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Single-Crystal Polarized Electronic Spectra, Ligand Field Analysis, and Vibronic Analysis of Olefin Complexes of Square-Planar Platinum(II)

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The 10 K single-crystal polarized electronic absorption spectra of $(Pr_4N)[PtCl_3(C_2H_4)]$ and $K[PtCl_3(C_3H_6)]\cdot H_2O$ are reported. These spectra are compared to those of Zeise's salt. The change of the cation from K^+ to Pr_4N^+ causes a red shift in the d–d transitions of about 900 cm^{-1}. The ligand field bonding properties of ethylene and propylene are analyzed by using the angular overlap form of ligand field theory. The olefins are good σ-donor and strong π-acceptor ligands. The spectrum of $(Pr_4N)[PtCl_3(C_2H_4)]$ contains well-resolved vibronic structure on several of the ligand field and charge-transfer bands. A Franck–Condon calculation of the intensities of the vibronic features shows that the metal–olefin bond is lengthened by 0.18 Å in the $^1B_2$ excited state. The vibrational frequency is decreased by 53 cm^{-1} in the excited state. The relationships between these changes and both the ligand bonding properties and the orbitals involved in the transition are discussed.

The series of square-planar monosubstituted $PtCl_3L^-$ compounds is proving very useful for studying the ligand field transitions, d-orbital energies, and metal–ligand interactions for ligands L of interest in organometallic chemistry such as olefins,[1] CO,[2] phosphine, arsine,[3] and isonitriles.[2] Techniques for measuring single-crystal polarized absorption spectra of compounds having absorption bands with extinction coefficients greater than 10^3 L/(M cm) have been developed.[1] Zeise's salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$ provided the prototypical compound for studying an olefin's interaction with platinum. In order to determine whether or not electronic spectroscopy is sensitive enough to measure subtle effects such as a minor change in the substituent on the olefin or a change in the cation, the spectra of complexes containing simple olefins other than ethylene and cations other than potassium have been obtained.

Changing the olefin from ethylene to propylene should cause subtle changes in the electronic structure of the platinum complex. Photoelectron spectroscopic studies[4] of the free ligand showed that the C═C π-electron ionization energy is lower for propylene than for ethylene. Hoffmann et al. performed EHMO calculations[5] on ethylene and substituted ethylenes. They concluded that a donor group would raise both the π-bonding and π-antibonding orbital energies. These studies suggest that the platinum to olefin charge-transfer bands should shift to higher energy when propylene is substituted for ethylene in a $PtCl_3L^-$ complex.

During the course of our studies of the effects of the cation on the electronic spectra, we observed that the resolution of vibronic structure on the electronic bands was strongly affected. The spectra of Zeise's salt contain poorly resolved vibronic structure[1] whereas in the spectra of $(Pr_4N)[PtCl_3(C_2H_4)]$ the vibronic structure is prominent. This type of counterion effect on the electronic spectra of ionic transition-metal compounds was recently used to experimentally obtain well-resolved vibronic structure in the absorption spectra of $[Cr(NH_3)_6](ClO_4)_2Cl\cdot KCl$ and $[Co(NH_3)_6](ClO_4)_2Cl\cdot KCl$.[6,7] The spectra of these complexes with other counterions that had been taken previously consisted of broad featureless bands.[8]

The presence of vibronic structure on an electronic absorption band allows a more detailed analysis of the excited-state properties to be made than is possible from only the featureless envelope. Bond length changes in excited electronic states can be determined by a Franck–Condon analysis of the intensities of the members of the vibronic progression. In mixed-ligand compounds, the appearance of a progression in a normal mode involving primarily one specific metal–ligand bond can implicate specific d-orbital involvement in the electronic transition. In this case the vibronic structure can aid in the assignment of the electronic states.

In this paper we report the spectroscopic results of making two small perturbations on Zeise's salt. First, we report the single-crystal polarized electronic absorption spectra of $K[PtCl_3(C_3H_6)]\cdot H_2O$ taken at 10 K and compare these spectra to those of Zeise's salt. The subtle changes in the d–d and charge-transfer band energies caused by the methyl substituent are measured. The σ and π interactions of propylene with platinum are analyzed by using the angular overlap formulation of crystal field theory. Second, we report the appearance of resolved vibronic structure in the electronic absorption spectrum of the tetra-*n*-propylammonium salt of $[PtCl_3(C_2H_4)]^-$. Both the intensities of the members of the progression in the $^1B_2$ band and the metal–ligand bond length change are calculated. The role of back-bonding between platinum and π-acceptor ligands in producing vibronic structure is analyzed. The use of the vibronic features in assigning the electronic transitions is discussed.

