Table I. Identity of the Principal Peaks in the Mass Spectrum of $HMn(CO)_5$

m/e	Identity
197	$HMn(CO)_4(^{13}CO)^+$
196	$HMn(CO)_5{}^+$
195	$Mn(CO)_5{}^+$
168	$HMn(CO)_4{}^+$
167	$Mn(CO)_4{}^+$
140	$HMn(CO)_3{}^+$
139	$Mn(CO)_3{}^+$
112	$HMn(CO)_2{}^+$
111	$Mn(CO)_2{}^+$
84	$HMn(CO)^+$
83	$Mn(CO)^+$
70	$HMn(CO)_3{}^{2+}$
69.5	$Mn(CO)_3{}^{2+}$
56	HMn^+, $HMn(CO)_2{}^{2+}$
55.5	$Mn(CO)_2{}^{2+}$
55	Mn^+
42	$HMn(CO)^{2+}$
41.5	$Mn(CO)^{2+}$
29	$^{13}CO^+$
28	CO^+
13	$^{13}C^+$
12	$^{12}C^+$

the loss of hydrogen and of neutral CO fragments are competitive processes.

The infrared spectra of $HMn(CO)_5$ and $DMn(CO)_5$ have been discussed by several investigators.[15–18] While no complete vibrational assignment has been made, Edgell, *et al.*,[15] and Cotton, *et al.*,[16] have identified the bands at 1783 cm^{-1} in the hydride and 1287 cm^{-1} in the deuteride as being due to a vibration primarily MnH stretching in character. From this evidence for a MnH bond, Edgell, *et al.*,[15] have estimated that the Mn–H stretching force constant is about 1.87 mdynes/A. Force field calculations on a number of related metal carbonyls show that M–C stretching force constants fall in the range 2.0–2.7 mdynes/A. Thus, the presence of a Mn–H bond and a competitive loss of H and CO fragments from $HMn(CO)_5$ are in keeping with conclusions from infrared investigations.

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Infrared Spectra and Normal Coordinate Analysis of Metal–Olefin Complexes. I. Zeise's Salt Potassium Trichloro(ethylene)platinate(II) Monohydrate[1]

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Abstract: To date the majority of infrared studies on platinum–olefin complexes have been limited to the NaCl region and particularly to the C=C stretching vibration. The present study was undertaken primarily to assign the platinum–olefin stretching vibration and to estimate the relative strength of the platinum–olefin bond in terms of force constants. For this purpose we have measured the infrared spectra of Zeise's salt, $K[Cl_3Pt(C_2H_4)]\cdot H_2O$, and its deuterio analog, $K[Cl_3Pt(C_2D_4)]\cdot H_2O$, from 4000 to 33 cm^{-1}, and have carried out approximate normal coordinate analysis for coordinated ethylene of V_h symmetry and for the remaining square-planar complex ion, in which the ethylene molecule is treated as a single atom having the mass of C_2H_4 or C_2D_4. The results indicate that the platinum–olefin stretching band is at 407 cm^{-1} (nondeuterated compound) and the corresponding force constant is 2.23 mdynes/A including repulsive force constants between nonbonded atoms. It has also been found that the C=C stretching vibration is coupled with the in-plane CH_2 scissoring vibration. This result suggests that the lowering of the C=C stretching frequency upon coordination can be used only as a qualitative measure of the strength of the platinum–olefin bond.

The infrared spectrum of Zeise's salt, $K[Cl_3Pt(C_2H_4)]\cdot H_2O$,[2a] has been observed by many investigators.[3,4] Chatt and Duncanson[3a] observed the infrared spectra of Zeise's salt and the dimer, $[Cl_2Pt(C_2H_4)]_2$,[2b] from 4000 to 650 cm^{-1}. From a comparison of the C–H stretching frequencies in saturated and

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(2) (a) Potassium trichloro(ethylene)platinate(II) monohydrate; (b) *sym-trans*-di-μ-chloro-dichlorobis(ethylene)diplatinum(II); (c) *sym-trans*-di-μ-chloro-dichlorobis(ethylene)dipalladium(II); (d) *trans*-dichloro(ammine)(ethylene)platinum(II).

(3) (a) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953); (b) H. B. Jonassen and J. E. Field, *J. Am. Chem. Soc.*, **79**, 1275 (1957); (c) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

(4) S. I. Shupack and M. Orchin, *Inorg. Chem.*, **3**, 374 (1964).

unsaturated hydrocarbons they concluded that, upon coordination to platinum, ethylene has scarcely been altered. In Zeise's dimer they found a very weak band at 1506 cm^{-1} and assigned it to the C═C stretching vibration, which upon coordination is shifted to a lower frequency by 117 cm^{-1}. Although this band was too weak to be observed in Zeise's salt, they concluded that the existence of this band in the spectrum of the dimer is evidence of the loss of a center of symmetry by the olefin. To explain the type of bonding necessary for this complex they proposed the well-known bonding scheme which requires that coordinated ethylene be orientated perpendicular to the plane of the $PtCl_3$ group. Later X-ray diffraction studies[5–7] have shown that coordinated ethylene is indeed perpendicular to the $PtCl_3$ group. Chatt and Duncanson also postulated that the hydrogen atoms in coordinated ethylene may deviate from the C_2H_4 plane.

