Infrared Spectra and Structure of Acetylacetonatoplatinum(II) Complexes. IV.   Infrared Spectra of Acetylacetonato Complexes Containing Both Platinum–Oxygen and Platinum–Olefinic Bonds[1,2]

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The infrared spectra of two acetylacetonato complexes containing both platinum–oxygen and platinum–olefinic bonds have been obtained from 4000 to 300 cm^{-1}.   It has been shown that the spectra of these compounds can be interpreted approximately as a superposition of spectra of the oxygen-bonded (chelated) acetylacetonate and the olefinic moiety.   The bonding between the Pt atom and the olefinic moiety has been discussed on the basis of infrared spectra.

Introduction

In 1827, Zeise[3] prepared the platinum–ethylene complex $K[C_2H_4PtCl_3] \cdot H_2O$ and its dimer, $[(C_2H_4)PtCl_2]_2$.   Subsequently many investigators have prepared a large variety of compounds containing uncharged ligands which may be considered substituted ethylene molecules.   Several investigators have studied the infrared spectra of one or more of these compounds.[4–7] Recently, Grogan and Nakamoto have assigned the infrared spectra of Zeise's salt[8] and Zeise's dimer[9] based on the results of normal-coordinate analyses.   Thus the band assignments for the coordinated ethylene portion of the Zeise's salt anion are well established.   In the previous papers of this series, we have reported the infrared spectra and normal-coordinate analyses on the O-bonded (chelated)[10] and C-bonded[11] acetylacetonato complexes of Pt(II).   In this investigation, we have prepared a novel Pt(II) complex containing the O-bonded acetylacetonato ligand and the π-bonded ethylene

I
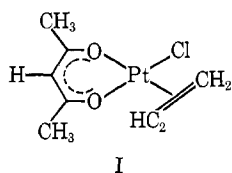
Using the technique demonstrated in the preceding paper,[12] the infrared spectrum of I may be approximated as a superposition of those of potassium dichloro-(acetylacetonato)platinate (II)[10] and Zeise's salt (III),[8] both of which have already been the subject of a detailed interpretation on the basis of normal-coordinate analysis.   Thus the detailed studies on the mag-

II

III
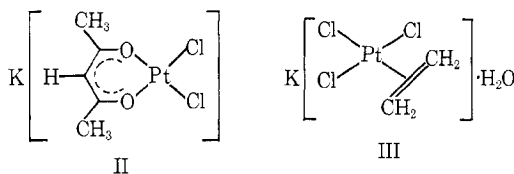
nitude and the direction of band shifts of I relative to II and III would provide valuable information about the nature of interaction between the acetylacetonato ring and the ethylene molecule.   It should be mentioned that the band assignment for the $Pt–C_2H_4$ stretching mode in compound III has been controversial; Paradilla-Sorzano and Fackler[13] assigned the bands at 491 and 403 cm^{-1} to the symmetric and antisymmetric stretching modes, respectively, while Grogan and Nakamoto[8] have assigned only the latter to the stretching mode.   The detailed analysis of the spectrum of I may be useful in solving this controversy.

The other example of acetylacetonato complexes containing the platinum–olefinic bond is

IVa
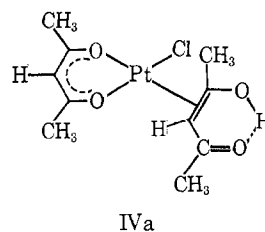
This complex was originally obtained by Allen, *et al.*,[14] by acidifying the solution of potassium chloroacetyl-acetonato(γ-acetylacetonato)platinum(II).   On the basis of nmr evidence, they suggested that the bonding between the enol ring of acetylacetone and the Pt atom is similar to that of Zeise's salt (IVa).   Their recent paper[15] indicated, however, that a wider choice among structures is possible and that the interpretation of their nmr is not unambiguous.   They have suggested

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(2) Submitted by G. T. B. to the faculty of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) W. C. Zeise, *Ann. Physik*, **9**, 632 (1827); **21**, 497 (1831).

(4) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(5) H. B. Jonassen and J. E. Field, *J. Am. Chem. Soc.*, **79**, 1275 (1957).