Experimental Section

$(Pr_4N)[PtCl_3(C_2H_4)]$ was prepared by reacting ethylene with $(Pr_4N)_2[Pt_2Cl_6]$. The dimer was prepared by the published method.[9–11] A solution of 0.195 g of the dimer in 10 mL of nitromethane was stirred under a continuous flow of ethylene for 48 h. The solution was filtered, and the filtrate was concentrated to 2 mL. A platelike yellow solid was obtained by slow addition of diethyl ether to the solution. The solid was collected by filtration, redissolved into nitromethane, and crystallized by adding diethyl ether.

The propylene analogue of Zeise's salt, $K[PtCl_3(C_3H_6)]\cdot H_2O$, was prepared according to the literature method.[12] Propylene was bubbled into an aqueous solution of K_2PtCl_4 under nitrogen. $SnCl_2$ was used as a catalyst to increase the reaction rate. The product was purified by recrystallization from carbon tetrachloride to remove unreacted K_2PtCl_4 and $SnCl_2$.

Single crystals of $(Pr_4N)[PtCl_3(C_2H_4)]$ for spectroscopic study were grown between quartz plates that were stored in a covered dish in the dark. A drop of a solution of the complex in nitromethane was put onto one plate and a second plate was pressed on top of the first. The dish was covered and allowed to stand for several hours until crystals formed. Rectangular plates of dimensions of the order of 100 × 500 × 1 μm micron were obtained. The spectrum labeled parallel was obtained with the electric vector of the incident radiation parallel to the extinction direction at an angle of 28° with the long crystal axis. Although the crystal structure is not known and the crystals are necessarily too small for analysis by X-ray diffraction, analysis of the spectrum suggests that the parallel spectrum is primarily *z*-polarized in the molecular axis system. The perpendicular spectrum was obtained in the orthogonal extinction direction. This direction probably consists of primarily the *x* and/or *y* molecular axes.

Single crystals of $K[PtCl_3(C_3H_6)]\cdot H_2O$ were grown from an aqueous solution. Long rectangular crystals usually formed. Crystals of usable

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size and thickness were obtained by putting a drop of very concentrated solution at the center of each pair of quartz plates. Water was introduced into the crystal growing dish to lengthen the solvent evaporation time. The aqueous solution spectrum was measured by using a Varian Cary 219 spectrophotometer.

The polarized absorption spectra of both compounds at 10 K were obtained by using the instrument described previously.[1] Because the extinction coefficients of several of the bands exceeded 10^3 L/(M cm), the use of thin microcrystals and the specially designed microspectrophotometer was mandated.

Results

The electronic absorption spectra of a thin single crystal of $(Pr_4N)[PtCl_3(C_2H_4)]$ taken at 10 K in the two orthogonal extinction directions are shown in Figure 1. The spectral region shown in the figure, 27 000–39 000 cm^{-1}, contains the spin-allowed d–d transitions as well as spin-forbidden charge-transfer transitions. The region to lower energy contains weak structureless bands arising from spin-forbidden d–d transitions. The energies of all of the bands are listed in Table I.

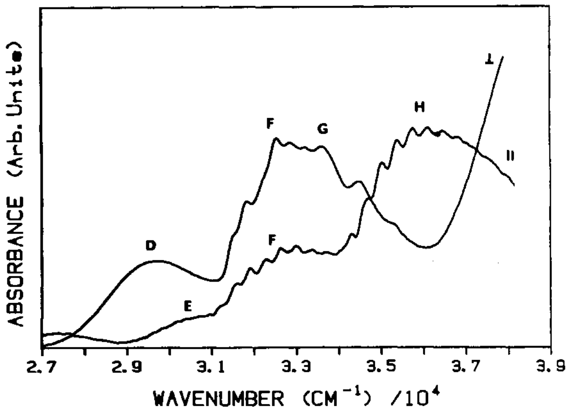

Figure 1. Single-crystal polarized electronic absorption spectra of $(Pr_4N)[PtCl_3(C_2H_4)]$ at 10 K in the region between 27 000 and 38 000 cm^{-1}.