Jonassen and Field[3b] observed the infrared spectra of Zeise's salt, Zeise's dimer, and some analogous compounds of butene-1 and isobutene, from 4000 to 650 cm^{-1}. A weak band was observed in all these compounds around 1500 cm^{-1}, and this band was assigned to the C═C stretching vibration. Using a simple two-body calculation, Jonassen and Field concluded that butene-1 upon coordination to platinum retains approximately 83% of its double bond character. Powell and Sheppard[3c] observed the infrared spectra of Zeise's salt, Zeise's dimer, the palladium analog of the dimer, $[Cl_2Pd(C_2H_4)]_2$,[2c] and the *trans*-ammine analog of Zeise's salt, $[Cl_2Pt(C_2H_4)(NH_3)]$,[2d] from 4000 to 400 cm^{-1}. By comparing the infrared spectrum of Zeise's salt with that of ethylene sulfide, they attempted to assign all the observed bands of Zeise's salt on the basis of C_{2v} symmetry, *i.e.*, with the four hydrogen atoms deviating equally from the C_2H_4 plane. Powell and Sheppard concluded that the fundamental frequencies of ethylene change only slightly upon coordination to the metal and suggested that a weak band near 400 cm^{-1} may be due to a stretching vibration associated with the platinum–ethylene bond. Recently, Shupack and Orchin[4] observed the infrared spectrum of Zeise's salt from 665 to 303 cm^{-1}. They assigned only one band, platinum–chlorine stretching at 330 cm^{-1}.

The main purpose of this investigation was to carry out an approximate normal coordinate analysis of Zeise's salt and its deuterio analog, to assign all the infrared bands, and to estimate the platinum–ethylene stretching force constant.

Experimental Section

Preparation of Compounds. $K[Cl_3Pt(C_2H_4)]\cdot H_2O$. This compound was prepared from $K_2[PtCl_4]$ according to the method described by MacNevin, *et al.*[8]

Anal. Calcd for $K[Cl_3Pt(C_2H_4)]\cdot H_2O$: C, 6.21; H, 1.55; Cl, 27.4. Found: C, 7.07; H, 1.36; Cl, 28.2.

$K[Cl_3Pt(C_2D_4)]\cdot H_2O$. $K_2[PtCl_4]$, 2.0 g, was dissolved in 30 ml of a 10% aqueous HCl solution. This solution was filtered to remove any $K_2[PtCl_6]$ and Pt. The filtrate was placed in a glass reaction vessel equipped with a high-pressure Teflon stopcock. The reaction vessel was evacuated and brought to Dry Ice–acetone temperature. C_2D_4 (purchased from Merck Sharp and Dohme, Montreal, Canada) was admitted to the reaction vessel. The reaction was continued for 4 days at room temperature until the solution had changed from red to yellow. The solution was removed from the reaction vessel, filtered, and placed in a crystallizing dish. This dish was placed in a vacuum desiccator over sulfuric acid and KOH pellets. Large yellow crystals were formed in 3 days at reduced pressure.

Anal. Calcd for $K[Cl_3Pt(C_2D_4)]\cdot H_2O$: C, 6.50; H, D, 2.57; Cl, 27.2. Found: C, 6.75; H, D, 2.57; Cl, 27.4.

Spectral Measurements. The infrared spectra from 4000 to 200 cm^{-1} were observed using a Beckman IR 12 spectrometer, and those from 500 to 33 cm^{-1} were obtained with a Beckman IR 11 far-infrared spectrometer. The regions between 4000 and 650 cm^{-1} and between 650 and 200 cm^{-1} were observed using the KBr pellet method and the Nujol mull technique with CsI plates, respectively. For the far-infrared (200 to 33 cm^{-1}) region the solid sample was mixed with polyethylene powder and fused into a melt.

Procedure of Calculation

Ethylene has 12 ((3 × 6) − 6) fundamental vibrations, and its lowest frequency mode,[9] the CH_2 rocking, absorbs at 810 cm^{-1}. The vibrational frequencies of ethylene are not expected to change markedly unless drastic changes occur in its structure and bonding. It is, therefore, safe to assume that all the ethylene vibrations will occur above 600 cm^{-1}. On the other hand, the $PtCl_3$ group has six ((3 × 4) − 6) vibrations, and the Pt–Cl stretching and the Cl–Pt–Cl bending vibrations are known to absorb in the regions 340–300 and 200–90 cm^{-1}, respectively.[10] Zeise's anion, $Cl_3Pt(C_2H_4)^-$, has 24 ((3 × 10) − 6) vibrations. This means that upon coordination of ethylene to the $PtCl_3$ group six new vibrations will be activated in addition to the 18 vibrations mentioned above. These six vibrations correspond to three translational and three rotational motions of the ethylene molecule with respect to the $PtCl_3$ group. It is evident that one of the translational motions along the Cl–Pt–C_2H_4 axis is the Pt–C_2H_4 stretching mode, and all the other five vibrations can be regarded as the bending modes of various types, which are expected to absorb at lower frequencies than the Pt–C_2H_4 stretching mode.

We have carried out normal coordinate analysis separately on the ethylene molecule, and on the square-planar $[PtCl_3(C_2H_4)]^-$ ion with C_2H_4 regarded as a single atom. This separation is justifiable since very little coupling is expected between the vibrations of the ethylene molecule (3100–810 cm^{-1}) and those of the $PtCl_3$ group (340–90 cm^{-1}). The Pt–C_2H_4 stretching may, however, appear between these two frequency ranges, and other bending modes activated by coordination may appear in a frequency range similar to that of the Cl–Pt–Cl bending modes (below 200 cm^{-1}).