(6) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

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

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

(9) M. J. Grogan and K. Nakamoto, *ibid.*, **90**, 918 (1968).

(10) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

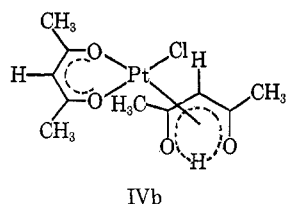(11) G. T. Behnke and K. Nakamoto, *ibid.*, **6**, 440 (1967).

(12) G. T. Behnke and K. Nakamoto, *ibid.*, **7**, 330 (1968).

(13) J. Paradilla-Sorzano and J. P. Fackler, *J. Mol. Spectry.*, **22**, 80 (1967).

(14) G. Allen, J. Lewis, R. F. Long, and C. Oldham, *Nature*, **202**, 589 (1964).

(15) D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc.*, A, 72 (1967).

that structure IVb shown below is more probable than structure IVa. In this structure, the π electrons of the

IVb

enol form of acetylacetone are completely delocalized, and the bonding between this ring and the Pt atom is similar to that found in metal-sandwich compounds. It is, therefore, of particular interest to discuss which structure is more consistent with the results of our infrared studies.

Experimental Section

Preparation of the Compounds.—Chloro(acetylacetonato)-(ethylene)platinum(II) (compound I) was prepared by dissolving 1.0 g of potassium trichloro(ethylene)platinum(II) in a minimum of water at room temperature. The addition of an excess of an aqueous solution of the sodium salt of acetylacetone resulted in the rapid formation of a yellow-green precipitate. This was removed by filtration, washed with ethanol, and dried under vacuum. Recrystallization was from anhydrous ether. *Anal.* Calcd for $C_7H_{11}O_2PtCl$: C, 24.60; H, 3.25. Found: C, 24.64; H, 3.04.

Chloro(acetylacetonato)(π-acetylacetonato)platinum(II) (compound IV) was prepared from a saturated aqueous solution at room temperature of potassium chloro(acetylacetonato)(γ-acetylacetonato)platinum(II) by acidification with dilute HCl. The bright yellow precipitate was immediately removed by filtration and was recrystallized from ether. *Anal.* Calcd for $C_{10}H_{15}$-O_4PtCl: C, 27.95; H, 3.52; Cl, 8.25. Found: C, 27.85; H, 3.65, Cl, 8.30.

Spectral Measurements.—The spectra between 4000 and 300 cm^{-1} were measured with a Beckman IR-12 infrared spectrophotometer. The KBr-disk method was employed for the region 4000–650 cm^{-1}. From 650 to 300 cm^{-1}, polyethylene pellets prepared as previously described[10] were employed. Calibration of the frequency readings was made with polystyrene film, 1,2,4-trichlorobenzene, and water vapor.

Results and Discussion

Chloro(acetylacetonato)(ethylene)platinum(II) (Compound I).—The infrared spectra and vibrational frequencies of I are shown in Figure 1 and Table I, respectively, together with those of II and III. The gross features of the high-frequency region (Figure 1) clearly demonstrate the feasibility of interpreting the infrared spectrum of I approximately as the simple sum of the spectra of II and III. The consistency of peak positions in these high-frequency modes indicates that large interactions between the O-chelated acetylacetonato ring and the ethylene molecule do not occur. For example, the carbonyl stretching modes of I (1567 (ν_1) and 1382 (ν_5) cm^{-1}) are only slightly higher than those of II (1563 and 1380 cm^{-1}). Although the position of ethylene in the *trans*-effect series indicates it to be one of the strongest *trans*-directing groups, it has not produced a secondary effect on the carbonyl bonds of a great magnitude. The C⋮C stretching band (ν_2) of II (1538 cm^{-1}) is shifted to 1527 cm^{-1} in I and has resulted in a clear separation between ν_1 and ν_2. The other
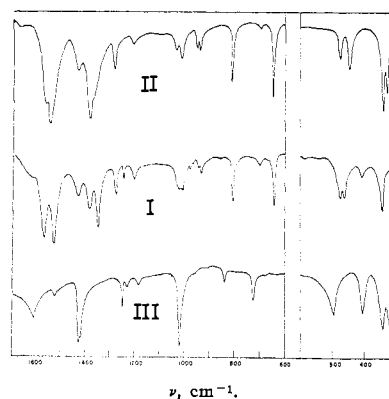

Figure 1.—Infrared spectra of chloro(acetylacetonato)(ethylene)platinum(II) (I), potassium dichloro(acetylacetonato)platinate(II) (II), and Zeise's salt (III).