Table I. Observed and Calculated Transition Energies (cm^{-1}) for $(Pr_4N)[PtCl_3(C_2H_4)]$

obsd	calcd[a]	assignt	label
	Singlet d–d		
29 700	29 705	$^1B_1$	D
30 350	30 375	$^1A_2$	E
32 800	32 809	$^1B_2$	F
35 900[b]	35 667	$^1A_1$	(H)
	Triplet d–d		
	19 256[c]	B_2	
	19 313	B_1	
	19 369	A_1	
22 315	22 048	A_2	
	22 449	B_1	
	23 293	A_1	
24 200	23 962	A_2	
	24 425	B_2	
	26 291	A_1	
26 724	26 344	B_2	
	26 450	A_2	
	28 367[d]	B_1	
	Triplet Charge Transfer		
33 570		$^3A_2$	G
(35 900)[b]		$^3B_1$	(H)

[a] The transition energies were calculated by using the following parameters (cm^{-1}): $e_\sigma^{Cl} = 12\,300$, $e_{\pi\parallel}^{Cl} = 2570$, $e_{\pi\perp}^{Cl} = 3710$, $e_\sigma^{\infty} = 14\,250$, $e_{\pi\parallel}^{\infty} = -150$, $e_{\pi\perp}^{\infty} = 70$, $B = 500$, $C = 2300$, $\sigma_{sd} = 12\,640$, $\xi = 2350$. [b] Both the width and energy of band H are in the range expected for the ^1A, d–d transition. However, assignment of this band to a triplet charge-transfer transition cannot be ruled out. [c] Nonzero intensity but no clearly defined peak is observed. [d] Obscured by the $^1B_1$ band.

The solution spectrum of the compound in acetonitrile consists of five broad featureless bands with energies (cm^{-1}) and extinction coefficients (L/(M cm)) of 22 200 (15), 29 700 (188), 33 300 (520), 37 800 (1800), and 40 700 (2230). The values of the extinction coefficients are typical for square-planar platinum(II) compounds where spin-forbidden d–d transitions typically are <100, spin-allowed d–d transitions are between 100 are 1000, and charge-transfer transitions are >1000.

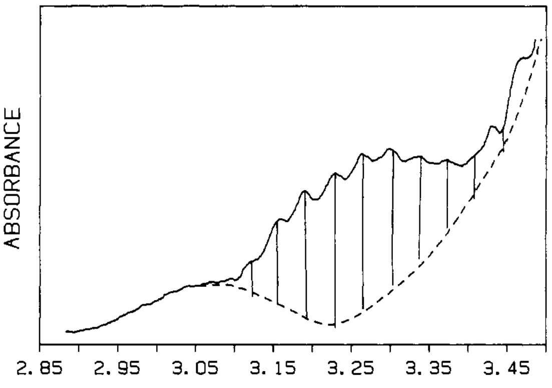

Figure 2. Vibronic structure on the $^1B_2$ absorption band of $(Pr_4N)[PtCl_3(C_2H_4)]$ at 10 K. The vertical bars are the intensities calculated by using a Franck–Condon analysis and a distortion between the platinum and the centroid of the carbon atoms of 0.18 Å.

Table II. Positions of the Vibronic Bands in the Electronic Absorption Spectrum of $[Pr_4N][PtCl_3(C_2H_4)]$

electronic band	vibronic max, cm^{-1}	sep, cm^{-1}	electronic band	vibronic max, cm^{-1}	sep, cm^{-1}
				(30 510)[a]	
				(30 870)[a]	
$^1B_2$ (∥)	31 479		$^1B_2$ (⊥)	31 225	
	31 819	322		31 601	376
	32 187	368		31 923	322
	32 535	348		32 295	372
	32 853	318		32 621	326
	33 196	343		33 005	384
		340 (av)		33 367	362
$^3B_1$	34 321			33 725	358
	34 682	361			357 (av)
	35 039	357			
	35 397	358	$^3A_2$	33 617	
	35 769	372		34 482	865
	36 130	361		35 338	856
	36 474	344			860 (av)
	36 825	351			
		357 (av)			

[a] The positions of these weak bands cannot be measured accurately enough to be used to determine the vibronic spacing.