A. Coordinated Ethylene. As stated previously, Chatt and Duncanson[3a] suggested that the hydrogen atoms of the coordinated ethylene in Zeise's salt may deviate from the C_2H_4 plane. On the other hand, Bokii and Kukina[7] have suggested that coordinated ethylene may be completely planar. Unfortunately, X-ray diffraction studies[5,7] of Zeise's salt have not been able either to locate the position of the hydrogen atoms or to determine the C═C distance accurately. We have, therefore, assumed that coordinated ethylene retains a planar configuration of V_h symmetry, although the

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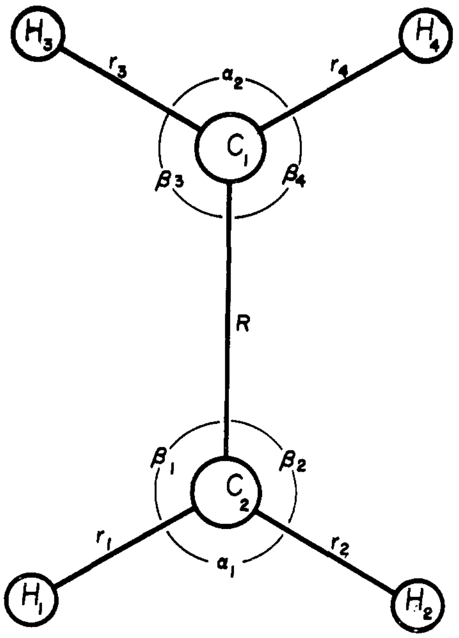

Figure 1. Structure and internal coordinates of coordinated ethylene.

C=C and the C—H bonds are slightly lengthened. The C=C distance in ethylene is 1.334 A.[11] According to Baenziger, *et al.*,[12] the C=C distance of norbornadienepalladium chloride is lengthened by 0.03 A upon coordination. Therefore, the C=C distance of the coordinated ethylene in Zeise's salt was estimated to be 1.364 A. The C—H distance depends upon the bond order of the C=C bond to which it is attached. In the present case, we estimate it to be 1.089 A assuming the C=C double bond character calculated from the bond distance used above. All the in-plane angles were taken to be 120.° Small errors in these values do not cause serious errors in the final results, since the frequency is much more sensitive to the force constants than to the bond distances. Figure 1 illustrates the molecular model and internal coordinates used for the calculation of coordinated ethylene.

Assuming V_h symmetry, the nine ((2 × 6) − 3) in-plane vibrations of coordinated ethylene are grouped into four species, $3A_g + 2B_{1g} + 2B_{2u} + 2B_{3u}$, and the three out-of-plane vibrations are grouped into three species, $A_u + B_{1u} + B_{2u}$. Figure 1 illustrates the eleven internal coordinates for the nine in-plane vibrations. Two redundant coordinates are easily removed if the symmetry coordinates shown in Table I are used. The *G* matrix elements are not listed here since they are listed by Morino, *et al.*[13] (in-plane vibrations), and by Dowling[14] (out-of-plane vibrations). The *F* matrix elements for the in-plane vibrations were expressed in terms of the modified Urey–Bradley force field, since it has already been used for ethylene.[9] For the out-of-plane vibrations we calculated the value of the *F* element, since each species contain only one mode.

B. Square-Planar Group (MX_2YZ). Figure 2 illustrates the molecular model used to calculate the in-plane vibrations of the MX_2YZ-type molecule, where M, X, Y, and Z are Pt, Cl, C_2H_4, and Cl_t (*trans* to C_2H_4), respectively. The Pt–Cl_t and Pt–Cl distances are reported to be 2.40 and 2.26 A, respectively.[7] Bokii and Kukina[7] estimated the Pt···CH_2 distance to be 2.55 A. Combining this value with that of the C=C bond (1.364 A) assumed previously, an approximate platinum–ethylene distance is estimated to be 2.45 A. Since the symmetry of this model is C_{2v}, the seven ((2 × 5) − 3) in-plane vibrations are grouped into two species, $4A_1 + 3B_2$, and the two (5 − 3) out-of-plane vibrations are grouped into one species, $2B_1$. To calculate seven in-plane vibrations, we used the internal coordinates shown in Figure 2. Evidently, one redundant coordinate is involved in this set which is easily removed if the symmetry coordinates shown in Table II are used. The *F* matrix was expressed in terms of a Urey–Bradley force field with modifications which will be explained later.

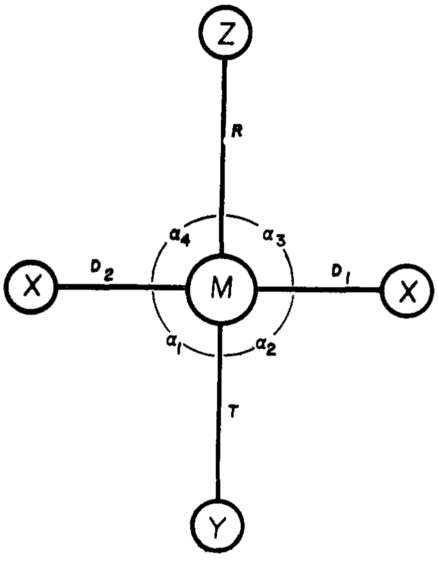

Figure 2. Structure and internal coordinates of the square-planar MX_2YZ-type molecule.

