206. *Infrared Spectra of Acetyl Complexes of Platinum and Palladium.*

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An assignment is made of the infrared absorption frequencies of the acetyl group in a series of complexes, *trans*-$[MX(CO{\cdot}CH_3)(PEt_3)_2]$, (M = Pt, Pd; X = anionic ligand). The shifts of these frequencies as X is varied are discussed in terms of the *trans*-effect of X.

In a recent note,[1] Booth and Chatt reported a new series of acyl complexes, *trans*-$[MX(CO{\cdot}R)(PEt_3)_2]$ (M = Pt, Pd; X = Cl, Br, I; R = Me, Ph). The infrared spectra of these and several similar complexes have been recorded in order to study the vibrational spectrum of the acetyl group bonded to a heavy metal atom. Other studies,[2,3] on the alkyl complexes, *trans*-$[PtMeX(PR_3)_2]$ (R = Me, Et; X = Cl, Br, I, NO_2, NO_3, CN, SCN), have characterised the methyl group attached to platinum and the effect of X upon the platinum–carbon stretching frequency.

The presence of a " ketonic " carbonyl group in metal acyl compounds has been inferred from infrared spectra by several authors.[4,5] Hieber, Braun, and Beck [5] published

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[1] Booth and Chatt, *Proc. Chem. Soc.*, 1961, 67.

[2] Adams, Chatt, and Shaw, *J.*, 1960, 2047.

[3] Adams, unpublished work.

[4] Coffield, Kozikowski, and Closson, *J. Org. Chem.*, 1957, **22**, 598; Breslow and Heck, *Chem. and Ind.*, 1960, 467; Heck and Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 4438; 1961, **83**, 1097; Hieber, Beck, and Linden, *Z. Naturforsch.*, 1961, **16b**, 229.

[5] Hieber, Braun, and Beck, *Chem. Ber.*, 1960, **93**, 901.

the frequencies of bands observed in the spectrum of [Re(CO)$_5$(CO·CH$_3$)] in the sodium chloride region but made no assignments other than of carbonyl and C–H stretching frequencies.

Assignment of Absorption Bands due to the Acetyl Group.—Comparison of the spectra of *trans*-[PtCl$_2$(PEt$_3$)$_2$] and *trans*-[PtCl(CO·CH$_3$)(PEt$_3$)$_2$] shows which bands are due to the acetyl group. These are listed in Tables 1 and 2 for platinum and palladium complexes.

TABLE 1.

Frequencies of the acetyl group in *trans*-[PtX(CO·CH$_3$)(PEt$_3$)$_2$], in carbon tetrachloride.

X = NO$_3$	NCS	Cl	Br	I	NO$_2$	X = NO$_3$	NCS	Cl	Br	I	NO$_2$
541w	545m	539m	537m	532m	554w	(985)sh	971w	969m	970w	967w	967vw
588m	588m	587m	584m	580m	581w	1087vs	1089vs	1085s	1080vs	1079vs	1084s
						1326m	1326m	1325m	1323m	1326m	1323s
913w	913w	910m	909m	905m	909w	1636vs	1628vs	1629vs	1630vs	1635vs	1629vs

TABLE 2.

Frequencies of the acetyl group in *trans*-[PdX(CO·CH$_3$)(PEt$_3$)$_2$], in carbon tetrachloride.

X = NO$_3$	NCS	Cl	Br	I	NO$_2$	X = NO$_3$	NCS	Cl	Br	I	NO$_2$
521m	520m	515m	513m	509m	517w	1076s	1074s	1074s	1073s	1071s	1074s
577m	576m	572m	571m	570m	575m	1326m	1321m	1323m	1324m	1324m	1326vs
						1675vs	1667vs	1665vs	1667vs	1668vs	1661vs
908w	906m	900w	903w	902m	908w		1653sh				
964w	963w	961w	961w	959w	961vw						

TABLE 3.