The energies and intensities of the absorption bands in $Pr_4N[PtCl_3(C_2H_4)]$ are very similar to those observed in $K[PtCl_3(C_2H_4)]\cdot H_2O$.[1] The major difference between the spectra of the two compounds is the well-resolved vibronic structure in the former. A minor systematic difference is that the d–d bands in the former are red-shifted by an average of about 900 cm^{-1} relative to the corresponding bands in the latter.

The positions of the prominent vibronic peaks shown in Figure 2 are listed in Table II. Note that the peaks on the band labeled F are also found on the band labeled both F and G in perpendicular polarization. The peaks in the latter polarization direction are the superposition of two different progressions from two different electron states. The lower frequency progression has a spacing of about 340 cm^{-1} while the higher frequency progression has a spacing of about 860 cm^{-1}. Because of the overlap between the two electronic bands in the perpendicular polarization spectrum and thus the corresponding overlap between the two vibrational progressions, neither the energies nor the intensities can be as accurately determined as is possible in the parallel polarization.

The single-crystal polarized absorption spectra of $K[PtCl_3(C_3H_6)]\cdot H_2O$ are shown in Figures 3 and 4. The band energies are listed in Table III. The spectra in Figure 3 were measured

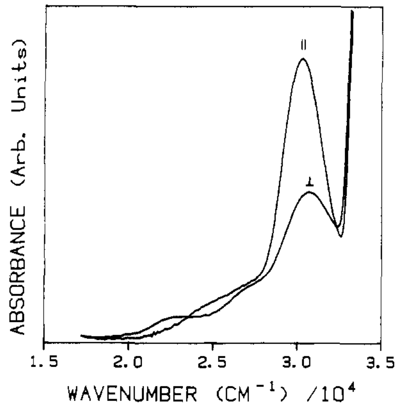

Figure 3. Single-crystal polarized electronic absorption spectra of $K[PtCl_3(C_3H_6)]\cdot H_2O$ at 10 K.

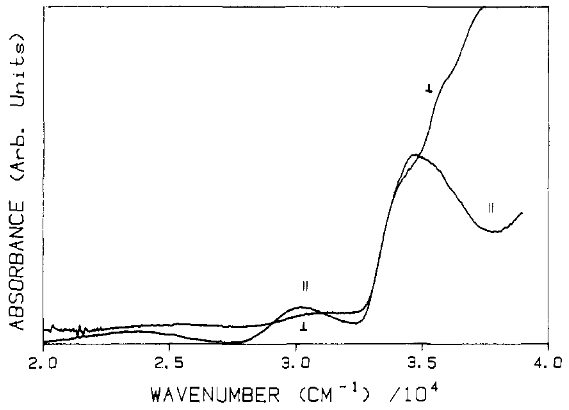

Figure 4. Single-crystal polarized electronic absorption spectra of $K[PtCl_3(C_3H_6)]\cdot H_2O$ at 10 K obtained from a crystal thinner than that used to obtain the spectra in Figure 3.

from a thick crystal to obtain information about the bands with low extinction coefficients in the spin-forbidden region of the spectrum. Three bands are observed in perpendicular polarization at 22 600, 27 200, and 30 570 cm^{-1}. Three unresolved features are observed in the region between 22 000 and 27 000 cm^{-1} in parallel polarization. A well-resolved but unsymmetrical band is also observed at 30 160 cm^{-1}.

The spectra in Figure 4 were obtained from an ultrathin crystal in order to obtain the peak positions of transitions with large extinction coefficients. An unsymmetrical band centered at about 34 600 cm^{-1} is observed in parallel polarization. This band is very well resolved, and the band maximum is very clear. The corresponding band in the ethylene analogue is not well resolved because it overlaps a second band at slightly higher energy. In the perpendicular polarization spectrum of the propylene compound in Figure 4, the beginning of a vibronic progression from a second peak of higher energy is observed on the high-energy side of the 34 600-cm^{-1} band. The maximum of the second peak is at a high energy out of the range of the instrument.