TABLE I

A COMPARISON OF THE OBSERVED FREQUENCIES OF CHLORO(ACETYLACETONATO)(ETHYLENE)PLATINUM(II) (I), POTASSIUM DICHLORO(ACETYLACETONATO)PLATINATE(II) (II), AND ZEISE'S SALT (III)

	I[a]	II[a]	III[a]	Band assignment[b]
ν_1	1567 s	1563 s	...	ν(C⋮O)
ν_2	1527 s	1538 s	...	ν(C⋮C)
ν_3	(Hidden)	...	1526 w	ν(C=C)
ν_4	1427 m	1429 m	1428 s	δ_d(CH$_3$), δ(CH$_2$) + ν(C=C),
			1418 s	δ(CH$_2$)
ν_5	1382 m	1380 s	...	ν(C⋮O)
ν_6	1352 s	1363 sh	...	δ_s(CH$_3$)
ν_7	1279 m	1288 m	...	ν(C⋮C)
ν_8	1248 w	...	1251 m	ρ_r(CH$_2$)
	1205 w			
ν_9		1212 w	...	δ(CH)
	1194 sh			
ν_{10}	1019	1033 m	1023 s	ρ_r(CH$_3$), ρ_w (CH$_2$)
	m, br	1018 m		
	956 w	952 m		
ν_{11}			...	ν(C—CH$_3$)
	936 w	941 m		
ν_{12}	872 vw	...	844 m	ρ_r(CH$_2$)
ν_{13}	808 s	817 s	...	π(CH)
ν_{14}	789 sh	...	730 m	ρ_t(CH$_2$)
ν_{15}	700 w	703 w	...	ν(Pt—O) + ν(C—CH$_3$) + ring def
ν_{16}	662 w	...	...	?
ν_{17}	645 s	650 s	...	ν(Pt—O)
ν_{18}	590 w	...	...	?
ν_{19}	470 s	478 m	...	ν(Pt—O)
ν_{20}	460 s	448 m	...	Ring def
ν_{21}	405 m	...	407 m	ν(Pt—C$_2$H$_4$)
ν_{22}	345 s	339 s	339 s	ν(PtCl)
		327 s	331 s	
			310 s	

[a] Intensity designations: s, strong; w, weak; m, medium; sh, shoulder; br, broad; v, very. [b] ν, stretching; δ, bending; δ_d, degenerate bending; δ_s, symmetric bending; ρ_r, rocking; ρ_w, wagging; ρ_t, twisting; π, out-of-plane bending.

C⋮C stretching band (ν_7) is also shifted from 1288 (II) to 1279 cm^{-1} (I).

The methyl group bending frequencies at 1427 and 1352 cm^{-1} of I again conform well to the group frequencies given for the degenerate and symmetric deformation modes, respectively. The CH in-plane bending band at 1212 cm^{-1} (ν_9) of II is found at 1205 and 1194 cm^{-1} for I. The origin of this very slight splitting is

not apparent; however, Fermi resonance with the first overtone of the very strong 645-cm^{-1} band may be responsible. Several bands in this region are due to the coordinated ethylene portion of the molecule. In free ethylene, the Raman-active C=C stretching mode appears at 1623 cm^{-1} and is shifted to 1526 cm^{-1} (ν_3) upon coordination to platinum.[8] This band is obscured by the intense carbon–carbon stretching band (ν_2) in I. The symmetric and asymmetric bendings of the CH$_2$ group of I are found at *ca.* 1427 cm^{-1} (ν_4) and are obscured by the methyl bending bands of the chelated ligand. However, the rocking mode of the CH$_2$ group at 1248 cm^{-1} (ν_8) is in a region which contains no bands due to the chelated ligand. This band has been shifted only slightly from the 1251-cm^{-1} band of Zeise's salt.