Frequencies (cm.$^{-1}$) of the acetyl group.

trans-[PtBr(CO·CX$_3$)(PEt$_3$)$_2$] in CCl$_4$ soln.				(CX$_3$·CO)$_2$ (from ref. 6)			[Re(CO)$_5$(CO·CH$_3$)] (from ref. 5)
X = H	X = D	ν_H/ν_D	Assignment	X = H	X = D	ν_H/ν_D	
537m	470w	1·14	ν_{M-C}				[b]
584m	522w	1·12	Skeletal deformation				
909m	838w	1·09	ν_{C-CH_3}	927	770	1·20	914m
970w	—	—					948w
1080vs	967s	1·12	Me rocking	1111	957	1·16	1072m
1323m	(1010) [a]	(1·31) [a]	$\delta_{CH_3(s)}$	1353	1025	1·32	1329m
(1380) [a]	1099s	(1·26) [a]	$\delta_{CH_3(a)}$	1421	1133	1·26	1409w
1630vs	1639vs	1·00	C=O	1718	1715	1·00	1617m

[a] Estimated value—see text. Not investigated.

To aid in their assignment to normal modes of vibration of the acetyl group, *trans*-[PtBr(CO·CD$_3$)(PEt$_3$)$_2$] was prepared. In Table 3 the frequencies of the CO·CX$_3$ group (X = H, D) are listed together with suggested assignments. A recent vibrational study of biacetyl and [^{2}H$_6$]biacetyl by Noak and Jones[6] is useful for comparison, and part of this is included in Table 3.

(i) *The carbonyl stretching frequency* (ν_{CO}). The acetyl ν_{CO} in our complexes is a little lower than that in organic saturated open-chain ketones[7] (1725—1705 cm.$^{-1}$), but this should not lead one to draw firm conclusions about the electronic effects of the metal atom on the acetyl group. Stretching of the $\rangle$C=O bond also changes the angles at the carbonyl carbon atom and some movements of neighbouring atoms. Overend and

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[6] Noak and Jones, *Z. Elektrochem.*, 1960, **64**, 707.

[7] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1956, p. 114.

Scherer[8] have shown that direct comparisons of observed ν_{CO} frequencies can be misleading for this reason. However, we believe it meaningful to draw conclusions from variations in ν_{CO} in closely related compounds, such as those in Tables 1 and 2.

(ii) *Methyl deformation frequencies* (δ_{CH_3}). The sharp band found near 1320 cm.$^{-1}$ in platinum and palladium acetyl complexes is the symmetric methyl deformation frequency, $\delta_{CH_3(s)}$. The antisymmetric deformation frequency, $\delta_{CH_3(a)}$, has not been observed directly but is assumed to be of low intensity and to lie beneath the absorption near 1400 cm.$^{-1}$ due to the phosphine ethyl groups; *trans*-[PtBr(CO·CX$_3$)(PEt$_3$)$_2$], where X = H or D, have identical spectra in the C–H deformation region, indicating that $\delta_{CH_3(a)}$ must be of low intensity.

Bands observed in the deuterated complex are best assigned as in Table 3, making 1099 cm.$^{-1}$ the lowered antisymmetric deformation, $\delta_{CD_3(a)}$. The lowered symmetric deformation, $\delta_{CD_3(s)}$, is now assumed to be weak and to lie beneath absorption near 1000 cm.$^{-1}$ due to the phosphine ligands. These assumptions regarding the intensities of $\delta_{CH_3(a)}$, $\delta_{CH_3(s)}$, $\delta_{CD_3(a)}$, and $\delta_{CD_3(s)}$ lead to very reasonable $\nu_H : \nu_D$ ratios. Further, the intensity changes postulated are in excellent agreement with those found for biacetyl and [^{2}H$_6$]biacetyl by Noak and Jones.[6] The frequencies and intensities observed[5] in the spectrum of [Re(CO)$_5$(CO·CH$_3$)] also support this assignment. Thus, the bands which may be assigned to the acetyl group (and which are included in Table 3) are close to those found in the present work. $\delta_{CH_3(s)}$ is at 1329m and $\delta_{CH_3(a)}$ at 1409(w—m) cm.$^{-1}$, *i.e.*, weaker than $\delta_{CH_3(s)}$. In the solid-state spectra $_{CH(s)}$ is at 1329(w—m) and $\delta_{CH_3(a)}$ at 1404vw cm.$^{-1}$.

