Contribution from the Department of Chemistry,
Illinois Institute of Technology,
Technology Center, Chicago, Illinois, 60616, U.S.A.

Far-Infrared Spectra of Metal-Olefin Complexes. I.
Potassium μ-1,3-Butadiene-Bis(Trichloroplatinate(II))[1a]

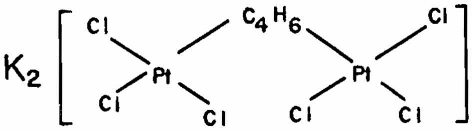
M. J. Grogan[1b] **and K. Nakamoto**

Received July 20, 1967

The infrared and Raman spectra of $K_2[(PtCl_3)_2(C_4H_6)]$ have been obtained in the crystalline state. The infrared spectrum of this complex in the high frequency region is similar to that of free butadiene (transoid configuration) and is markedly different from that of $Fe(CO)_3(C_4H_6)$ where butadiene is planar-cisoid. The infrared spectrum of the Pt(II) complex in the low frequency region is strikingly similar to that of Zeise's salt. Based on these observations, a new structure of the Pt(II) complex has been proposed in which the symmetrical transoid butadiene molecule is sandwiched between two $PtCl_3$ groups.

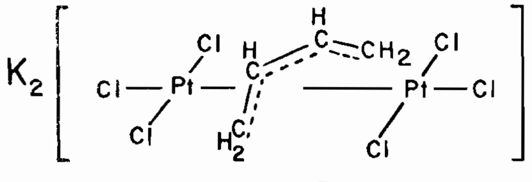
Introduction

The infrared spectrum of $K_2[(PtCl_3)_2(C_4H_6)]$[2a] from 4000 to 650 cm^{-1} has been observed by several investigators. Slade and Jonassen[3] suggested a stucture in which both the C=C bonds of butadiene are involved in coordination (Structure A).



Structure A

Although the bonding between butadiene and the Pt atoms is not clear in this structure, Chatt[4,5] proposed a sandwhich structure (Structure B) in which the butadiene molecule takes the cisoid configuration and lies between the two Pt atoms:



Structure B

Hendra and Powell[6] have reported the infrared spectrum of the Pt complex from 4000 to 400 cm^{-1}. However, their results could not provide any new information about the structure and bonding of this complex.

The purpose of this work is to elucidate the structure of the Pt(II) butadiene complex based on its infrared and Raman spectra.

Experimental Section

Preparation of Compounds. $K_2[(PtCl_3)_2(C_4H_6)]$ was prepared from $K_2[PtCl_4]$ according to the method described by Chatt.[5] Anal : Calcd. for $K_2[(PtCl_3)_2(C_4H_6)]$: C, 6.53; H, 0.82; Cl, 28.9. Found: C, 6.02; H, 1.12; Cl, 27.8. $Fe(CO)_3(C_4H_6)$[2b] was purchased from Alfa Inorganics, Inc., Beverly, Mass., and was used without purification.

Spectral Measurements. The infrared spectrum of $K_2[(PtCl_3)_2(C_4H_6)]$ was observed from 4000 to 500 cm^{-1} on a Beckman IR 12 infrared spectrophotometer using the KBr pellet technique, and from 600 to 50 cm^{-1} on a Beckman IR 11 far-infrared spectrophotometer using Nujol mull between polyethylene plates. The Raman spectrum (solid phase) was observed on a Cary Model 81 Raman spectrophotometer with a He-Ne gas laser. The infrared spectrum of $Fe(CO)_3(C_4H_6)$ was observed on a Beckman IR 12 infrared spectrophotometer with a CsI capillary cell.

