Infrared Spectra and Normal Coordinate Analysis of Metal–Olefin Complexes. II. Zeise's Dimer and Its Palladium(II) Analog[1]

Michael J. Grogan and Kazuo Nakamoto

Contribution from the Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago, Illinois 60616. *Received July 18, 1967*

Abstract: The infrared spectra of Ziese's dimer, $[Pt(C_2H_4)Cl_2]_2$, and its deuterated and Pd(II) analogs have been obtained from 4000 to 50 cm^{-1}. The Raman spectrum of crystalline Zeise's dimer has also been obtained. A normal coordinate analysis has been carried out on the planar $[MXYR]_2$ system of C_{2h} symmetry where M is Pt(II) or Pd(II), R is C_2H_4, and X and Y are terminal and bridging Cl atoms, respectively. The bands at 408 and 427 cm^{-1} of Zeise's dimer and its Pd(II) analog have been assigned to the Pt–ethylene and Pd–ethylene stretching modes, respectively. The corresponding force constants (mdyn/Å) are: Pt–ethylene stretching, 2.25, and Pd–ethylene stretching, 2.14, including repulsive force constants between nonbonded atoms. All the other bands in the low-frequency region have been assigned based on potential energy distribution.

According to X-ray analysis,[2] the two palladium atoms in $[Pd(C_2H_4)Cl_2]_2$[3a] are joined by two bridging chlorine atoms, and the other chlorine atoms and ethylene molecules are bonded to each palladium atom to form a *trans*-planar structure such as shown in Figure 1 (two ethylene molecules are oriented perpendicular to the square-planar plane). No X-ray analysis has been carried out on the analogous Pt(II) complex, $[Pt(C_2H_4)Cl_2]_2$.[3b] The purpose of this work is to determine the structure of the latter from its infrared and Raman spectra and to assign all the bands observed for these compounds based on normal coordinate analysis. Recently, Pradilla-Sorzano and Fackler[4] have made a similar attempt. However, our results in the low-frequency region are markedly different from theirs.

Experimental Section

Preparation of Compounds. $[Pt(C_4H_4)Cl_2]_2$. This compound was prepared from Zeise's salt, $K[Pt(C_2H_4)Cl_3]\cdot H_2O$,[5a] according to the method described by Chatt and Searle.[5b]

Anal. Calcd for $[Pt(C_2H_4)Cl_2]_2$: C, 8.46; H, 1.42; Cl, 24.96. Found: C, 8.02; H, 1.24; Cl, 24.20.

$[Pt(C_2D_4)Cl_2]_2$.[6] This compound was prepared from Zeise's salt-d_4, $K[Pt(C_2D_4)Cl_3]\cdot H_2O$, according to the method described by Chatt and Searle.[5b]

$[Pd(C_2H_4)Cl_2]_2$. $Pd(C_6H_5CN)_2Cl_2$[7a] (3.0 g) was dissolved in 60 ml of dry benzene.[7b] The solution was heated to 80° and filtered. The filtrate was placed in a glass reaction vessel equipped with a high-pressure Teflon stopcock.[8] The reaction vessel was evacuated, and dry C_2H_4 (Matheson CP) was admitted. Over a period of 30 min the reaction solution changed from a clear brown red to a turbid dark yellow color. The solution was removed from the vessel, and dry Skellysolve B was added, resulting in more precipitate. The yellow product (unstable to water) was placed in a desiccator over $CaCl_2$. No analysis was performed because of the instability of the complex toward moist air.

Spectral Measurements. The infrared spectra from 4000 to 500 cm^{-1} were observed using the KBr pellet technique on a Beckman IR 12 spectrophotometer. Also, Nujol and hexachlorobutadiene mulls were used to observe the spectra (4000–650 cm^{-1}) on a Perkin-Elmer Model 21 spectrophotometer. The low-frequency spectra were observed using a Nujol mull between polyethylene plates on a Beckman IR 11 spectrophotometer.