(iii) C–H *Stretching frequencies* (ν_{C-H}). ν_{C-H} and ν_{C-D} absorptions are extremely weak in these complexes. In a concentrated mull of *trans*-[PtBr(CO·CD$_3$)(PEt$_3$)$_2$], bands due to ν_{C-D} are found at 2232 and 2212 cm.$^{-1}$. In the light-hydrogen complex, no evidence could be found of ν_{C-H} due to acetyl. The extreme weakness of ν_{C-H} of a methyl group vicinal to a carbonyl group has been noted previously,[5,9] and explained by Halmann and Pinchas.[10]

(iv) *Methyl rocking* (ρ_{CH_3}) *and carbon–carbon stretching* (ν_{C-CH_3}) *frequencies*. These are assigned to the bands found near 1080 and 900 cm.$^{-1}$ respectively and show no features of particular interest, being well within the wide range in which these modes commonly occur.

The weak band found near 970 cm.$^{-1}$ may be either a combination band or a second methyl rocking mode.

(v) *Low-frequency modes*. In the 500—600 cm.$^{-1}$ region we expect to find the ν_{Pt-C} (or ν_{Pd-C}) mode,[2,11] and two bands are found there for each of the complexes. Since all the stretching and C–H deformation modes are accounted for, one of these low-frequency bands must be due to a skeletal deformation, the other being ν_{M-C} (M = Pt or Pd). It is not possible to make a firm choice between these two possibilities. However, we favour the assignment of ν_{M-C} to the lower band for the following reason: the amount of bond weakening in passing from platinum to corresponding palladium complexes is likely to be similar for both alkyl[2,11] and acetyl complexes. The difference, $\nu_{Pt-C} - \nu_{Pd-C}$, for the pairs of complexes *trans*-[MX(CH$_3$)(PEt$_3$)$_2$] (X = Br, SCN), *cis*-[M(CH$_3$)$_2$(PEt$_3$)$_2$] and [M(CH$_3$)$_2$(EtS·[CH$_2$]$_2$·SEt)] (M = Pt[2] or Pd[11]), lies between 30 and 46 cm.$^{-1}$. The corresponding difference for the lower of the two low-frequency bands in the spectra of the acetyl complexes lies between 20 and 37 cm.$^{-1}$; for the higher band it is 6—15 cm.$^{-1}$. These figures therefore point to the lower of the two bands being ν_{M-C}.

Effect of X *upon Acetyl Frequencies in* trans-[MX(CO·CH$_3$)(PEt$_3$)$_2$] (M = Pt, Pd). In a study of *trans*-[PtX(CH$_3$)(PEt$_3$)$_2$] (X = anionic ligand) it was shown[2] that ν_{Pt-C} was sensitive to the nature of X and that it decreased with increasing *trans*-effect of X,

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[8] Overend and Scherer, *Spectrochim. Acta*, 1960, **16**, 773.
[9] Nolin and Jones, *J. Amer. Chem. Soc.*, 1953, **75**, 5626.
[10] Halmann and Pinchas, *J.*, 1958, 3264.
[11] Calvin and Coates, *J.*, 1960, 2008.

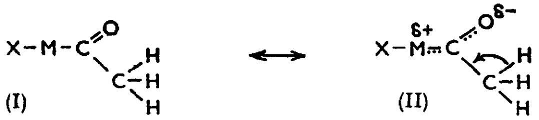
with the exception of X = SCN. We suggested that if the complex contained an isothiocyanate group, then ν_{Pt-C} would place this group between nitrate and chloride in the *trans*-effect series.

Turco and Pecile have shown[12] that the stretching frequency of the sulphur–carbon bond clearly distinguishes thiocyanate from isothiocyanate complexes. Thus for –SCN, $\nu_{S-C} = 690$—720 cm.$^{-1}$ and for –NCS, $\nu_{S-C} = 780$—860 cm.$^{-1}$. In *trans*-[Pt(SCN)CH$_3$(PEt$_3$)$_2$], $\nu_{S-C} = 812$ cm.$^{-1}$, whilst in *trans*-[Pt(SCN)(CO·CH$_3$)(PEt$_3$)$_2$], $\nu_{S-C} = 819$ cm.$^{-1}$. Both are therefore isothiocyanato-complexes.