Results and Discussion

Butadiene at room temperature is in the symmetric trans configuration[7] (C_{2h} symmetry), and its normal vibrations are grouped into $9A_g$, $4A_u$, $3B_g$ and $8B_u$ species. Table I lists the observed infrared and Raman frequencies of these twenty-four normal vibrations and their band assignments as given by Harris.[8] In the third column of Table I, we have listed the observed infrared frequencies of butadiene in $K_2[(PtCl_3)_2(C_4H_6)]$. These band assignments have been made by assuming that the frequency order observed for free butadiene holds for the complex, except the CH_2 wagging and

---

[1] (a) This work was supported by Grant 2096-A3,5 from the Petroleum Research Fund. To be submittend by M. J. Grogan to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree, Doctor of Philosophy. (b) Present address: Shell Chemical Company, Plastic Technical Center, Woodbury, New Jersey 08096.

[2] (a) Potassium μ-1,3-butadiene-bis(tricholoroplatinate(II)). (b) Tricarbonyl(butadiene)iron(O).

[3] P. E. Slade Jr. and H. B. Jonassen, *J. Am. Chem. Soc.*, *79*, 1277 (1957).

[4] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2039 (1953).

[5] J. Chatt, Conf. Inorg. Chem. Varenna 1959, Accadamia Najionale dei Tircei, p. 161 (1961).

[6] P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, *18*, 1195 (1962).

[7] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Chem. Phys.*, *11*, 432 (1943).

[8] R. K. Harris, *Spectrochim. Acta*, *20*, 1129 (1964).

Table I. Observed Butadiene Frequencies and their Band Assignments for Free State, $K_2[(PtCl_3)_2(C_4H_6)]$ and $[Fe(CO)_3(C_4H_6)]$ (cm^{-1})*

	C_4H_6 (IR and R)	$K_2[(PtCl_3)_2(C_4H_6)]$ (IR)	$Fe(CO)_3(C_4H_6)$ (IR)	Assignment
ν_1	3102 (IR)	3070 (m)	3060 (m)	$\nu(=CH_2)$
ν_2	3101 (R)	3060 (w, sh)	3060 (m)	$\nu(=CH_2)$
ν_3	3056 (IR)	3010 (w)	3005 (m)	$\nu(=CH)$
ν_4	3014 (R)	2995 (w, sh)	2960 (w)	$\nu(=CH)$
ν_5	3014 (R)	2985 (w, sh)	2960 (w)	$\nu(=CH_2)$
ν_6	2985 (IR)	2945 (w)	2920 (m)	$\nu(=CH_2)$
ν_7	1643 (R)	1521 (w)	?	$\nu(C=C)$
ν_8	1599 (IR)	1471 (s)	1479 (s)	$\nu(C=C)$
ν_9	1442 (R)	1402 (vw)	1443 (m)	$\delta(=CH_2)$
ν_{00}	1385 (IR)	1340 (w)	1368 (m)	$\delta(=CH_2)$
ν_{11}	1285 (IR)	1238 (m)	1201 (s)	$\delta(=CH)$
ν_{12}	1279 (R)	1310 (vw)	1170 (m)	$\delta(=CH)$
ν_{13}	1205 (R)	1205 (vw)	1049 (s)	$\nu(C\text{-}C)$
ν_{14}	1013 (IR)	849 (vs)	790 (m)	$\rho_t(=CH_2)$
ν_{15}	987 (IR)	959 (vs)	925 (m)	$\rho_r(=CH_2)$
ν_{16}	967 (R)	810 (w)	772 (w)	$\rho_t(=CH_2)$
ν_{17}	910 (R)	1039 (s)	975 (m)	$\rho_w(=CH_2)$
ν_{18}	909 (IR)	1008 (vs)	951 (m)	$\rho_w(=CH_2)$
ν_{19}	890 (R)	888 (w)	895 (m)	$\rho_r(=CH_2)$
ν_{20}	686 (R)	---	668 (s)	π(skeletal)
ν_{21}	520 (IR)	553 (s)	510 (vs)	π(skeletal)
ν_{22}	513 (R)	---	493 (m, sh)	$\delta(C=C\text{-}C)$
ν_{23}	301 (IR)	305 (sh)	380 (m)	$\delta(C=C\text{-}C)$
ν_{24}	163 (IR)	162 (sh)	135 (w)	ρ_t(skeletal)