The infrared spectrum of Zeise's dimer in solution (550–275 cm^{-1}) was observed on a Perkin-Elmer Model 21 spectrophotometer equipped with CsBr optics. The following solvents were used: carbon disulfide, benzene, and dichloromethane. The dimer was dissolved in the solvent until the solution was saturated at room temperature, and the solution was placed in a polyethylene cell (Barnes Engineering Co., Part No. 118-0011, 5.0 mm). The solution of the Pd(II) dimer was also observed in dichloromethane. No decomposition of the dimer molecule occurred in these solvents; the compound was recovered completely after each spectral measurement.

Procedure of Calculation. As stated in our previous paper on Zeise's salt,[8] the vibrations due to ethylene can be treated separately from those of the rest of the molecule. We have, therefore, carried out a normal coordinate analysis on the molecular model shown in Figure 1 where ethylene is treated as a single dynamic group. In Figure 1, M is either Pt(II) or Pd(II), Y is the bridging Cl, X is the terminal Cl, and R is ethylene. Although X-ray analysis has not yet been made on the Pt(II) compound, the similarity of the spectra between the Pt(II) and Pd(II) complexes definitely indicates that the Pt(II) analog also takes the *trans*-planar structure shown in Figure 1. For this structure, we anticipate only one Pt–C_2H_4 stretching, one Pt–Cl (terminal), and two Pt–Cl (bridging) stretching bands in the infrared spectrum. As will be shown later, these predictions were confirmed for both compounds. It should be noted that the number of these infrared-active fundamentals would be doubled if the molecule were *cis*-planar (C_{2v} symmetry).

The molecular model shown in Figure 1 has 18 $[(3 \times 8) - 6]$ normal vibrations, which are classified into $7\,A_g + 3\,A_u + 2\,B_g + 6\,B_u$ species under C_{2h} symmetry. To calculate the 13 in-plane vibrations ($7\,A_g + 6\,B_u$), we have used 18 internal coordinates, shown in Figure 1. Apparently, this set of internal coordinates involves five redundancies (two involving the four angles around each metal, and three involving the four angles inside the central ring) which were not removed from the calculations. Thus the final results yield five "zero-frequencies" (two in A_g and three in B_u) which provide a good check on our calculations. Table I lists the symmetry coordinates used in the present work. The *G*-matrix elements were evaluated using the molecular parameters (Å):[2] $R = 2.3$, $S = 2.18$, $T = 2.43$, and $U = 2.33$. All the angles were

---

[1] Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. This work was supported by Grant 2096-A3,5 from the Petroleum Research Fund. Submitted by M. J. Grogan to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. N. Dempsey and N. C. Baenziger, *J. Am. Chem. Soc.*, 77, 4984 (1955).

[3] (a) *sym,trans*-Di-μ-chloro-dichlorobis(ethylene)dipalladium(II); (b) *sym,trans*-di-μ-chloro-dichlorobis(ethylene)diplatinum(II).

[4] J. Pradilla-Sorzano and J. P. Fackler, *J. Mol. Spectry.*, 22, 80 (1967).

[5] (a) Potassium trichloro(ethylene)platinate(II) monohydrate; (b) J. Chatt and M. L. Searle, *Inorg. Syn.*, 5, 210 (1957).

[6] Potassium trichloro(ethylene-d_4)platinate(II) monohydrate.

[7] (a) Dichlorobis(benzenecarbonitrile)palladium(II); (b) M. S. Kharasch and T. A. Ashford, *J. Am. Chem. Soc.*, 58, 1735 (1936).

[8] M. J. Grogan and K. Nakamoto, *ibid.*, 88, 5454 (1966).

Table I. Symmetry Coordinates for the In-Plane Vibrations of the Planar $[MXYR]_2$-Type Molecule