Table I. Symmetry Coordinates for the In-Plane Vibrations of Ethylene[a]

$S_1 = (^1/_2)(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$	A_g	ν(C—H)
$S_2 = \Delta R$	A_g	ν(C=C)
$S_3 = (1/\sqrt{6})(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)$		Redundant
$S_4 = (1/\sqrt{6})(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4)$		Redundant
$S_5 = (1/\sqrt{12})(2\Delta\alpha_1 + 2\Delta\alpha_2 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4)$	A_g	$\delta_s(CH_2)$
$S_6 = (^1/_2)(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$	B_{1g}	ν(C—H)
$S_7 = (^1/_2)(\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4)$	B_{1g}	$\rho_r(CH_2)$
$S_8 = (^1/_2)(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$	B_{2u}	ν(C—H)
$S_9 = (^1/_2)(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)$	B_{2u}	$\rho_r(CH_2)$
$S_{10} = (^1/_2)(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$	B_{3u}	ν(C—H)
$S_{11} = (1/\sqrt{12})(2\Delta\alpha_1 - 2\Delta\alpha_2 - \Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)$	B_{3u}	$\delta_{as}(CH_2)$

[a] ν, stretching; δ_s and δ_{as}, symmetric and antisymmetric scissoring; ρ_r, rocking.

C. Calculation of Frequencies and Potential Energy Distribution. A matrix secular equation of the form,

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Table II. Symmetry Coordinates for the In-Plane Vibrations of the Square-Planar MX_2YZ-Type Molecule

$S_1 = (1/\sqrt{2})(\Delta d_1 - \Delta d_2)$	A_1	ν_s(M-X)
$S_2 = \Delta R$	A_1	ν(M-Z)
$S_3 = \Delta T$	A_1	ν(M-Y)
$S_4 = (^1/_2)(\Delta\alpha_1 + \Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_4)$	A_1	Bending
$S_5 = (^1/_2)(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4)$	A_1	Redundant
$S_6 = (1/\sqrt{2})(\Delta d_1 - \Delta d_2)$	B_2	ν_{as}(M-X)
$S_7 = (1/\sqrt{2})(\Delta\alpha_3 - \Delta\alpha_4)$	B_2	Bending
$S_8 = (1/\sqrt{2})(\Delta\alpha_1 - \Delta\alpha_2)$	B_2	Bending

Table III. Force Constants for Ethylene, Coordinated Ethylene, and the Square-Planar Group (mdynes/A)

	Stretching	Bending	Repulsive	Interaction	Out-of-plane
Coordinated ethylene	K(C=C) = 6.00 K(C—H) = 4.64	H(H-C-H) = 0.31 H(H-C-C) = 0.22	F(C···H) = 0.70 F(H···H) = 0.00	$S(CH_2)$ = 0.22	$F1$ = 0.061 $F2$ = 0.283 $F3$ = 0.050
Ethylene[9]	K(C=C) = 7.40 K(C—H) = 4.70	H(H-C-H) = 0.31 H(H-C-C) = 0.22	F(C···H) = 0.70 F(H···H) = 0.00	$S(CH_2)$ = 0.19	$F1$ = 0.138 $F2$ = 0.237 $F3$ = 0.035
Square-planar group	K(Pt-Cl) = 1.82 K(Pt-C_2H_4) = 2.23 K(Pt-Cl_t) = 1.78	H(C_2H_4-Pt-Cl) = 0.16 H(Cl-Pt-Cl_t) = 0.15	F(C_2H_4···Cl) = 0.14 F(Cl···Cl_t) = 0.14	S(Pt-Cl) = 0.20	

Table IV. Comparison of Calculated and Observed Frequencies for Zeise's Salt and Its Deuterio Analog (cm^{-1})

		Zeise's salt		Zeise's salt-d_4		
Group	Vibration	Obsd	Calcd	Obsd	Calcd	Assignment[a,d]
Coordinated ethylene	ν_1 (A_g)	2920	2977	2115	2155	ν(C—H)
	ν_2 (A_g)	1526	1528	1428	1443	ν(C=C) + $\delta_s(CH_2)$[b]
	ν_3 (A_g)	1418	1330	978	974	$\delta_s(CH_2)$ + ν(C=C)[b]
	ν_5 (B_{1g})	2975	3080	2219	2289	ν(C—H)
	ν_6 (B_{1g})	1251	1242	1021	1011	$\rho_r(CH_2)$
	ν_9 (B_{2u})	3098	3105	2335	2310	ν(C—H)
	ν_{10} (B_{2u})	844	792	536	570	$\rho_r(CH_2)$
	ν_{11} (B_{3u})	3010	3017	2185	2192	ν(C—H)
	ν_{12} (B_{3u})	1428	1471	1067	1084	$\delta_{as}(CH_2)$
	ν_4 (A_u)	730	680	450	481	$\rho_t(CH_2)$
	ν_7 (B_{1u})	1023	1051	811	795	$\rho_w(CH_2)$
	ν_8 (B_{2g})	1023	1010	818	829	$\rho_w(CH_2)$
Square-planar	ν_1' (A_1)	331	330	329	329	ν_s(Pt-Cl)
	ν_2' (A_1)	407	407	387	387	ν(Pt-C_2H_4)
	ν_3' (A_1)	310	309	305	307	ν(Pt-Cl_t)[c]
	ν_4' (A_1)	183	174	185	174	δ(Cl-Pt-Cl)
	ν_5' (B_2)	339	343	339	342	ν_{as}(Pt-Cl)
	ν_6' (B_2)	210	214	198	211	δ(Cl-PtC_2H_4) + δ(Cl-Pt-Cl)
	ν_7' (B_2)	161	168	160	163	δ(Cl-Pt-Cl_t) + (Cl-Pt-C_2H_4)
	ν_8' (B_1)	121	...	117	...	π(C_2H_4-Pt-Cl_t)
	ν_9' (B_1)	92	...	92	...	π(Cl-Pt-Cl)

[a] Assignments are in terms of the nondeuterated compound. [b] Coupling occurs only in the nondeuterated compound. [c] The subscript (t) refers to the chloride *trans* to the olefin. [d] ν, stretching; δ, bending; ρ_r, rocking; ρ_t, twisting; ρ_w, wagging; π, out-of-plane bending; s, symmetric; and as, asymmetric.