The solution spectrum of the propylene compound in water consists of two peaks and one shoulder. The lowest energy band occurs at 30 000 cm^{-1} with an extinction coefficient of 200 L/(M cm). The other band is at 42 700 cm^{-1}, with an extinction coefficient of 1500 L/(M cm). The shoulder is at about 35 700 cm^{-1}.

Discussion

1. Assignments of the Electronic Transitions and Calculations of the Ligand Field Transition Energies and the Ligand Field Parameters. The absorption bands in the electronic spectra of $(Pr_4N)[PtCl_3(C_2H_4)]$ have a one to one correspondence with those of Zeise's salt. The assignments of the bands in the former compound are thus analogous to those made previously for Zeise's salt.[1] These assignments are given in Table I. (As before, we have used an axis system with the z axis perpendicular to the square plane and the x axis along the ethylene–platinum bond. The B_1 irreducible representation is defined as the one symmetric to reflection in the xy mirror plane.) The one-electron transitions corresponding to the state assignments in Table I are d_{xy} to $d_{x^2-y^2}$ (A_1 to B_1), d_{yz} to $d_{x^2-y^2}$ (A_1 to A_2), d_{xz} to $d_{x^2-y^2}$ (A_1 to B_2), and d_{z^2} to $d_{x^2-y^2}$ (A_1 to A_1).

Table III. Observed and Calculated Transition Energies (cm^{-1}) for $K[PtCl_3(C_3H_6)]\cdot H_2O$

obsd	calcd[a]	assignt
	Singlet d–d	
30 160	30 157	$^1B_1$
30 570	30 571	$^1A_2$
34 680	34 671	$^1B_2$
b	35 618	$^1A_1$
	Triplet d–d	
	19 124[c]	B_2
	19 205	B_1
22 600	19 363	A_1
	23 274	A_2
	23 770	B_1
24 500	23 977	A_2
	24 601	A_1
	24 726	B_2
27 000	26 424	B_2
	27 124	A_2
	27 135	A_1
	28 814	B_1

[a] The transition energies were calculated by using the following parameters (cm^{-1}): $l_\sigma^{Cl} = 12\,300$, $l_{\pi\parallel}^{Cl} = 2570$, $l_{\pi\perp}^{Cl} = 3710$, $l_\sigma^{C=C} = 14\,050$, $l_{\pi\parallel}^{C=C} = -600$, $l_{\pi\perp}^{C=C} = -2250$, $B = 500$, $C = 2300$, $\sigma_{sd} = 12\,780$, $\xi = 2560$. [b] Obscured by the charge-transfer band. [c] Nonzero intensity but no clearly defined peak observed.

The spectra of the propylene compound are very similar to those of the ethylene analogue, and the absorption bands are assigned in a similar way. The lowest energy d–d band at 30 160 cm^{-1} is more intense in parallel polarization. This band is assigned as the $^1A_1$ to $^1B_1$, d_{xy} to $d_{x^2-y^2}$ transition. The next d–d band at 30 570 cm^{-1} is assigned as $^1A_1$ to $^1A_2$, d_{yz} to $d_{x^2-y^2}$ transition. The energies of these two bands are very similar, but they are separable by using polarized light as shown in Figure 3. The third d–d band is observed at 34 600 cm^{-1} and is allowed in parallel polarization as shown in Figure 4. It is assigned to the $^1A_1$ to $^1B_2$, d_{xz} to $d_{x^2-y^2}$ transition.

All of the d–d transitions of $(Pr_4N)[PtCl_3(C_2H_4)]$ are lower in energy than those of $K[PtCl_3(C_2H_4)]\cdot H_2O$. However, the magnitude of the red shift of each of the bands is different. The magnitudes of the red shifts of the $^1A_2$ band, the $^1B_1$ band, and the $^1B_2$ band are 900, 600, and 1320 cm^{-1}, respectively.

There is no general trend in the d–d band energies of $K[PtCl_3(C_3H_6)]\cdot H_2O$ compared to those of $K[PtCl_3(C_2H_4)]\cdot H_2O$. The B_1 and A_2 bands shift to lower energy by 1500 and 670 cm^{-1}, respectively, while the B_2 band shifts 560 cm^{-1} to higher energy.