	Symmetry coordinate	Vibrational mode[a]
Ag	$S_1 = 1/\sqrt{2}(\Delta R + \Delta R')$	ν(M-R)
	$S_2 = 1/\sqrt{2}(\Delta S + \Delta S')$	ν(M-X)
	$S_3 = 1/\sqrt{2}(\Delta T + \Delta T')$	ν(M-Y)
	$S_4 = 1/\sqrt{2}(\Delta U + \Delta U')$	ν(M-Y)
	$S_5 = 1/\sqrt{2}(\Delta A + \Delta A')$	δ(R-M-X)
	$S_6 = 1/\sqrt{2}(\Delta B + \Delta B')$	Ring def
	$S_7 = 1/\sqrt{2}(\Delta C + \Delta C')$	Ring def
	$S_8 = 1/\sqrt{2}(\Delta E + \Delta E')$	Ring def
	$S_9 = 1/\sqrt{2}(\Delta D + \Delta D')$	Ring def
Bu	$S_{10} = 1/\sqrt{2}(\Delta R - \Delta R')$	ν(M-R)
	$S_{11} = 1/\sqrt{2}(\Delta S - \Delta S')$	ν(M-X)
	$S_{12} = 1/\sqrt{2}(\Delta T - \Delta T')$	ν(M-Y)
	$S_{13} = 1/\sqrt{2}(\Delta U - \Delta U')$	ν(M-Y)
	$S_{14} = 1/\sqrt{2}(\Delta A - \Delta A')$	δ(R-M-X)
	$S_{15} = 1/\sqrt{2}(\Delta B - \Delta B')$	Ring def
	$S_{16} = 1/\sqrt{2}(\Delta C - \Delta C')$	Ring def
	$S_{17} = 1/\sqrt{2}(\Delta E - \Delta E')$	Ring def
	$S_{18} = 1/\sqrt{2}(\Delta D - \Delta D')$	Ring def

[a] ν, stretching; δ, bending

taken as 90°. These values were used both for the Pt(II) and Pd(II) compounds since the dsp^2 covalent radii of these atoms are similar.[9] The F-matrix elements were expressed in terms of the simple Urey-Bradley force field.[10] Finally, a matrix secular equation of the form $|GF - E\lambda| = 0$ [11] 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 II. Table III compares the observed frequencies with those calculated by using these sets of force constants. The band assignments given in the last column of Table III were made on the basis of the calculation of potential energy distribution[12] in each symmetry coordinate which is shown in Table IV.

Table II. Force Constants for the Pt(II) and Pd(II) Dimeric Planar Group (mdyn/Å)

Type of force constant	M = Pt(II)	M = Pd(II)
Stretching		
$K(M\text{-}C_2H_4)$	2.25	2.14
$K(M\text{-}Cl_t)$[a]	2.17	1.71
K(M-Cl)	0.69	0.65
$K(M\text{-}Cl_b)$[a]	0.69	0.65
Bending		
$H(C_2H_4\text{-}M\text{-}Cl_t)$	0.14	0.12
$H(C_2H_4\text{-}M\text{-}Cl_b)$	0.35	0.31
$H(Cl_t\text{-}M\text{-}Cl_b)$	0.35	0.31
$H(M\text{-}Cl_b\text{-}M)$	0.11	0.09
$H(Cl_b\text{-}M\text{-}Cl_b)$	0.07	0.05
Repulsive		
$F(C_2H_4\cdots Cl_t)$	0.15	0.13
$F(C_2H_4\cdots Cl_b)$	0.14	0.12
$F(Cl_t\cdots Cl_b)$	0.15	0.13
$F(Cl_b\cdots Cl_b)$	0.13	0.11
$F(M\cdots M)$	0.05	0.07

[a] Subscripts t and b indicate terminal and bridging chlorides, respectively.

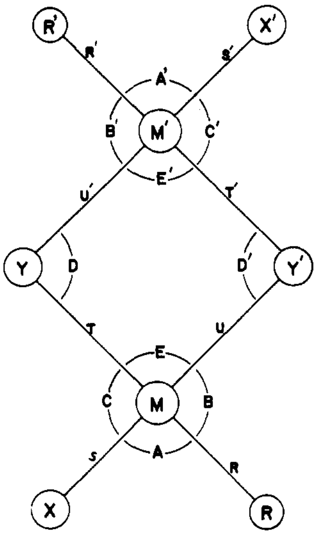


Figure 1. Structure and internal coordinates of Zeise's dimer and its analogs.

Results and Discussion

The infrared spectra of Zeise's dimer and its deuterio and Pd(II) analogs are illustrated in Figure 2. Table V lists the vibrational frequencies of ethylene in these compounds, Zeise's salt, and its deuterio analog.[8] The similarity of these frequencies among the compounds studied indicates that the electronic structures of these coordinated ethylenes are also similar. Thus, Zeise's salt and Zeise's dimer are rather difficult to distinguish from their infrared spectra in the high-frequency region. As noted in our previous paper,[8] the bands that show appreciable shifts upon coordination to a metal are the C=C stretching, asymmetric CH_2 rocking, and CH_2 twisting modes.