The methyl rocking bands at 1033 and 1018 cm^{-1} of II are close to the 1023-cm^{-1} band (CH$_2$ wagging) of Zeise's salt. This has resulted in a very complex and broad band of high intensity at 1019 cm^{-1} (ν_{10}). The carbon–carbon stretchings of the acetylacetone methyl groups have not shifted and are found near 946 cm^{-1} (ν_{11}). A very weak band at 872 cm^{-1} (ν_{12}) may correspond to the low-frequency CH$_2$ rocking at 844 cm^{-1} of Zeise's salt. This shift may be due to changes in vibrational coupling. The intense CH out-of-plane bending band at 808 cm^{-1} (ν_{13}) is shifted only slightly from the 817-cm^{-1} band of II. Being of high intensity, this band is again one of the most characteristic absorptions of the chelated ligand. A shoulder at 789 cm^{-1} (ν_{14}) may be assigned to a twisting mode of the CH$_2$ group.

The most important region is that of coordinate bond stretchings below 700 cm^{-1}. The chelated ligand continues to exhibit a weak band at 700 cm^{-1} (ν_{15}), which, though it contains significant platinum–oxygen stretching character, also contains large contributions of C–CH$_3$ stretching and of an in-plane ring deformation.[9] The main platinum–oxygen stretching band (ν_{17}) is found lowered from 650 cm^{-1} in II to 645 cm^{-1} here. Similarly, the low-frequency platinum–oxygen stretching band (ν_{19}) is found to have shifted from 478 to 470 cm^{-1}. Two additional weak bands at 662 (ν_{16}) and 590 cm^{-1} (ν_{18}) of very low intensity are also observed. Since no corresponding bands are present in either II or III, they are not assigned. Their low intensity is, however, consistent with interpretation either as an overtone or combination band or as an out-of-plane ring deformation such as that observed in bis(acetylacetonato)platinum(II).[9] A well-characterized ring deformation at 460 cm^{-1} (ν_{20}) has shifted from the 448 cm^{-1} of II. The direction and magnitude of this shift is consistent with the small changes in bond order evidenced in the high-frequency region discussed above. The stretching frequency of the platinum–olefin bond is found at 405 cm^{-1} (ν_{21}), nearly identical with that of the corresponding mode in Zeise's salt at 407 cm^{-1}. The platinum–chloride stretching frequency at 345 cm^{-1} also shows a small shift from the 339 cm^{-1} band of III.

Many bonding arguments have been suggested for the platinum–olefin bonds. Babushkin, *et al.*,[16] pro-

posed a triangular coordination (scheme A), in which all three bonds in the ring are essentially single bonds.

A
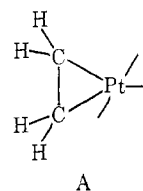
This scheme which involves the sp^3 hybridized carbons was quickly rejected by Powell and Sheppard[17] from their infrared (1500-cm^{-1} region) and nmr (chemical shifts) evidence. For such a triangular structure, one would expect two Pt–C stretching bands per Pt–C$_2$H$_4$ bond unless they are symmetrically forbidden. As is seen in Figure 1, I exhibits only one Pt–C$_2$H$_4$ stretching band at 405 cm^{-1}. It is noted that I, which contains no water of hydration, does not show any absorption near 490 cm^{-1}. This result confirms our interpretation that the 490-cm^{-1} band of Zeise's salt is due to crystal water. Although Zeise's dimer, [Pt(C$_2$H$_4$)Cl$_2$]$_2$, exhibits a strong band at 408 cm^{-1} and a weak band near 490 cm^{-1}, it has been shown[9] that the former is the only infrared-active Pt–C$_2$H$_4$ stretching band and the latter is not a fundamental. Furthermore, [Pd(C$_2$H$_4$)-Cl$_2$]$_2$ exhibits the Pd–C$_2$H$_4$ stretching at 427 cm^{-1} without any absorption between 500 and 430 cm^{-1}.[9] These observations together with other evidence cited by Powell and Sheppard definitely rule out bonding scheme A.