The $^1B_2$ band of the propylene compound is not obscured by a charge-transfer band, and its position can be accurately determined. A spin-forbidden platinum to olefin charge-transfer band is centered at 34 600 cm^{-1} in Zeise's salt. The *n*-propylammonium salt of the ethylene compound has two spin-forbidden charge-transfer bands at 33 570 and 35 900 cm^{-1} which overlap the $^1B_2$ ligand field band. The charge-transfer band in the propylene compound occurs at significantly higher energy. The introduction of a methyl group into the ethylene ligand raises the energy of the π^* orbitals, which causes the platinum to olefin charge-transfer band to shift to higher energy. The band maximum of this charge-transfer band is out of the range of the instrument. Thus, only the beginning of the vibronic progression (with a spacing of about 1500 cm^{-1}) is observed in perpendicular polarization as shown in Figure 4. This shift of the charge-transfer band toward high energy enables the energy of the $^1B_2$ transition to be more accurately determined in the propylene compound than is possible in the case of Zeise's salt.

Ligand Field Parameters. The transition energies and the angular overlap σ and π parameters for all the compounds discussed in this work are calculated by using the full-matrix angular overlap calculation including spin–orbit coupling. The matrix elements[13] and the parameters used in this calculation have been discussed previously.[14] The results of the calculation and the values of the parameters are given in Tables I and III.

The quantitative agreement between the calculated and observed singlet-state transition energies is excellent for both compounds. The mean discrepancies between the measured and calculated energies are 5 cm^{-1} for the propylene compound and 13 cm^{-1} for the *n*-propylammonium compound. The calculations are also in agreement with the assignments. The calculated transition energies of the triplet states also agree well with the observed transitions. The calculation, including spin–orbit coupling, shows that the observed spin-forbidden bands do not arise from a single "triplet" state such as $^3B_2$ but instead are composed of clusters of spin–orbit-coupled components. The irreducible representations and the energies of the components comprising the clusters are given in Tables I and III.

The AOM parameters for the ethylene complex given in Table I are different from and more accurate than those reported previously.[1] The values in Table I were calculated by using the full-matrix calculation whereas those in ref 1 were estimated by using only the diagonal matrix elements. All of the values quoted in this paper and in those subsequent to the original work are determined by the full-matrix calculation.

The angular overlap σ and π parameters for the olefins derived from the full-matrix calculations enable the σ-donor and π-acceptor interactions of these ligands to be compared with those for other ligands of interest in organometallic chemistry. The olefins' σ parameters show that they are good σ-donor ligands. The σ-donor series that has been determined to date is $PEt_3 > NMe_3 > PPh_3 > AsPh_3 >$ olefin $> Cl > Br$.[2] The π parameters provide a relative ordering of the metal–ligand π interactions. The more positive the value the better the π-donor properties while the less positive (or more negative) the value the better the π-acceptor properties. Of the compounds studied to date only carbon monoxide is a better π acceptor than the olefins. The π-interaction series, ordered in terms of π-acceptor ability, is CO > olefin > $AsPh_3 > PPh_3 > PEt_3$.[2,15] The values of the AOM parameters for the ligands in the above series are different enough for reliable comparisons to be made.

The electronic absorption spectra have more than enough resolution to allow the ethylene and propylene complexes to be differentiated. For example, the difference between the $^1B_1$ band energies of the potassium salts of the ethylene and propylene complexes is -1500 cm^{-1} and the difference between the $^1B_2$ band energies is $+560$ cm^{-1}. Although the experimental resolution is high and the bands shift in opposite directions, the angular overlap model cannot reliably provide a measure of the relative σ and π interactions of the ligands. In an attempt to determine these relative interactions, the best fits to the experimental spectra were obtained by holding all of the AOM parameters constant except for the σ and π parameters of the olefins. The ethylene ligand's σ parameter is 15 200 cm^{-1} compared to the propylene's σ parameter of 14 050 cm^{-1}. The respective π parameters are -330 and -1425 cm^{-1}. Equally good fits yielding different values for the olefin parameters can be obtained when the other AOM parameters in the calculation such as the halide parameters or the Racah parameters are allowed to vary slightly.