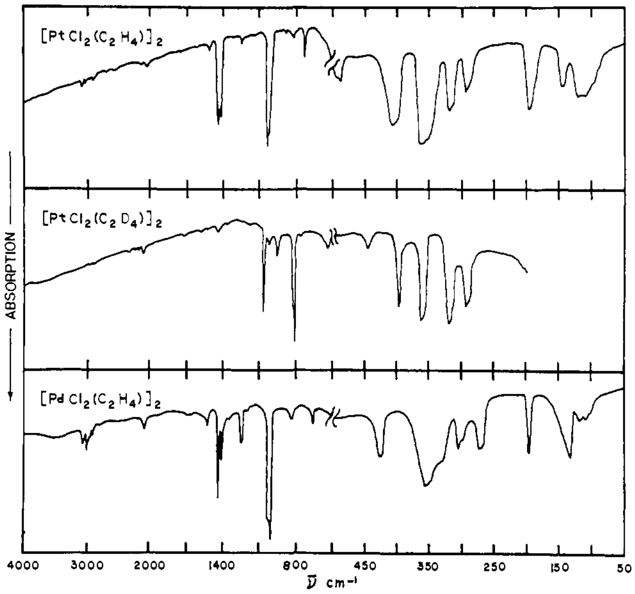


Figure 2. Infrared spectra of Zeise's dimer and its deuterio and Pd(II) analogs, 4000–50 cm^{-1}.

---

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 253.

(10) T. Shimanouchi, *J. Chem. Phys.*, 17, 245 (1949).

(11) E. B. Wilson, *ibid.*, 7, 1047 (1939); 9, 76 (1941).

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

Table III. Comparison of Observed and Calculated Frequencies of Zeise's Dimer and Its Deuterio and Pd(II) Analogs below 500 cm^{-1} [a]

Vibration	$[Pt(C_2H_4)Cl_2]_2$ Obsd (R)	$[Pt(C_2H_4)Cl_2]_2$ Calcd (A_g)	$[Pt(C_2H_4)Cl_2]_2$ Obsd (ir)	$[Pt(C_2H_4)Cl_2]_2$ Calcd (B_u)	$[Pt(C_2D_4)Cl_2]_2$ Obsd (ir)	$[Pt(C_2D_4)Cl_2]_2$ Calcd (B_u)	$[Pd(C_2H_4)Cl_2]_2$ Obsd (ir)	$[Pd(C_2H_4)Cl_2]_2$ Calcd (B_u)	Assignment[b]
ν_1'/ν_1	406 (s)	406	408 (s)	406	392 (s)	385	427 (s)	423	$\nu(Pt–C_2H_4)$
ν_2'/ν_2	362 (vs)	359	364 (vs)	364	364 (vs)	364	357 (vs) 333 (sh)	364	$\nu(Pt–Cl_t)$
ν_3'/ν_3	308 (s)	319	321 (s)	329	322 (s)	326	306 (s)	315	$\nu(Pt–Cl_b) + \nu(Pt–Cl_t) +$ ring def
ν_4'/ν_4	248 (s)	249	293 (s)	293	294 (s)	291	271 (s)	277	$\nu(Pt–Cl_b) + \delta(C_2H_4–Pt–Cl_t)$
ν_5'/ν_5	...[c]	207	197 (s)	198	...	194	198 (s)	197	$\delta(C_2H_4–Pt–Cl_t)$
ν_6'/ν_6	...[c]	184	138 (m)	125	...	121	131 (s)	120	Ring def
ν_7'	...[c]	109	...	...	...	...	...	...	Ring def
				Frequencies Not Calculated					
	...		...		450 (w)		...		$\rho_t(CD_2)$
	480 (w)		485 (w)		...		...		Combination or overtone
	...[c]		120 (s)		...		118 (m)		$\pi(Pt–C_2H_4)$
	...[c]		111 (s)		...		108 (m)		$\pi(Pt–Cl_t)$
	...[c]		99 (sh)		...		103 (sh)		?