According to the well-known bonding scheme of the Pt–C$_2$H$_4$ bond by Chatt, *et al.*,[18] the σ-type bond is formed by the overlap of the filled bonding 2pπ molecular orbital of the olefin with the vacant dsp^2 bonding orbital in the plane of hybridization of the platinum atom, and the π-type bond is formed by the overlap of the 2pπ* antibonding orbital of the olefin with a filled dp hybrid orbital of the platinum atom. The back-donation of electrons from the metal atom to the olefin through the π bond may occur since it prevents the accumulation of electrons on the metal atom. This bonding scheme has been used by many investigators to account for the nature of the metal–olefin bond. It should be noted, however, that the relative importance of these two types of bonding is not apparent in this scheme. It will probably change from metal to metal, and the π bonding may become more important as the oxidation state of the metal becomes lower.

Let us consider two bonding schemes shown below.

B   C
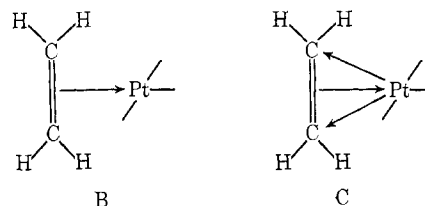
(16) A. A. Babushkin, L. A. Gribov, and A. D. Gelman, *Dokl. Akad. Nauk URSS*, **123**, 461 (1958).

(17) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

(18) J. Chatt, L. A. Duncanson, and R. G. Guy, *Nature*, **184**, 526 (1959).

B represents an almost pure σ bond, whereas C represents a bonding scheme in which both σ and π bonds are involved. We have several types of evidence supporting the view thrt, in the Pt(II) complexes with ethylene, π bonding is not significant enough to require the introduction of scheme C.

(1) In the bonding scheme of Chatt, *et al.,*[18] the dπ (platinum)–2pπ* (ethylene) bond shown in scheme C uses the filled platinum 5d orbital hybridized with the 6p orbital. This hybridization was necessary to give sufficient overlap between the 5dπ and 2pπ* orbitals. The immediate consequence of this hybridization is the contraction of the electron-lobe in the direction *trans* to ethylene. It is generally accepted that the Pt–O (acetylacetone) bond has a partial dπ (platinum)–pπ(oxygen) bond character.[19,20] Then, the latter bond is expected to be weakened by the coordination of ethylene *trans* to the Pt–O bond (I). The relatively minor shifts in the coordinate bond stretching frequencies observed in this work suggest that a competition does not seem to occur, again suggesting that the π bonding is not significant in the platinum–ethylene bond.

(2) It may be noted that a recent nmr study of $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$[21] indicates that the ethylene molecule coordinated to Rh(0) rotates relatively freely about the $Rh\text{-}C_2H_4$ bond, thus indicating that bonding scheme B is favored even for Rh(0).

Choro(acetylacetonato)(π-acetylacetonato)platinum-(II) (Compound IV).
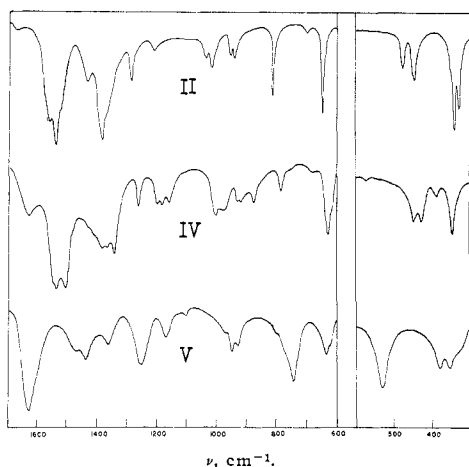
—Figure 2 compares the infrared

Figure 2.—Infrared spectra of chloro(acetylacetonato)(π-acetylacetonato)platinum(II) (IV), potassium dichloro(acetylacetonato)platinate(II) (II), and the enol form of acetylacetone (V).

spectrum of IV with those of II and the enol form of acetylacetone (V). Table II lists the observed frequencies of these three compounds. The infrared spectrum of V has already been studied extensively by Ogoshi and Nakamoto.[22] The spectrum of IV is roughly approximated by the sum of the spectra of II and V. We have, therefore, related each band of IV to

(19) D. W. Barnum, *J. Inorg. Nucl. Chem.,* **21**, 221 (1961); **22**, 183 (1961).

