2.045	Cl(2)–Pt–N	90.1(5)
Pt–C(1)	2.15(2)	Cl(2)–Pt–M	178.5
C(1)–C(1)′	1.35(3)	N–Pt–M	91.4
N–C(2)	1.53(2)	C(1)–Pt–C(1)′	36.6(8)
C(2)–C(3)	1.51(2)	Pt–N–C(2)	111.6(8)
C(3)–C(4)	1.52(2)	C(2)–N–C(2)′	112.4(13)
C(2)–C(5)	1.50(2)	N–C(2)–C(3)	110.0(12)
		N–C(2)–C(5)	110.1(12)
		C(3)–C(2)–C(5)	111.3(13)
		C(2)–C(3)–C(4)	113.4(14)
		C(3)–C(4)–C(3)′	109.4(14)

[a] M is the midpoint of the uncoordinated double bond. Primed and unprimed symbols refer to atoms related by the mirror plane.

The platinum atom has the expected square-planar coordination with the piperidine ligand in *cis* position to the η-coordinated ethylene. The coordination plane, containing the $NPtCl_2$ framework, coincides with the crystallographic mirror plane and bisects the coordinated piperidine and ethylene molecules. The direction of the coordinated double bond is therefore exactly perpendicular to the coordination plane. The angles subtended at the metal centre coincide with, or deviate only slightly from, the regular values of 90° and 180°.

The two Pt–Cl bonds are significantly different, Pt–Cl(1) [2.285(6) Å] *trans* to the piperidine ligand being shorter (by *ca.* 8.7 σ) than Pt–Cl(2) [2.337(6) Å] which is *trans* to the ethylene. A similar difference in the Pt–Cl bond lengths was also found in the complexes *cis*[$PtCl_2$(*trans*-but-2-ene)L] [6] and *cis*[$PtCl_2$(but-1-ene)L] [7] (L = α-methylbenzylamine) and is a consequence of the *trans* influence of the η-coordinated olefins.

The Pt–N bond length [2.111(17) Å] compares well with the values [2.14(3), 2.076(15) Å] observed in the already mentioned complexes containing the α-methylbenzylamine *trans* to a chlorine atom [6, 7]. It is slightly higher than the values [average 2.025(10) Å] found in *cis*[$PtCl_2$(pyridine)$_2$] containing the heteroaromatic amines *trans* to chlorine atoms [8].

Bond lengths and angles in the piperidine ligand are quite regular. The piperidine ring maintains its chair conformation with the internal torsion angles equal to −54.2(17), 55.3(18) and −55.5(22)°, starting from the N–C(2) bond. The two methyl groups and the Pt atom are bonded to the piperidine ring in equatorial positions.

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5 C–H = 1.0 A, C–C–H = 120° (sp^2), H–C–H = 109.5° (sp^3); each hydrogen atom was assigned the isotropic thermal parameter of the carbon atom to which it is attached. The positions of the atoms were readjusted after each cycle of refinement.

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