$|GF - E\lambda| = 0$,[15] was constructed for each species and solved by using an IBM 7094 computer. The best sets of force constants thus obtained are listed in Table III. Table IV compares the observed frequencies with those calculated by using these sets of force constants. The band assignments given in the last column of Table IV were made on the basis of the calculation of potential energy distribution in each symmetry coordinate for each normal vibration.[16] The potential energy distribution is shown in Table V.

Results and Discussion

Figure 3 illustrates the infrared spectra of Zeise's salt (designated as I) and its d_4 analog (designated as II). The spectra are divided into three regions according to the method of sampling (see Experimental Section). Table VI compares the observed frequencies of I and II with those of C_2H_4, C_2D_4, and the $PtCl_4^{2-}$ ion.

Coordinated Ethylene. Four weak bands of varying intensity were observed between 3100 and 2900 cm^{-1} for I and between 2350 and 2100 cm^{-1} for II, and are assigned to the C–H or C–D stretching modes (ν_9, ν_{11}, ν_5, and ν_1). As is seen in Table VI, these frequencies are slightly lower than those of free ethylene. The appearance of four stretching bands suggests that the symmetry of coordinated ethylene is lower than C_{2v}. As stated previously, it is not obvious at the present whether this lowering is due to the distortion of ethylene itself or the attachment of the $PtCl_3$ group to ethylene. A weak band at 1526 cm^{-1} of I was assigned to the coordinated C=C stretching mode (ν_2). In free ethylene, this vibration (Raman active) appears at 1623 cm^{-1}. Thus, it is shifted by 97 cm^{-1} to a lower frequency upon coordination to the Pt atom. According to the calculation of potential energy distribution, this mode couples strongly with the CH_2 scissoring mode. Therefore, the use of this frequency as a quantitative measure of the strength of the coordinate bond is questionable. A strong band at 1428 cm^{-1} and a shoulder at 1418 cm^{-1} of I have been assigned to the antisymmetric and

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(16) Y. Morino and K. Kuchitsu, *ibid.*, **20**, 1809 (1952).

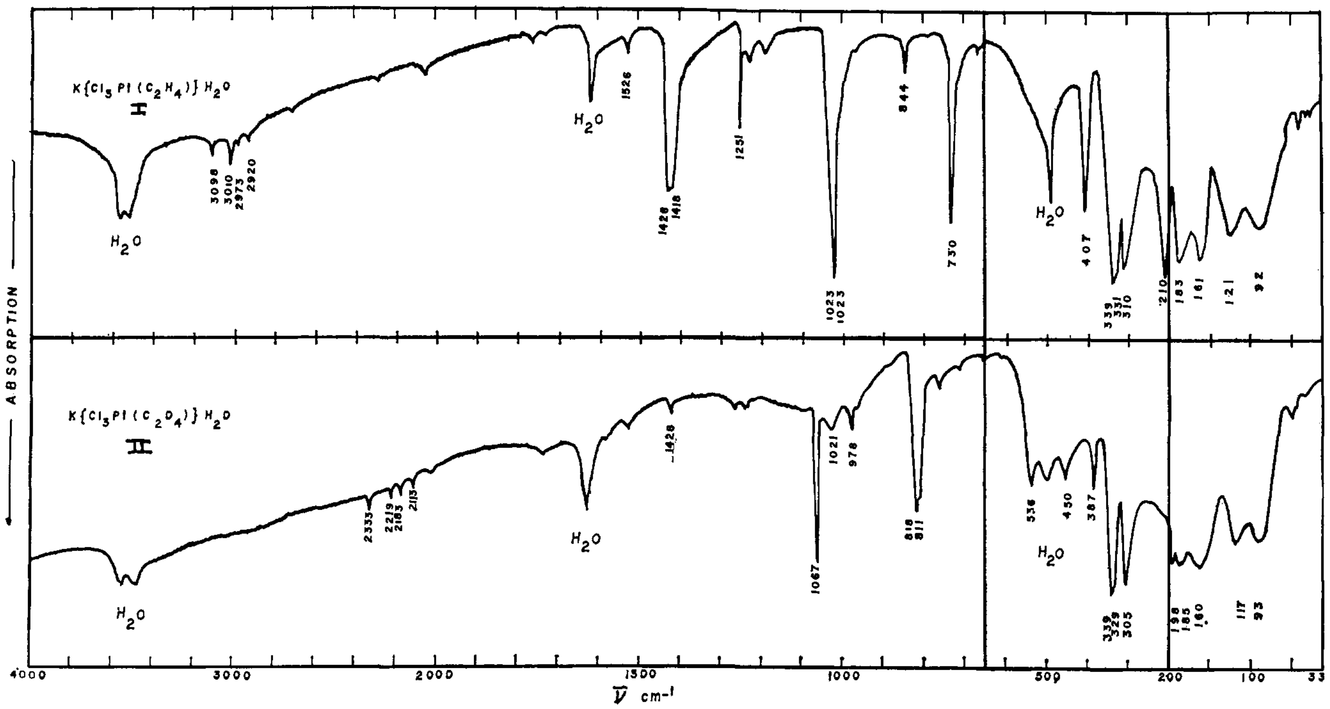

Figure 3. Infrared spectra of Zeise's salt and Zeise's salt-d_4 from 4000 to 33 cm^{-1}.

symmetric CH$_2$ scissoring vibrations (ν_{12} and ν_3), respectively. Upon deuteration, they are shifted to 1067 and 978 cm^{-1}, respectively. According to potential energy distribution, ν_3 of I couples strongly with the C=C stretching mode. However, this coupling disappears in II since the CD$_2$ scissoring frequency is too low to couple with the C=C stretching mode.