(20) K. Nakamoto and A. E. Martell, *J. Chem. Phys.,* **32**, 588 (1960).

(21) R. Cramer, *J. Am. Chem. Soc.,* **86**, 217 (1964).

(22) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.,* **45**, 3113 (1966).

TABLE II

A COMPARISON OF THE OBSERVED FREQUENCIES OF CHLORO(ACETYLACETONATO)(π-ACETYLACETONATO)PLATINUM(II) (IV), POTASSIUM DICHLORO(ACETYLACETONATO)PLATINATE(II) (II), AND THE ENOL FORM OF ACETYLACETONE (V)[a]

	IV	II	V	Band assignment
ν_1	1627 m	...	1623 s	ν(C=O)
ν_2	1550 sh	...	1623 s	ν(C=C)
ν_3	1542 s	1563 s	...	ν(C⋯O)
ν_4	1512 s	1538 s	...	ν(C⋯C)
ν_5	1450 vw	...	1460 m	δ(OHO)
ν_6	1429 vw	...	1432 m	ν(C—O) + δ_d(CH₃)
ν_7	1415 vw	1429 m	...	δ_d(CH₃)
ν_8	1380 m, br	1380 s	...	ν(C⋯O)
ν_9	1367 s	1363 sh	...	δ_s(CH₃)
ν_{10}	1347 m	...	1368 m	δ_s(CH₃)
ν_{11}	1267 m	1288 m	...	ν(C⋯C)
ν_{12}	1202 m	...	1250 s	ν(C—C) + ν(C=C)
ν_{13}	1188 m	1212 w	...	δ(C—H)
ν_{14}	1163 m	...	1170 m	δ(C—H)
ν_{15}	1005 m	1033 m / 1018 m	...	ρ_r(CH₃)
ν_{16}	990 w	...	995 sh	ρ_r(CH₃)
ν_{17}	978 m	...	945 m	π(OH)
ν_{18}	932 m	952 m / 941 m	...	ν(C—CH₃)
ν_{19}	918 m	...	908 m	ν(C—CH₃)
ν_{20}	881 m	...	810 vw	ν(C—CH₃)
ν_{21}	790 s	817 s	...	π(C—H)
ν_{22}	766 w	...	764 s	π(C—H)
ν_{23}	678 m	703 w	...	ν(Pt—O) + ν(C—CH₃) + ring def
ν_{24}	642 s	650 s	...	ν(Pt—O)
ν_{25}	632 sh	...	640 m	Ring def (out-of-plane)
ν_{26}	587 w	...	515 s	Ring def
ν_{27}	452 m	478 m	...	ν(Pt—O)
ν_{28}	433 m	448 m	...	Ring def
ν_{29}	388 w	...	388 m	δ(C—CH₃)
ν_{30}	355 sh	...	364 m	Ring def
ν_{31}	347 s	339 s / 327 s	...	ν(Pt—Cl)
ν_{32}	324 w	...	320 sh	δ(C—CH₃)

[a] See Table I for meanings of intensity designations and band assignments.

a band of either II or V. Table II gives the band assignments thus obtained. In addition, IV exhibits the OH stretching band characteristic of the enol form at 2905 cm⁻¹. This band corresponds to the 2750-cm⁻¹ band of V. The fact that this band is shifted to a high frequency upon coordination is not consistent with structure IVb which predicts the weakening of the O–H bond upon coordination.

Both of the CO stretching frequencies (ν_1 and ν_6) of the enol ring are little altered whereas both of the CC stretching frequencies (ν_2 and ν_{12}) are shifted by 70–50 cm⁻¹ to lower frequencies upon coordination to the Pt-(II) atom. This result is again consistent with structure IVa where the CC bond order is expected to be reduced upon coordination. It has been shown previously[22] that the 1623-cm⁻¹ band of V is the overlap of ν_1 and ν_2. Upon coordination, ν_2 is now shifted to 1550 cm⁻¹. It is noted that this shift from 1623 to 1550 cm⁻¹ (73 cm⁻¹) is smaller than, but comparable to, that of the C=C stretching band of ethylene upon coordination to the Pt atom (97 cm⁻¹).[8] The CO stretchings

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(ν_3 and ν_8) and the CC stretchings (ν_4 and ν_{11}) of the O-chelated ring are shifted by 20–0 cm^{-1} to lower frequencies in going from II to IV.