* s, strong; m, medium; w, weak; sh, shoulder; vs, very strong; vw, very weak; ν, stretching; δ, bending; π, out-of-plane bending; ρ_w, wagging; ρ_r, rocking; ρ_t, twisting; IR, infrared; R, Raman.

twisting modes. According to our previous work on Zeise's salt,[9] the frequency order of these two modes is reserved upon coordination to the Pt atom. Thus, the CH_2 wagging frequencies are higher than the CH_2 twisting modes in Table I. It is interesting to note that the C-H stretching frequencies ($\nu_1 \sim \nu_6$) are slightly lowered and the C=C stretching frequencies (ν_7 and ν_8) are lowered by ca. 125 cm^{-1} upon coordination of butadiene to the Pt atoms.

In general, the infrared active modes of free butadiene appear relatively strongly and the Raman active modes appear relatively weakly in the Pt complex. Thus, these results support the local symmetry of C_{2h} for the butadiene molecule in the Pt complex. As is shown in Table I, several bands which should be forbidden under C_{2h} smmetry appear weakly, probably because the over-all symmetry of the complex ion is lower than C_{2h}.

The infrared frequencies of $Fe(CO)_3(C_4H_6)$ in which butadiene is definitely cis-planar[10] are listed in the fourth column of Table I. Figure 1 compares the infrared spectrum of this complex with that of the Pt complex in the region from 4000 to 300 cm^{-1}. The former exhibits several strong CO stretching bands near 2000 cm^{-1} and the C-Fe-C bending modes near 600 cm^{-1}. It is seen that the Fe complex exhibits much more bands than the Pt complex in the region between 1500 and 700 cm^{-1}. The Fe complex exhibits three bands (ν_3, ν_9 and ν_{10}) between 1500 and 1350 cm^{-1}, whereas the Pt complex shows only one band (ν_8) in the same region. Two bands are seen at 1201 (ν_{11}) and 1170 cm^{-1} (ν_{12}) for the Fe complex, whereas only one band (1238 cm^{-1}) is present in the Pt complex. It is also seen that two

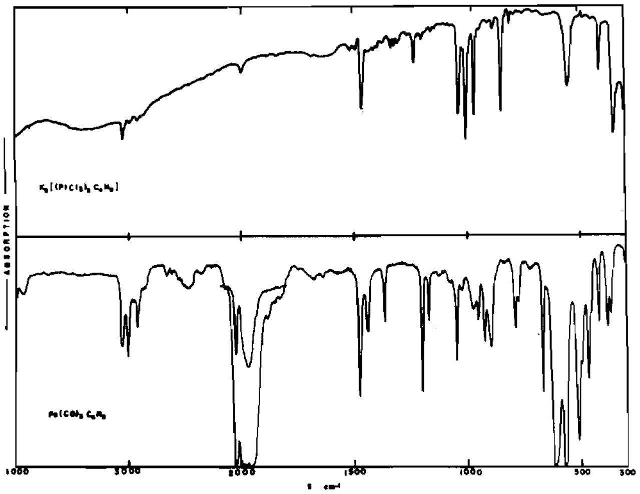


Figure 1. Infrared spectra of $K_2[(PtCl_3)_2C_4H_6]$ and $Fe(CO)_3$-C_4H_6.

bands at 975 and 951 cm^{-1} of the Fe complex correspond to the 1008 cm^{-1} (ν_{18}) of the Pt complex, and that two bands at 925 and 895 cm^{-1} of the Fe complex correspond to the 959 cm^{-1} band (ν_{15}) of the Pt complex. These spectral differences between the two complexes can be accounted for satisfactorily if the planar-transoid structure is assigned to the butadiene molecule of the Pt complex.

Figure 2 compares the infrared spectrum of $K_2[(PtCl_3)_2(C_4H_6)]$ with that of Zeise's salt, $K[Pt(C_2H_4)Cl_3]H_2O$ [9] below 550 cm^{-1}. The similarity of these two spectra is striking. This is more clearly demonstrated by the comparison of observed frequen-

---

(9) M. J. Grogan and K. Nakamoto, *J. Am. Chem. Soc.*, *88*, 5454 (1966).