Table V. The Potential Energy Distribution for the In-Plane Vibrations of Coordinated Ethylene and the Square-Planar Group (Nondeuterated Only)[a]

Coordinated ethylene				Square-planar group				
(A$_g$)	ν_1	ν_2	ν_3	(A$_1$)	ν_1'	ν_2'	ν_3'	ν_4'
S_1	*1.00*	0.13	0.00	S_1	*1.00*	0.0	*0.90*	0.00
S_2	0.00	*1.00*	*0.51*	S_2	0.00	*1.00*	0.00	0.00
S_5	0.00	*0.53*	*1.00*	S_3	*0.93*	0.00	*1.00*	0.00
				S_4	0.00	0.00	0.00	*1.00*
(B$_{1g}$)	ν_5	ν_6		(B$_2$)	ν_5'	ν_6'	ν_7'	
S_6	1.00	0.00		S_6	1.00	0.00	0.00	
S_7	0.00	*1.00*		S_7	0.00	*1.00*	*0.52*	
				S_8	0.000	*0.50*	1.00	
(B$_{2u}$)	ν_9	ν_{10}						
S_8	*1.00*	0.00						
S_9	0.00	*1.00*						
(B$_{3u}$)	ν_{11}	ν_{12}						
S_{10}	*1.00*	0.00						
S_{11}	0.00	*1.00*						

[a] If there are more than two relatively large contributions, only the term which contributes more than 0.5 is used to represent the vibrational coupling.

A strong, sharp band at 1251 cm^{-1} and a medium band at 844 cm^{-1} of I are assigned to the symmetric and antisymmetric rocking modes (ν_6 and ν_{10}), respectively, and a very strong band at 1023 cm^{-1} is assigned to both the symmetric and antisymmetric wagging modes (ν_8 and ν_7). The latter band splits into two bands in the Nujol mull spectrum. As is seen in Table IV, these four bands are all sensitive to deuteration and are shifted to lower frequencies in good agreement with the calculation. Table VI shows that both the rocking and wagging frequencies of Zeise's salt are higher than those of the corresponding modes

Table VI. Comparison of Observed Frequencies of Zeise's Salt, Its Deuterio Analog, Ethylene, Ethylene-d_4, and Tetrachloroplatinate Anion

Zeise's salt	Zeise's salt-d_4	C$_2$H$_4$[9]	C$_2$D$_4$[9]	[PtCl$_4$]$^{2-}$[10]	Assignment
3564 (s)	3550 (s)				ν_a (H$_2$O)
3491 (s)	3480 (s)				ν_s (H$_2$O)
3098 (w)	2335 (w)	3106	2345		ν_9
3010 (w)	2185 (w)	2990	2200		ν_{11}
2975 (vw)	2219 (w)	3108	2304		ν_5
2920 (vw)	2115 (w)	3019	2251		ν_1
2098 (sh)	1557 (vw)	2046	1595		$\nu_6 + \nu_{10}$
2048 (w)	1629 (sh)	1889	1497		$\nu_7 + \nu_8$
1612 (s)	1616 (s)				δ (H$_2$O)
1526 (w)	1428 (w)	1623	1515		ν_2
1428 (vs)	1067 (vs)	1444	1078		ν_{12}
1418 (sh)	978 (m)	1342	981		ν_3
1251 (s)	1021 (m)	1236	1009		ν_6
1023 (vs)	818 (vs)	949	721		ν_8
1023 (vs)	811 (vs)	943	780		ν_7
844 (m)	536 (m)	810	586		ν_{10}
730 (s)	450 (m)	1007	726		ν_4
493 (s)	498 (s)				ν_L[a] (H$_2$O)
407 (s)	387 (s)				ν_2'
$\begin{pmatrix}339\\335\end{pmatrix}$ (vs) (sh)	$\begin{pmatrix}339\\335\end{pmatrix}$ (vs) (sh)			335 (A$_{1g}$)	ν_5'
$\begin{pmatrix}310\\307\end{pmatrix}$ (s) (s)	$\begin{pmatrix}305\\303\end{pmatrix}$ (sh) (sh)			304 (B$_{1g}$)	ν_3'
$\begin{pmatrix}331\\327\end{pmatrix}$ (vs) (sh)	$\begin{pmatrix}329\\325\end{pmatrix}$ (vs) (sh)			320 (E$_u$)	ν_1'
210 (s)	198 (s)				ν_6'
183 (s)	185 (s)			183 (E$_u$)	ν_4'
161 (s)	160 (s)			164 (B$_{2g}$)	ν_7'
121 (m)	117 (m)				ν_8'
92 (m)	92 (m)			93 (A$_{2u}$)	ν_9'
66 (sh)					
49 (w)	50 (w)				
46 (sh)	46 (sh)				
40 (w)	41 (w)				
37 (w)					

[a] ν_L, librational mode.

of free ethylene except ν_{10} of II. According to Table IV, the calculated frequencies of ν_{10} and ν_4 of II give *ca.* 6% deviation from the observed values. This may be due to the coupling between these low-frequency ethylene modes and the vibrations due to the $PtCl_3$ group, which was neglected in our treatment. Finally, a strong band at 730 cm^{-1} of I was assigned to the torsional mode (ν_4). It is interesting to note that, different from the rocking and wagging modes, the torsional frequency of Zeise's salt is much lower than that of free ethylene. This is understandable, since the torsional mode involves the twisting of the C=C double bond which is weakened considerably upon coordination.