[a] Intensity designation: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. R = Raman; ir = infrared. [b] The assignments are given for the B_u species of $[Pt(C_2H_4)Cl_2]_2$. π, out-of-plane bending. [c] These Raman lines could not be observed.

Table IV. Potential Energy Distribution for the In-Plane Vibrations of $[Pt(C_2H_4)Cl_2]_2$[a]

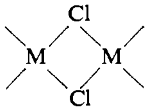
	Sym coord	ν_1'	ν_2'	ν_3'	ν_4'	ν_5'	ν_6'	ν_7'
A_g	S_1	*1.00*	0.02	0.00	0.00	0.00	0.00	0.00
	S_2	0.01	*1.00*	0.00	0.00	0.00	0.00	0.00
	S_3	0.00	0.00	*1.00*	0.30	0.05	*0.76*	0.06
	S_4	0.00	0.00	*0.79*	*0.76*	0.03	*0.58*	0.08
	S_5	0.00	0.00	0.12	0.00	*1.00*	0.00	0.02
	S_6	0.00	0.01	0.00	*1.00*	0.00	*1.00*	0.20
	S_7	0.00	0.00	0.23	0.11	0.00	0.21	*1.00*
		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	
B_u	S_{10}	*1.00*	0.03	0.21	0.02	0.02	0.00	
	S_{11}	0.08	*1.00*	*0.62*	0.02	0.00	0.00	
	S_{12}	0.07	0.30	*1.00*	*0.83*	0.49	0.27	
	S_{13}	0.08	0.28	*0.86*	*1.00*	0.47	0.27	
	S_{14}	0.01	0.01	0.08	*0.88*	*1.00*	0.01	
	S_{15}	0.04	0.16	*0.50*	0.03	0.01	*1.00*	

[a] These numbers denote relative contribution of potential energy from each symmetry coordinate. If there are more than two relatively large contributions, only the term which contributes more than 0.5 was used to represent the vibrational coupling shown in the last column of Table III.

The low-frequency bands of Zeise's dimer and its deuterio and Pd(II) analogs were assigned based on normal coordinate analysis described in the preceding section. As is shown in Table III, the strong band at 408 cm^{-1} of Zeise's dimer (ν_1) was assigned to the Pt–C_2H_4 stretching mode (B_u). The Raman spectrum of Zeise's dimer also exhibits a band at 406 cm^{-1} (A_g). The closeness of these two frequencies does not violate the mutual exclusion rule for C_{2h} symmetry, since two ethylene molecules in Zeise's dimer are far apart and their vibrations do not couple appreciably. The corresponding Pt–C_2H_4 stretching force constant was calculated to be 2.25 mdyn/Å, including repulsive force constants between nonbonded atoms.[8] Again, this value is similar to that found for Zeise's salt.[8] This band is shifted to 392 cm^{-1} in the deuterio analog and to 427 cm^{-1} in the Pd(II) analog. As is seen in Table II, the Pd–C_2H_4 stretching force constant is smaller than the Pt–C_2H_4 stretching force constant. Therefore, the lighter mass of Pd relative to Pt is responsible for the higher frequency of the Pd–C_2H_4 stretching relative to that of the Pt–C_2H_4 stretching mode.

The next strong band at 364 cm^{-1} of Zeise's dimer (ν_2) is due to the terminal Pt-Cl stretching mode. This vibration is observed at 362 cm^{-1} (ν_2') in the Raman spectrum. These frequencies are in good agreement with those reported by Adams and Chandler[13] for the terminal Pt-Cl stretching frequencies (365–340 cm^{-1}). The previous investigators[4] assigned this band to one of the Pt-C_2H_4 stretching modes. The strong bands near 320 cm^{-1} are assigned to the bridging Pt–Cl stretching coupled with terminal Pt-Cl stretching and a ring deformation mode (ν_3). These frequencies are also in good agreement with those reported by Adams and Chandler[13] for bridging metal-chloride frequencies (335–300 cm^{-1}). This band was previously assigned to the terminal Pt-Cl stretching mode.[4]