Four sources of uncertainty can cloud the comparison of AOM parameters when they are as similar as those for the olefins. First, the angle between the direction of the olefinic double bond and the coordination plane is unknown. Ethylene is assumed to be symmetrical and perpendicular to the square plane when bonded to the metal. When a substituent is attached to the olefin double bond, the metal olefinic carbon bonds become unequal, with the longer bond being that to the methyl-substituted carbon. The olefin double bond is no longer perpendicular to the square plane. These structural changes are not considered in the AOM calculation. Second, uncertainties of the energies of the bands in Zeise's salt contribute to the uncertainties in the AOM parameters for that compound. For example, the $^1B_2$ band, whose maximum is estimated at about 34 100 cm^{-1}, is overlapped by the charge-transfer band. Third, the olefin's AOM parameters are dependent on those chosen for chloride. When the chloride sigma parameter is changed, the olefin's σ parameter changes by three times that amount in the opposite direction. There is a one to one relationship of opposite sign between the chloride and olefin π parameters. Small modifications of the chloride parameters can still produce good fits to the experimental spectrum and give different sets of parameters for L. Fourth, interaction of the metal compound with its environment is observed in the experimental spectrum but is not explictly included in the AOM calculation. For example, changing the cation from K^+ to Pr_4N^+ changes the σ AOM parameter for ethylene by 950 cm^{-1} and the π parameter by 290 cm^{-1}. The total magnitudes of the uncertainties in the parameters are difficult to determine. From experience with the transferability of the parameters in the square-planar Pt(II) compounds, the uncertainties of the σ and π parameters are estimated to be on the order of ± 500 cm^{-1}. When all of the uncertainties discussed above are considered, the parameters for the ethylene and propylene are too similar to allow reliable comparisons between the bonding properties of the two ligands to be made.

2. Vibronic Structure. Three electronic absorption bands in Figure 1 show pronounced vibronic structure: band F ($^1B_2$), band G (MLCT), and band H (MLCT). The spacing between the peaks in band F in parallel polarization is 357 cm^{-1}. The spacing between the peaks in band G, 860 cm^{-1}, is most clearly seen at the high-energy side of the electronic band in perpendicular polarization. In this polarization direction, the spectrum consists of two overlapping absorption bands, bands F and G. The overlapping of the vibronic peaks with spacings of 860 and 357 cm^{-1} is seen on the low-energy side of the combined peaks. The spacing between the peaks in band H is 357 cm^{-1}.

The totally symmetric metal–ligand stretching vibrational frequencies in the ground state are 410 cm^{-1} for the platinum–ethylene stretch, 303 cm^{-1} for the cis platinum–chloride stretch, and 331 cm^{-1} for the trans platinum–chloride stretch.[16,17] These frequencies are expected to decrease in the d–d excited electronic states because σ-antibonding orbitals are populated (vide infra). In all of the $PtCl_3L^{n-}$ complexes (including L = Cl) that have been studied to date, the vibrational frequencies observed in ligand field electronic excited states were lower than those in the ground electronic state.[2,18,19] If the MIME effect is occurring, the observed 357-cm^{-1} frequency could be a result of both metal–chloride and metal–olefin modes.[20-22] A detailed calculation is not possible here because the vibrational frequencies in the excited electronic state are not known. The 357-cm^{-1} frequency observed on band F is assigned to primarily the Pt–C stretch, which is decreased from its 410 cm^{-1} value in the ground electronic state.

The vibrational frequencies in the MLCT excited states cannot at present be assigned. The progression with a frequency of 357 cm^{-1} on band H could be caused by a Pt–Cl stretch with an increased frequency in the excited state or the Pt–C stretch with a decreased frequency. (Note that the frequency is coincidentally about the same as that in band F. The progression in band H is separated from that in band F by a gap of 596 cm^{-1}.) In the metal to olefin charge transfer, the platinum is formally oxidized and the olefin reduced. The electrostatic interaction between the

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more positively charged metal and the chloride ligand would be expected to increase, resulting in an increase in the Pt–Cl stretching frequency. A prediction of the direction of change in the Pt–C stretch cannot be made as easily, although most probably the frequency would be expected to decrease because of decreased metal–olefin back-bonding.

