The Crystal and Molecular Structure of Chloro-(2-methoxycyclo-octa-1,5-dienyl)pyridineplatinum

By C. PANATTONI, G. BOMBIERI, E. FORSELLINI, and B. CROCIANI

(Istituto di Chimica Generale and Centro di Strutturistica, Università di Padova, Via Loredan 4, Padova, Italy)

and U. BELLUCO*†

(Istituto di Chimica Organica e di Chimica Industriale, Universita di Bologna, Italy)

DIMERS of the type [PtLCl]$_2$ [L = methoxy-cyclo-octa-1,5-diene (codOMe) and cyclopentadiene dimer (cpdOMe)] undergo bridge-splitting reactions by treatment with neutral ligands L.[1,2] A recent X-ray investigation on the chloro-bridged dimer [Pt (cpdOMe)Cl]$_2$ has shown that the central metal is linked to the organic moiety through both a σ and a π olefinic bond.[3] The position of the ligand relative to the two 'teeth' of the bidentate ligand was uncertain.

MeO ⎯⎯ L   MeO ⎯⎯ Cl
      Pt   Pt
⎯⎯ Cl   ⎯⎯ L
   (I)   (II)
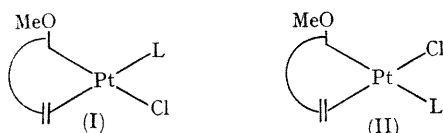
A crystal structure determination of [Pt(CodOMe) py Cl] was therefore undertaken. The compound crystallizes in the space group $P2_1/c$ with $a = 9.84 \pm 0.02$, $b = 18.52 \pm 0.04$, $c = 8.15 \pm 0.02$ Å; $\beta = 104° \pm 20'$ and $Z = 4$. A total of 1470 independent reflections were collected with Cu-K_α radiation by the multiple film equi-inclination Weissenberg technique for reciprocal lattice levels 0–8 kl. The structure was solved by the heavy-atom method and refined by Fourier and block-diagonal least-squares methods to R 11·1 for all observed intensities with individual isotropic thermal parameters for all atoms. The molecular configuration is shown in the Figure.

The environment of the platinum atom is essentially square-planar with the chlorine atom trans to the π-olefinic bond and the pyridine trans to the Pt–C(10) σ-bond (structure II). The σ bond-length, Pt–C(10) (2·04 Å), is very close to that found in the dimer [Pt(cpdOMe)Cl]$_2$,[3] and in the dehydrohexamethyl Dewar benzene Pt^{II} complex, [Pt(C$_{12}$H$_{17}$)Cl]$_2$.[4] This occurs also for the Pt–C(6) and Pt–C(7) bond distances of the π-olefinic bond (2·16 Å).

The far i.r. spectrum of [Pt(CodOMe) py Cl] is consistent with the structure shown in the Figure. The ν(Pt–Cl) stretch at 300 cm.$^{-1}$ is very close to ν(Pt-Cl) for Cl trans to the ethylene in Zeise's salt (307 cm.$^{-1}$).[5] This similarity is reflected also in the Pt–Cl bond distances which are 2·345 and 2·40 Å respectively.[6] Owing to the high trans effect of the σ-bonded carbon, the pyridine is easily replaced by other neutral ligands, such as p-toluidine, triarylphosphine, etc. Although the structure of these reaction products cannot be asessed with certainty, i.r. data indicate that structure (II)
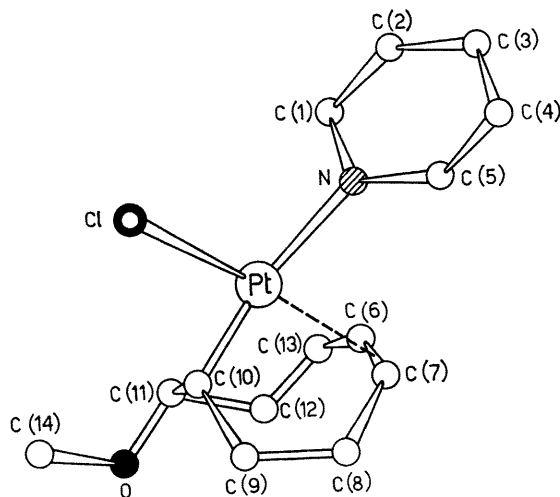

FIGURE. Molecular configuration of chloro-(2-methoxycyclo-octa-1,5-dienyl)pyridineplatinum.

Bond distances		Angles	
Pt–Cl	2·345 (10)	Cl–Pt–N	87° (1)
Pt–N	2·16 (3)	Cl–Pt–C(10)	91° (1)
Pt–C(6)	2·17 (4)	C(11)–C(10)–Pt	106° (2)
Pt–C(7)	2·16 (4)	C(9)–C(10)–Pt	107° (2)
Pt–C(10)	2·04 (3)	C(7)–Pt–C(6)	40° (2)
		Cl–Pt–C(7)	162° (1)

is retained for p-toluidine [ν(Pt–Cl) = 301 cm.$^{-1}$], whereas structure (I) should be extant for triphenylphosphine [ν(Pt–Cl) = 274 cm.$^{-1}$], when the Pt–Cl stretching frequency corresponds to that of a chloride in the trans position to a platinum–carbon σ-bond (270—283 cm^{-1}).[7,8]

† Present address: as for other authors at Padova.

[1] J. Chatt, M. L. Vallarino, and M. L. Venanzi, J. Chem. Soc., 1957, 2496, and 3413.
[2] J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, J. Amer. Chem. Soc., 1965, 87, 3282.
[3] W. A. Whitla, H. M. Powell, and L. M. Venanzi, Chem. Comm., 1966, 310.
[4] R. Mason, G. B. Robertson, P. O. Whim, B. L. Shaw, and G. Shaw, Chem. Comm., 1968, 868.
[5] M. J. Grogan and K. Nakamoto, J. Amer. Chem. Soc., 1966, 88, 5454.
[6] G. E. Bokii and G. A. Kukina, Kristallografiya, 1957, 2, 395.
[7] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, J. Chem. Soc., 1964, 734.
[8] P. L. Goggin and R. J. Goodfellow, J. Chem. Soc. (A), 1966, 1462.