Two bands at 1188 (ν_{13}) and 1163 (ν_{14}) cm^{-1} of IV are attributed to the CH in-plane bending modes of II and V, respectively. Upon deuteration at the γ position, these bands are shifted to 916 and 868 cm^{-1}, respectively. The region 1005–978 cm^{-1} (ν_{15}–ν_{17}) consists of a complex band structure due to the methyl rocking modes. Upon deuterium substitution of the enol OH proton, a change in this region occurs, with the disappearance of a weak band at 978 cm^{-1} (ν_{17}) attributed to the out-of-plane bending of the OH group. The carbon–carbon stretching frequencies involving each of the methyl groups again occur in the same region, but in this case they are slightly separated, with the higher frequency band at 932 cm^{-1} (ν_{18}) being attributed to the chelated ligand and the lower frequencies 918 (ν_{19}) and 881 (ν_{20}) cm^{-1} attributed to V. The separation of the latter two bands may be attributed to the lower symmetry of this moiety. The very strong band at 790 cm^{-1} (ν_{21}) is highly characteristic of the chelated acetylacetone and is attributed to the out-of-plane bending of the CH group. It is shifted to 595 cm^{-1} upon deuterium substitution at this position. A similar observation is made for the weak band at 766 cm^{-1} (ν_{22}) which is attributed to the analogous mode of V.

Again, the most significant region in which interaction between ligands would be expected to be found is the coordinate bond stretching region. The four vibrational modes contain significant contributions due to platinum–oxygen stretching modes. Each frequency is found to be lowered by 26–8 cm^{-1} from the frequencies observed in II. The bands formerly at 703 (ν_{23}), 650 (ν_{24}), 478 (ν_{27}), and 448 cm^{-1} (ν_{28}) in II are thus now found at 678, 642, 452, and 433 cm^{-1}, respectively. In this region two ring deformations at 632 (ν_{25}) and 587 cm^{-1} (ν_{26}) are attributed to V. Three weak bands at 388 (ν_{29}), 355 (ν_{30}), and 324 cm^{-1} (ν_{32}) originate in V, while the strong band at 347 cm^{-1} (ν_{31}) is definitely due to the Pt–Cl stretching mode.

As has been discussed previously, the Pt–C_2H_4

stretching band is seen at 407 cm^{-1} in III and at 405 cm^{-1} in I. In order to demonstrate the differences to be expected in the spectra of structures IVa and IVb, it is necessary to discuss the low-frequency spectral region of this compound in more detail.

(1) The frequency of the platinum–ligand stretching vibration will be affected by two factors in structure IVa, namely, the mass of the ligand and the bond order of the carbon–carbon double bond of the ligand. If a calculation is made assuming a simple diatomic model, with the same metal–ligand stretching force constant as used for Zeise's salt[8] (2.45 mdyn/Å), it is found that the frequencies of 407 and 250 cm^{-1} are predicted for III and IVa, respectively. This low frequency for IV is due only to the large mass of acetylacetone relative to ethylene. Since, however, the carbon–carbon bond order in the free acetylacetone ligand is undoubtedly lower than that in free ethylene owing to delocalization effects in the enol-ring structure, it is anticipated that the metal–ligand bond would be correspondingly weaker in IVa. Thus this frequency could be lower than 250 cm^{-1}.

(2) It is rather difficult to predict a similar platinum–acetylacetone stretching frequency for structure IVb. A comparison may be made, however, with the metal–ring stretching and metal–ring tilting modes observed by Fritz,[23] who has assigned these modes for a number of cyclopentadienyl and benzene complexes. Although his list does not include sandwich-type acetylacetone complexes, these modes have been assigned above 300 cm^{-1} for π-bonded cyclopentadienyl complexes of W, Os, and Pt. In this case, no such bands have been observed above 300 cm^{-1}. This result may indicate the likelihood of structure IVa. Although the metal–ligand stretching frequency for this compound has not been observed, the considerations discussed above and the character of the spectra in both high- and low-frequency regions seem to support structure IVa rather than structure IVb.

(23) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 283 (1964).