According to the potential energy distribution, the bands near 293 cm^{-1} of Zeise's dimer and at 271 cm^{-1} of the Pd(II) analog are due to the bridging metal-halogen stretching coupled with the bending mode involving the C_2H_4–metal–Cl (terminal) angle (ν_4). These frequencies are in the same region as those given by Adams and Chandler[13] for the second metal-halogen (bridging) stretching mode. Theoretically, a ring structure of the type



is expected to show at least two infrared-active metal–chloride (bridging) stretching bands. These band assignments are further confirmed by the fact that each metal–halogen stretching band is accompanied by a shoulder band on the lower frequency side of the main band due to the presence of Cl^{37}. The Pd(II) analog of Zeise's dimer is unusual in that the terminal Pd–Cl stretching band at 357 cm^{-1} is accompanied by a well-separated shoulder band at 333 cm^{-1}. The latter band

(13) D. M. Adams and P. J. Chandler, *Chem. Commun.*, 69 (1966).

Table V. Observed Frequencies of Coordinated Ethylene in Zeise's Salt, Zeise's Dimer, Pd(II) Analog of Zeise's Dimer, and Their Deuterio Analogs (cm^{-1})

Vibration	$K[Pt(C_2H_4)Cl_3]\cdot H_2O$	$[Pt(C_2H_4)Cl_2]_2$	$[Pd(C_2H_4)Cl_2]_2$	$K[Pt(C_2D_4)Cl_3]\cdot H_2O$	$[Pt(C_2D_4)Cl_2]_2$	Assignment[a]
ν_1'' (A_g)	2920	2925	2925	2115	2115	ν(C—H)
ν_2'' (A_g)	1526	1516	1527	1428	1428	$\nu(C{=}C) + \delta_s(CH_2)$
ν_3'' (A_g)	1418	1418	1423	978	978	$\delta_s(CH_2) + \nu(C{=}C)$
ν_4'' (A_u)	730	722	675	450	448	$\rho_t(CH_2)$
ν_5'' (B_{1g})	2975	2970	2975	2219	2220	ν(C—H)
ν_6'' (B_{1g})	1251	1242	1258	1021	1021	$\rho_r(CH_2)$
ν_7'' (B_{1u})	1023	1020	1018	811	810	$\rho_w(CH_2)$
ν_8'' (B_{2g})	1023	1206	1027	818	819	$\rho_w(CH_2)$
ν_9'' (B_{2u})	3098	3090	3090	2335	2330	ν(C—H)
ν_{10}'' (B_{2u})	844	812	824	536	529	$\rho_r(CH_2)$
ν_{11}'' (B_{2u})	3010	3010	3010	2185	2185	ν(C—H)
ν_{12}'' (B_{3u})	1428	1430	1437	1067	1058	$\delta_{as}(CH_2)$

[a] Assignments are given for nondeuterated ethylene (V_h symmetry). δ_{as}, asymmetric bending; δ_s, symmetric bending; ρ_w, wagging; ρ_r, rocking; ρ_t, twisting

Table VI. The C=C and Pt–Olefin Stretching Frequencies of Various Monoolefin Complexes (cm^{-1})

Complex	ν(C=C) of free olefin	ν(C=C) of coord olefin	Magnitude of shift	ν(metal–olefin)
$K[Pt(C_2H_4)Cl_3]\cdot H_2O$	1623	1526	97	407
$K[Pt(C_2D_4)Cl_3]\cdot H_2O$	1515	1428	87	387
$K[Pt(C_2H_4)Br_3]\cdot H_2O$	1623	1511	112	395
$K[Pt(C_3H_6)Cl_3]$	1649	1505	144	393
$K[Pt(\textit{trans}\text{-}C_4H_8)Cl_3]$	1681	1522	159	387
$K[Pt(\textit{cis}\text{-}C_4H_8)Cl_3]$	1672	1505	167	405
trans-$[Pt(C_2H_4)(NH_3)Cl_2]$	1623	1521	102	383
trans-$[Pt(C_2H_4)(NH_3)Br_2]$	1623	1517	106	383

disappears when the spectrum is observed in a dichloromethane solution. According to X-ray analysis,[2] this compound contains two crystallographically different dimers which do not have exactly the same molecular dimensions. We have, therefore, assigned this shoulder band to one of the dimers.