Table III compares the force constants of Zeise's salt with those of free ethylene.[9] In addition to stretching, bending, and repulsive force constants, these include the interaction constant between two HCH angle-bending coordinates. The necessity of this constant was justified by Shimanouchi[9] in terms of the flexibility of the C=C bond. Upon coordination, both the C—H and C=C stretching constants decrease, mainly because the C=C bond order is decreased; *K*(C=C) decreases *ca.* 30%, and *K*(C—H) decreases by *ca.* 19%. According to the theory of bond flexibility, the interaction constant is expected to increase with the decrease in the C=C bond order. It was found that the calculated frequencies of Zeise's salt can be fit reasonably well to the observed ones with the same bending and repulsive force constants as used for free ethylene. This result seems to suggest that they are much less sensitive to coordination than the stretching and interaction constants.

In general, all the out-of-plane bending force constants are expected to increase upon coordination because of the repulsive forces between the ligand atoms and the metal atom. This was found to be the case for the wagging force constant (*F*2) and the interaction constant between wagging and torsional modes (*F*3). However, the torsional force constant (*F*1) decreased drastically upon coordination for the reason mentioned earlier.

Square-Planar Group. It has been well established that the Pt–Cl stretching bands appear in the region between 340 and 300 cm^{-1}.[10] In Zeise's salt, three strong bands are clearly seen in this region, 339 (ν_5'), 331 (ν_1'), and 310 (ν_3') cm^{-1}, and they are not sensitive to deuteration. Each of these bands has a slight shoulder which may be attributed to the $Pt-Cl^{37}$ stretching mode. As stated before, the lowest frequency band of coordinated ethylene (I) is at 730 cm^{-1} (ν_4). There are two bands between ν_4 and ν_5', the highest Pt–Cl stretching mode. One is at 493 cm^{-1} and is assigned to an absorption due to lattice water,[3] since it is sensitive to the condition of dehydration. The other is at 407 cm^{-1} (ν_2') and was suggested by Powell and Sheppard[3] to be the $Pt-C_2H_4$ stretching mode. We have found in this investigation that this is the only band which provides the reasonable deuteration shift and reasonable stretching force constant for this type of metal π bonding. Zeise's dimer and all other olefin complexes of Pt(II) exhibit similar bands which cannot be assigned to other vibrations, and these will be discussed in a subsequent paper.

Three strong bands of I at 210, 183, and 161 cm^{-1} are assigned to the three in-plane bending modes involving changes in the four angles around the Pt atom (ν_6', ν_4', and ν_7'). Of these bands, that at 210 cm^{-1} is most sensitive to the deuteration of ethylene. The potential energy distribution shows that this mode involves mainly the change in the $Cl-Pt-C_2H_4$ angles. The $PtCl_4^{2-}$ ion (D_{4h} symmetry) exhibits two Cl–Pt–Cl bending modes in this region. Two bands at 121 and 92 cm^{-1} of I are assigned to the out-of-plane bending modes (ν_8' and ν_9') of the square-planar skeleton. Although we have not calculated these frequencies, it is anticipated that the former may involve mainly the change in the out-of-plane $C_2H_4-Pt-Cl_t$ angle since it is slightly sensitive to deuteration. On the other hand, the latter involves the change in the out-of-plane Cl–Pt–Cl angle because it is not sensitive to deuteration. In fact, the $PtCl_4^{2-}$ ion exhibits the same mode at 93 cm^{-1}. We have observed several bands below 90 cm^{-1} which may be due to the bending modes of the ethylene molecule as a whole or to lattice modes. The assignments of these low-frequency modes are, however, beyond the scope of the present work.

Table III lists all the force constants used to calculate the square-planar group. The most important force constant obtained is the $Pt-C_2H_4$ stretching force constant. It takes the value of 2.23 mdynes/A on the assumption that the ethylene molecule is a single atom. A simple diatomic approximation ($Pt-C_2H_4$) gives a value of 2.45 mdynes/A if the frequency is fitted to the band at 407 cm^{-1}. It should be noted that these values in the Urey–Bradley force field contain a contribution from repulsive forces between nonbonded atoms. It is rather difficult, however, to estimate accurately the repulsive force constants between the C and H atoms of ethylene and the Pt atom. Thus far, a repulsive force constant of this type is known only for the Pt···O repulsion in the $Pt(NO_2)_4^{2-}$ ion.[17] If the value of 0.03 mdyne/A obtained for this latter complex is assumed for both the Pt···C and Pt···H repulsions, the $Pt-C_2H_4$ stretching force constant may be near to 2.05 mdynes/A ($2.23 - 6 \times 0.03$). Table VII lists the coordinate bond stretching force constants in various Pt(II) complexes which have been obtained using the Urey–Bradley force field. If the $Pt-C_2H_4$ stretching force constant obtained above is compared with those listed in Table VII, we find that the $Pt-C_2H_4$ stretching constant is almost the same as those of $Pt-NH_2$ (glycine),