In Tables 1 and 2 the complexes have been arranged in the order of the *trans*-effect of X, placing isothiocyanate between nitrate and chloride.

General trends are evident from these data and can be clearly seen in a plot of the figures in Tables 1 and 2, but there are several exceptions; in particular, the nitro-complexes have frequencies which place the group in a different position in the order of X depending on which frequency of the acetyl group is considered. The possibility that these complexes may contain the nitrito-group is ruled out by the observed ν_{N-O} frequencies which are typical of a normal nitro-complex. The behaviour of the carbonyl stretching frequency is also difficult to understand in detail. Nevertheless, two general trends in the data are adequately accounted for by two simple resonance structures: (*a*) ν_{M-C}, the skeletal deformation frequency, δ_{Me} and ν_{C-CH_3} move to lower frequencies as the *trans*-effect of X increases; and (*b*) when X = –NCS, Cl, Br, or I, ν_{CO} tends to move to higher frequencies as the frequencies in (*a*) move in the opposite direction.

These trends can be explained in terms of the resonance structures (I) and (II), closely similar to those invoked by Hieber, Braun, and Beck[5] in discussing the spectra of rhenium acyl complexes. A partial double bond between the metal and the acetyl group is obtained at the expense of the carbonyl double bond. Strengthening of the C–C bond can arise through hyperconjugation; this contribution will probably depend on the amount of M–C double bonding and the consequent availability of the carbonyl carbon atom *p*-orbital for overlap with the molecular orbitals of the methyl hydrogen atoms. The electron-withdrawing power of X will affect the strength of the M–C bond and a change in X will therefore cause a change in the M–C bond order. This will alter the relative contributions of the two resonance structures and cause the observed variations in the frequencies of the acetyl group.



(I) (II)

The general validity of this scheme is supported by the observed spectral difference between the platinum and palladium series of acetyl complexes. The force constant of the Pd–C bond is less than that of the Pt–C bond[13] in complexes of the type [M(CH$_3$)$_2$(PEt$_3$)$_2$] (M = Pt, Pd), and the same is likely to be true in our acetyl complexes. A weaker M–acetyl bond will mean a higher contribution from resonance form (I) resulting in lower ν_{Pd-C} and ν_{C-CH_3} and a higher ν_{CO} than in the corresponding platinum complexes. These trends are observed.

Experimental.—trans-*Bromo*([^{2}H$_3$]*acetyl*)*bis*(*triethylphosphine*)*platinum*, *trans*-[PtBr(CO·CD$_3$)(PEt$_3$)$_2$]. The *compound*, *trans*-bromo([^{2}H$_3$]methyl)bis(triethylphosphine)-platinum (Found: C, 29·5%. $C_{13}H_{30}BrD_3P_2Pt$ requires C, 29·5%) was prepared by the method of Chatt and Shaw,[14] by using MgBr(CD$_3$). This alkylplatinum complex was treated with

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[12] Turco and Pecile, *Nature*, 1961, **191**, 66.

[13] Coates, " Organo-Metallic Compounds," Methuen, London, 1960, p. 321.

[14] Chatt and Shaw, *J.*, 1959, 705.

carbon monoxide at 90°/70 atm., as described by Booth and Chatt,[15] to give the *complex* as colourless needles, m. p. 65—66° [from light petroleum (b. p. 30—40°)] (Found: C, 30·45%. $C_{14}H_{30}BrD_3OP_2Pt$ requires C, 30·2%).

The preparation of the other complexes used in this work is described elsewhere.[15]

Infrared spectra were recorded on a Grubb–Parsons GS2A spectrometer for carbon tetrachloride solutions (0·1 mm. cell) and for Nujol and hexachlorobutadiene mulls.

We thank Mr. D. Green and Mr. H. Lintott for experimental assistance.

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[*Received, September* 19*th*, 1961.]

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[15] Booth and Chatt, unpublished work.