The strong bands near 200 cm^{-1} observed for all the compounds were assigned to the in-plane C_2H_4–metal-Cl (terminal) bending mode (ν_5). A similar band appears at 210 cm^{-1} in Zeise's salt.[8] Other bands below 200 cm^{-1} were assigned to the ring deformations (ν_6, ν_7) and to several out-of-plane bending modes which were not calculated in this paper.

As is seen in Figure 2, Zeise's dimer exhibits a weak band at 485 cm^{-1} (the band at 450 cm^{-1} of Zeise's dimer-d_8 is due to the CD_2 twisting mode[8]). Pardilla-Sorzano and Fackler[4] assigned three bands at 482, 410, and 365 cm^{-1} to the infrared-active Pt–C_2H_4 stretching modes of the dimer. On the other hand, we assign only one band at 408 cm^{-1} to this mode. Figure 3 illustrates the infrared spectrum of Zeise's dimer in the CH_2Cl_2, C_6H_6, and CS_2 solutions. The 485-cm^{-1} band appears very weakly in the former two solutions and disappears completely in the CS_2 solution. This result may suggest that the structure of the dimer molecule is perturbed differently by these solvents and that the 485 cm^{-1} band is due to a combination or an overtone which is sensitive to the structural changes.[14]

Another evidence supporting this interpretation is that a number of other monoolefin complexes we have studied exhibit only one metal-olefin stretching band for each metal-olefin bond unless it is forbidden by symmetry requirements. Table VI lists the Pt-olefin stretching frequencies of various monoolefin complexes. It is seen that this vibration appears between 410 and 380 cm^{-1}. Table IV also lists the C=C stretching frequencies of olefins (free and coordinated) and the low-frequency shifts of this mode upon coordination. Apparently, the magnitude of the shift is not parallel to the Pt–olefin stretching frequency. As pointed out in our previous paper,[8] the C=C stretching mode of an olefin often couples with other modes such as the CH_2 scissoring. Thus, the magnitude of the shift in this mode upon coordination cannot be used as a quantitative measure of the strength of the coordinate bond. It is clear that the metal–olefin stretching force constant serves as the best measure for the strength of coordination.

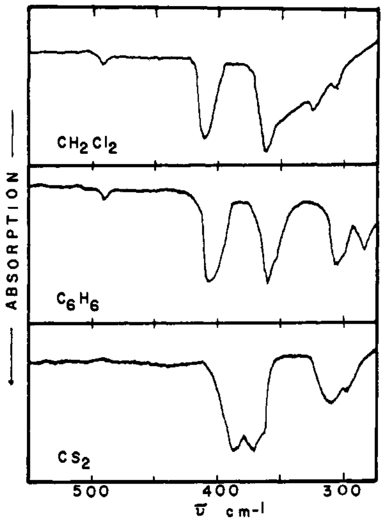


Figure 3. Far-infrared spectra of Zeise's dimer in various solvents.

Finally, it is interesting to note in Table II that the Pt–Cl (terminal) stretching force constant is slightly larger than those of Zeise's salt (~1.82–1.78 mdyn/Å),[8]

---

(14) Zeise's salt exhibits a band at 493 cm^{-1} which was assigned to a vibrational mode of the crystal water.[8] Although the shape of this band is sensitive to the condition of dehydration, it always remains as a weak band even after complete dehydration. It is probable that this band is an overlap of a librational mode of the crystal water and a combination or an overtone discussed above for Zeise's dimer.

whereas the Pt–Cl (bridging) stretching force constant is much smaller than those of Zeise's salt. This result suggests that the bridging Pt–Cl bond is much weaker than the terminal Pt–Cl bond. A similar result has been obtained from the normal coordinate analysis of the Al_2Cl_6 molecule[15] which yielded the values of 2.35 and 1.05 mdyn/Å for the terminal and bridging Al–Cl stretching force constants, respectively.

Acknowledgments. The authors wish to express their sincere thanks to Mr. H. S. Haber of Applied Physics Corp. for obtaining the Raman spectrum of Zeise's dimer. The Beckman IR 11 far-infrared spectrophotometer used in this investigation was purchased by a NSF research equipment grant (GP-5417).