(10) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960).

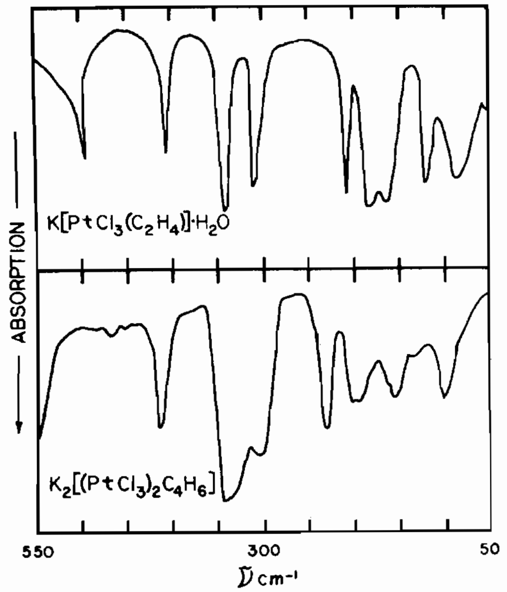
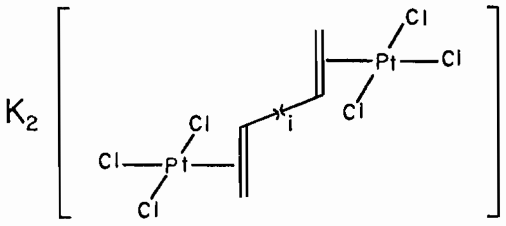


Figure 2. Infrared spectra of K[PtCl$_3$(C$_2$H$_4$)]H$_2$O and K$_2$[(PtCl$_3$)$_2$C$_4$H$_6$].

Table II. Observed Skeletal Frequencies of K$_2$[(PtCl$_3$)$_2$(C$_4$H$_6$)] and K[PtCl$_3$(C$_2$H$_4$)] . H$_2$O

K$_2$[(PtCl$_3$)$_2$(C$_4$H$_6$)] IR	R	[KPtCl$_3$(C$_2$H$_4$)] . H$_2$O IR	Assignment[9]
---	---	493 (s)	H$_2$O
415 (s)	415 (w)	407 (s)	ν(Pt-olefin)
339 (vs) 332 (vs) 308 (s)	350 (s) 335 (m) 298 (w)	339 (vs) 331 (vs) 310 (s)	ν(Pt-Cl)
231 (s)	237 (m)	210 (s)	δ(Pt-olefin)
203 (s) 155 (s)	206 (m) 187 (sh)	183 (s) 161 (s)	δ(PtCl$_2$)
128 (w)	---	121 (m)	π(Pt-olefin)
101 (m)	---	92 (m)	π(skeletal)

cies listed in Table II. In our previous paper,[9,11] we have noted that the Pt-olefin stretching bands appear between 420 and 380 cm^{-1}. The butadiene Pt(II) complex exhibits only one band in this region (415 cm^{-1}), and, therefore, must have a center of symmetry. This result together with those obtained in the high frequency region leads to a new structure shown below :



Structure C

This structure consists of two units of Zeise's anion bonded through the C-C bond. The butadiene molecule thus formed has a center of symmetry at the midpoint of the C-C bond. (C$_i$ symmetry). Since the local symmetry of butadiene in this structure is C$_{2h}$, its high-frequency infrared spectrum is similar to that of free butadiene. Its low-frequency spectrum is similar to that of Zeise's salt, since it consists of two units of Zeise's anion connected through a center of symmetry. Thus, structure C can best account for all the spectroscopic observations.

Acknowledgement. The Beckman IR 11 far-infrared spectrophotometer used in this investigation was purchased by a NSF research equipment grant (GP-5417). The Raman spectrum of solid butadiene platinum complex was obtained by Dr. H. Haber of Cary Instruments, Monrovia, California.

(11) M. J. Grogan and K. Nakamoto, to be published.