The high-frequency 860-cm^{-1} spacing on charge-transfer band G is unusual because it is much larger than any of the metal–ligand stretching or bending modes and it is much smaller than the 1515-cm^{-1} C=C stretching mode. If the MIME effect is occurring, the observed spacings could arise from a mixture of many normal modes.[20–22]

The magnitude of the bond lengthening in the ligand field excited states of $[PtCl_3(C_2H_4)]^-$ can be calculated from the Franck–Condon factors. The calculational procedure has been discussed in detail previously.[18] In the cases of the bands shown in Figure 1, the accuracy of the calculation is limited because of the overlapping of several electronic transitions. An estimate of the distortion of the platinum–carbon bond length in the $^1B_2$ excited state can be obtained from the spectrum taken in parallel polarization. The vibronic intensities calculated by using the ground- and excited-state frequencies, a spectral origin of 30 511 cm^{-1}, and a distortion of 0.18 Å are shown superimposed on the experimental spectrum in Figure 2. This distortion in the platinum–olefin bond has an uncertainty of about ±0.03 Å because of the uncertainty in the intensities of the tails of the bands from the overlapping electronic transitions.

The change of the Pt–olefin bond length of about 0.18 Å from its ground-state value of 2.02 Å is typical for Pt(II) complexes. Large changes are apparently not uncommon in systems of this type. In the case of the $PtCl_3CO^-$ complex, for example, the platinum–carbon bond length change was also 0.18 Å.[2] The platinum–carbonyl stretching frequency in the excited state was 80% of that in the ground state. The 0.18 Å bond length change and the 13% change in the platinum–olefin stretching frequency are evidence for a significant change in the electronic structure of the molecule in the $^1B_2$ excited state.

3. Relationships between Vibronic Structure and Ligand Bonding Properties. The coupling of the Pt–C vibration with the $^1A_1$ to $^1B_2$ transition can be explained in terms of the orbital properties of the transition.[23] This transition corresponds to a one-electron promotion from the d_{xz} orbital to the $d_{x^2-y^2}$ orbital. In the molecular orbitals involved in this transition, the d_{xz} orbital participates in π bonding between the Pt and the olefin while the $d_{x^2-y^2}$ orbital participates in metal–olefin σ antibonding. Thus the transition weakens both the π bonding and the σ bonding between the metal and the carbon leading to a large displacement of the excited-state potential surface along the totally symmetric Pt–C stretching normal mode relative to the ground electronic state.

The smaller coupling of the Pt–Cl vibrations with the $^1B_2$ transition is the result of the simultaneous metal–ligand π-bond strengthening and small σ-bond weakening. The d_{xz} orbital is π antibonding between the platinum and the trans chloride. Depopulation of this orbital strengthens the π bond, which opposes the small σ-bond weakening. The metal–olefin σ bond is more strongly weakened than the metal–chloride bond because its σ parameter, 14 250 cm^{-1}, is larger than that for the chloride, 12 300 cm^{-1}. The metal–olefin π bond is more strongly weakened than the metal–chloride bond because its π parameter, −120 cm^{-1}, is much smaller than that for the chloride, 3370 cm^{-1}.

The experimental observation of a vibronic progression in the Pt–olefin stretching normal mode provides additional aid in the assignment of the d–d transition. Only the transition to the $^1B_2$ state involves the metal–olefin π interaction whereas all of the d–d transitions involve identical values of the Pt–C σ interaction. Also, in this example the progression is identified as the Pt–olefin stretch because it is larger than any of the other metal–ligand stretches. A similar set of circumstances occurred in the spectra of $PtCl_3CO^-$, and similar reasoning was used. In these cases, the identification of the Pt–C stretching mode vibronic structure on the electronic band provides additional support for the assignment of that band as $^1B_2$.

The experimental results show that well-defined vibronic structure in ionic square-planar platinum compounds can be observed when a suitable counterion is found and a large distortion along a single normal mode of relatively high frequency exists in the molecule. To date no systematic method is known for predicting what type of counterion will produce a crystal that will give well-resolved vibronic structure in its spectra. The results do show that vibronic structure is likely to be prominent when primarily one normal mode with a relatively large vibrational frequency is involved. These latter conditions are met for light ligands with both strong π-acceptor and σ-donor abilities.

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Registry No. $(Pr_4N)[PtCl_3(C_2H_4)]$, 33480-45-4; $K[PtCl_3(C_3H_6)]\cdot H_2O$, 12144-27-3.

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