---

[15] T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, **20**, 325 (1964).

Kinetics of Ligand Exchange in Tetrahedral Complexes. Ligand Exchange with Some Tertiary Phosphine Complexes of Nickel(II) and Cobalt(II) by Proton Magnetic Resonance[1]

Louis H. Pignolet and William DeW. Horrocks, Jr.

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey 08540.

Received July 17, 1967

Abstract: The kinetics of exchange of ligand, L, in pseudo-tetrahedral complexes of the type ML_2X_2 (where M = Co, Ni; X = Cl, Br, I; and L = triphenylphosphine, tri-*p*-tolylphosphine, or *n*-butyldiphenylphosphine) with excess phosphine has been studied in deuteriochloroform solution. Kinetic parameters for the exchange between −60 and 60° have been obtained by proton magnetic resonance by using shift and line-width techniques. The ligand exchange follows second-order kinetics with the nickel(II) complexes being more labile than their cobalt(II) analogs. The lability of a particular series increases slightly in the order I < Br < Cl. The new dihalobis(*n*-butyldiphenylphosphine)cobalt(II), $Co(BPP)_2X_2$, complexes have kinetic parameters for ligand exchange similar to those of the triarylphosphines.

A kinetic study of triphenylphosphine (TPP) exchange with some pseudo-tetrahedral complexes was recently reported by us in a preliminary communication.[2] This was the first reported investigation of ligand exchange in "tetrahedral" divalent first-row transition metal complexes. Results of this sort are important in establishing the mechanism of ligand exchange and assessing the importance of ligand-field effects in this class of compound. We present here a more comprehensive account of this work and have extended the study to chloro as well as bromo and iodo complexes. The study of tri-*p*-tolylphosphine (TTP) complexes enabled us to use an alternative nmr shift technique in addition to the line-width method employed earlier.[2] The pmr spectra of these complexes are well known[3–5] as is their pseudo-tetrahedral structure in solution.[6–10] The new dihalobis(*n*-butyldiphenylphosphine)cobalt(II) complexes were synthesized in order to determine the effect on the ligand-exchange kinetics of substitution of an aryl group by an alkyl group.

Procedure

Nuclear magnetic resonance techniques for studying exchange kinetics are well known and have frequently been applied to systems reported in the current literature.[11–15] Two of these methods were used in this study.

Method I. Kinetic parameters can be obtained from the measured line width at half-height, $\Delta\nu_{1/2}$ (cps), of an isotropically shifted[3] resonance of a proton on a coordinated ligand. In such a system the effective transverse relaxation time of a ligand proton, T_2, is given by $(1/T_2) = \pi\Delta\nu_{1/2}$. This is related to $T_{2\mathrm{m}}$, the transverse relaxation time in the absence of exchange, and τ_{m}, the average residence time of a ligand in the complex, by[12,16]

$$1/T_2 = 1/T_{2\mathrm{m}} + 1/\tau_{\mathrm{m}} \qquad (1)$$

---

[1] This research was supported by the National Science Foundation through Grant GP 6321.

[2] W. D. Horrocks, Jr., and L. H. Pignolet, *J. Am. Chem. Soc.*, **88**, 5929 (1966).

[3] G. N. LaMar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

[4] E. A. LaLancette and D. R. Eaton, *J. Am. Chem. Soc.*, **86**, 5145 (1964).

[5] G. N. LaMar, *J. Phys. Chem.*, **69**, 3212 (1965).

[6] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

[7] M. C. Browning, R. F. B. Davies, D. J. Morgan, L. E. Sutton, and L. M. Venanzi, *ibid.*, 4816 (1961).

[8] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **83**, 344 (1961).

[9] F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *ibid.*, **83**, 1780 (1961).

[10] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).

[11] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[12] Z. Luz and S. Meiboom, *ibid.*, **40**, 1058 (1964).

[13] Z. Luz and S. Meiboom, *ibid.*, **40**, 2686 (1964).

[14] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

[15] J. S. Babiec, Jr., C. H. Langford, and T. R. Stengle, *ibid.*, **5**, 1362 (1966).

[16] L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).