

Crystal and Molecular Structure of the Butadiene Complex $[\text{NMe}_3\text{Et}]_2[\text{Pt}_2\text{Cl}_6(\text{C}_4\text{H}_6)]^{2-}$

By VIVIENNE C. ADAM, J. A. J. JARVIS, B. T. KILBOURN, and P. G. OWSTON*

(Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire)

Summary In the complex anion $[\text{Pt}_2\text{Cl}_6(\text{C}_4\text{H}_6)]^{2-}$ the two planar (PtCl_3) groups are linked by a *trans*-butadiene bridge in which the central C-C bond is shorter than the two terminal bonds; the bonding between platinum and the butadiene ligand is similar to the π -type bond in Zeise's salt.

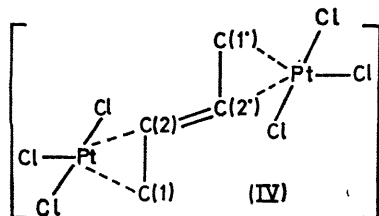
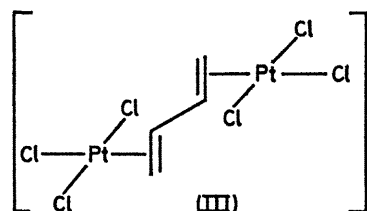
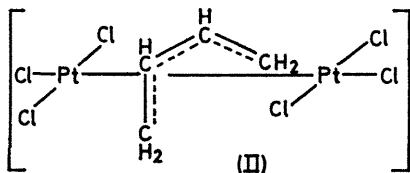
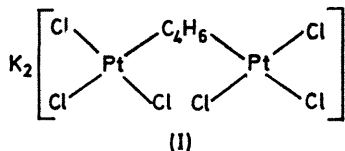
SLADE and JONASSEN¹ first prepared the butadiene complex $\text{K}_2[\text{Pt}_2\text{Cl}_6(\text{C}_4\text{H}_6)]$, and pointed out its great stability compared with other butadiene complexes of transition metals; they formulated it as (I). Chatt, Johnson, and Shaw² proposed the structure (II), analogous to that of $[\text{Fe}(\text{CO})_3\text{C}_4\text{H}_6]$ in which the butadiene can be regarded as a *cis*-conjugated hydrocarbon.³ Grogan and Nakomoto,⁴ however, interpreted their i.r. results as favouring the *trans*-diene structure (III) in which the co-ordination is similar to that in Zeise's salt.

We have prepared a series of salts $\text{M}_2[\text{Pt}_2\text{Cl}_6(\text{C}_4\text{H}_6)]$, ($\text{M} = \text{K}, \text{Na}, \text{Cs}, \text{NH}_4, \text{NEt}_4, \text{and NEtMe}_3$; $\text{M}_2 = \text{Ca}$). To a stirred, nearly saturated solution of the potassium salt, prepared by Slade and Jonassen's method, in 5% aqueous HCl, solid MCl was added until an orange-yellow precipitate was formed; this was recrystallised by slow evaporation of a solution in 5% aqueous HCl. For substituted ammonium salts, acetone-5% aqueous HCl (1:1) was used. Crystals of the complexes with $\text{M} = \text{Na}, \text{K}, \text{Cs}, (\text{NEt}_4)$, and Ca , though visually satisfactory, showed evidence of disorder when X-ray photographs were taken. Only the complex $\text{M} = \text{NEtMe}_3$ proved suitable for X-ray work.

Crystal Data: $\text{C}_{14}\text{H}_{34}\text{N}_2\text{Cl}_6\text{Pt}_2$, $M = 833.6$; monoclinic, $a = 5.996(3)$, $b = 10.528(2)$, $c = 20.233(4)$ Å, $\beta = 101.09(3)$, $U = 1253.3$ Å³; $D_m = 2.215$ (by flotation), $Z = 2$, $D_c = 2.208$, $F(000) = 780$, space group $P2_1/c$, μ (Mo- K_α) = 124.1 cm⁻¹.

The structure was solved and refined by standard

methods using 1175 reflections for which $|F| > 20\sigma$ and $\sin \theta/\lambda < 0.60$, on a four-circle diffractometer; corrections for absorption and anomalous dispersion were applied, and refinement converged to $R = 0.052$.



The structure of the $[\text{Pt}_2\text{Cl}_6(\text{C}_4\text{H}_6)]^{2-}$ ion is at first sight that of formula (III). It is centro-symmetric with the bond-lengths and angles as in the Table. The butadiene molecule is *trans*-planar. Each terminal C-C bond forms a π -type bond with a platinum atom, similar to that in Zeise's salt.⁵ The bonding of the platinum atom also resembles that in Zeise's salt in other ways: the three chlorine atoms and the centre of the C-C bond are almost

coplanar; the C-C bond is inclined at 81° to this co-ordination plane rather than exactly at 90° and the Pt-Cl bond-length *trans* to the hydrocarbon is not significantly different

TABLE

Pt-Cl <i>cis</i> to butadiene ..	2.32(1), 2.29(1) Å
<i>trans</i> to butadiene ..	2.29(1)
C(1)-C(2)	1.51(3)
C(2)-C(2)'	1.36(3)
Pt-C(1)	2.20(3)
Pt-C(2)	2.18(2)
C-C-C	118(2)°

from that of the two *cis*-bonds. The C-C bond-lengths, however, indicate that the structure can be represented as (IV) rather than (III), since the two terminal C-C bonds are approximately single and the central C-C bond is approximately a double bond. This structure suggests that co-ordination involves 1,4 addition to the butadiene, but there is no evidence that the terminal carbon atoms differ from the central ones either in their degree of interaction with the platinum atoms or in their chemical reactivity.

Other complexes are known^{6,7} in which the central bond of a butadiene or butadiene-like molecule, co-ordinated to a metal atom, is shorter than the terminal bonds. It has been suggested that an alternation of bond-lengths in the opposite sense to that in the free ligand indicates a bonding state similar to that in the first excited state of the ligand.⁶ In these complexes,^{6,7} however, the *cis*-conformation is adopted, and the 'butadiene fragment' is co-ordinated to one metal atom only. A *trans*-conformation in a butadiene molecule linked to two metal atoms occurs⁸ in $[\{(\text{C}_5\text{H}_5)(\text{CO})_2\text{Mn}\}_2\text{C}_4\text{H}_6]$; here the central C-C bond is longer (1.50 Å) than the terminal bonds (1.43 Å).

The $(\text{NMe}_3\text{Et})^+$ group is an independent ion, with no evidence of specific interaction between it and the complex anion. There is some disorder in the positions of the carbon atoms of the ethyl group; two alternative conformations appear equally possible.

Copies of the tables of bond-lengths and angles, atomic parameters, and structure factors may be obtained, on request from the authors.

(Received, November 30th, 1970; Com. 2064.)

¹ P. E. Slade and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1957, **79**, 1277.

² J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1662.

³ O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 1960, 421.

⁴ M. J. Grogan and K. Nakamoto, *Inorg. Chim. Acta*, 1967, **1**, 228.

⁵ J. A. J. Jarvis, B. T. Kilbourn, and P. G. Owston, *Acta Cryst. B*, in the press.

⁶ M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1967, **A301**, 433.

⁷ L. Parri, G. Vitelli, M. Zocchi, and G. Allegra, *Chem. Comm.*, 1969, 276; V. G. Adrianov, V. P. Martinov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *ibid.*, 1970, 1252.

⁸ M. Ziegler, *Zeit. Anorg. Allgem. Chem.*, 1967, **355**, 12.