Table VII. Comparison of Urey–Bradley Stretching Force Constants for Various Pt(II) Complexes

Coordinate bond	Compound	Stretching force constant, mdynes/A	Ref
Pt–CN	$K_2[Pt(CN)_4]$	3.425	*a*
$Pt-NO_2$	$K_2[Pt(NO_2)_4]$	3.40	17
$Pt-NH_2$	$Pt(gly)_2$	2.10	*b*
Pt–OOC	$Pt(gly)_2$	2.10	*b*
$Pt-NH_3$	*trans*-$[Pt(NH_3)_2Cl_2]$	2.09	18
Pt–Cl	*trans*-$[Pt(NH_3)_2Cl_2]$	1.82	18

[a] D. M. Sweeney, I. Nakagawa, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 889 (1956). [b] R. A. Condrate, and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965).

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(17) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

Pt-OOC (glycine), and Pt-NH_3. This result may indicate that the strength of the coordinate bonds in these compounds is similar.

The Pt–Cl stretching force constant used in this investigation is the same as used previously for *trans*-$Pt(NH_3)_2Cl_2$.[18] Also the interaction constant between two Pt–Cl stretching modes takes a similar value as that used for *trans*-$Pt(NH_3)_2Cl_2$ (0.23 mdyne/A). The Pt–Cl (*trans*) stretching force constant is slightly less than the Pt–Cl (*cis*) stretching force constant. This is reasonable since the Pt–Cl (*trans*) bond is slightly weakened compared with the Pt–Cl (*cis*) bonds because of the *trans* effect of ethylene. Other bending and repulsive force constants used in this work are similar to those of other Pt(II) complexes.[17–19]

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(18) K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, **4**, 36 (1965).

(19) See footnotes *a* and *b* in Table VII.

Organometallic Exchange Reactions. V. Proton Magnetic Resonance Study of Methyl Group Exchanges among the Trimethyl Derivatives of Group III. The Cage Effect in Organometallic Dissociations[1]

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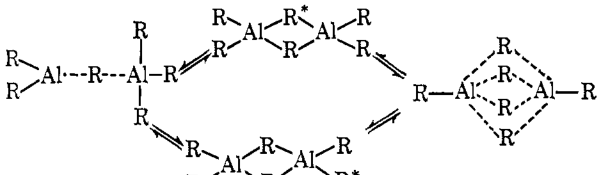
Abstract: The exchange of methyl groups between bridge and terminal positions in trimethylaluminum has been studied in toluene solution using proton magnetic resonance spectroscopy. The rate and activation energy are essentially the same as reported for cyclopentane solution. The process is strictly first order in trimethylaluminum. Exchange of methyl groups between trimethylaluminum and trimethylgallium has been observed in cyclopentane and toluene. Trimethylaluminum–trimethylindium exchange has been observed in toluene. From a detailed study of the temperature and concentration dependences of the pmr spectra it is concluded that the over-all rate-determining process in these exchanges is formation of solvent-separated $Al(CH_3)_3$ from $Al_2(CH_3)_6$. Comparison of these exchange data with the results for bridge-terminal exchange in $Al_2(CH_3)_6$ leads to the conclusion that the latter process requires dissociation into solvent-caged monomers. The cage effect favors recombination of monomers in cyclopentane, whereas monomer–solvent interactions prevent extensive intracage recombination in toluene.

The nature of the association of trialkyl derivatives of the group III metals in solution has been extensively studied. It now appears that aluminum is the only metal whose saturated alkyl derivatives are associated in solution.[3] The bridge structure of dimeric trimethylaluminum in hydrocarbon solutions was nicely confirmed by Muller and Pritchard through observation of two peaks in the pmr spectrum of trimethylaluminum in cyclopentane at −75°.[4] At room temperature, only one pmr peak is observed, as a result of methyl group exchange between bridging and terminal positions. Two possible mechanisms were suggested for the exchange: (1) the breaking of one Al–C bond, which may re-form with a different methyl group in the bridging position; or (2) a deformation of the molecule in which no bonds are broken, leading to structure having four bridging methyl groups at the corners of a square. These processes are depicted in eq 1. Since the estimated activation energy (6–14 kcal/mole) was considerably less than the heat of dissociation of the dimer to the monomer, reported to be 20.2 ± 1 kcal/mole in the gaseous phase,[5] an intramolecular process was deemed the more likely. Ramey and co-workers[6] have carried out a more quantitative study of the temperature dependence of the pmr spectra of a number of trialkylaluminum compounds in an attempt to elucidate the mechanism by which alkyl groups are transferred from bridging to terminal positions. For $(Al(CH_3)_3)_2$ the enthalpy of activation for exchange of bridge and terminal groups was found to be 15.6 ± 0.2 kcal/mole. The authors suggested that the exchange occurs by one of the intramolecular processes suggested by Muller and Pritchard. They also studied the interconversion of mixed aluminum alkyls and concluded that the exchange involved rupture of one Al–C bond. Ziegler has discussed the interconversion of mixed aluminum alkyls in some detail.[7] He postulates the following reaction scheme to account for rapid exchange of alkyl groups.



(1)

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(2) Alfred P. Sloan Research Fellow.

(3) N. Muller and A. L. Otermat, *Inorg. Chem.*, **4**, 296 (1965).

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(6) K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Barchert, *J. Phys. Chem.*, **69**, 3418 (1965).

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