

FAR-INFRARED SPECTROSCOPY
OF SOME HALIDE COMPLEXES.

A thesis
presented for the degree of
Doctor of Philosophy in the Faculty of Science
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by
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Statement

The experimental work in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, under the supervision of Dr. D. M. Adams.

The work has not been presented and is not being currently presented for any other degree.

P. J. Chandler.

November, 1967.

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SUMMARY

A survey of the published data on M-X bond vibrations (M = Pt, Pd; X = Cl, Br, I) highlighted several gaps in the information.

A full assignment of the infrared spectra of anionic bridged complexes of platinum and palladium identified stretching modes in terminal and bridged positions and bending modes. These assignments provide the basis for an extended examination of substituted halogen-bridged complexes of Pt(II), Pd(II) and Rh(I). The terminal and higher bridge $\nu(\text{MX})$ have relatively constant frequencies, whilst the lower bridge mode varies with the nature of the ligand, L. In the first systematic study of Pt(IV) complexes, the infrared spectra of cis- and trans- $[\text{PtX}_4\text{L}_2]$ are assigned. The number of $\nu(\text{PtX})$ and $\nu(\text{PtL})$ modes observed relate to the stereochemistry of the complexes and distinguish between cis- and trans- isomers. In trans- $[\text{PtX}_4\text{L}_2]$, $\nu(\text{PtX})$ is ligand insensitive whereas for the cis- complexes, vibrations of the Pt-X bonds trans to L show a marked ligand dependence.

From an extensive review of M-L bond vibrations (L = S, Se, Te, As, P, py, olefin) and the corresponding low-frequency ligand spectra, assignments of $\nu(\text{ML})$ and $\delta(\text{LML})$ are made for the platinum, palladium and rhodium complexes.

Finally the first assignments of infrared-active metal-metal bond vibrations are recorded for transition metal-tin complexes.

INTRODUCTION

1. General

Platinum and to a lesser extent palladium and rhodium form a wide variety of halide and substituted halide complexes and thus are ideal metals for an extensive study of metal-halogen and metal-ligand modes. The general approach has been to record the far-infrared spectra of related series of complexes and to make empirical assignments based upon group theoretical predictions. Metal-ligand vibrations are the subject of an extensive review in Chapter V, where the evidence for their assignment is collated, and are not discussed here. Chapters I, II and IV are concerned with platinum- and palladium-halogen vibrations and many new assignments are made. Therefore it is pertinent here to review the state of knowledge of these modes upto and during the course of this work. Subsequently vibrational interactions are discussed as the assumption has been made that in general it is realistic to talk in terms of M-L and M-X modes rather than of complex vibrations of the whole molecule.

2. Platinum- and palladium-halogen vibrations.

In 1957, Brame¹² assigned $\nu(\text{PtCl})$ for

PtCl₂ and PtCl₄ at 320 and 343 cm.⁻¹ respectively and found ν (PtCl) bands at corresponding frequencies in several ammine and ethylenediamine complexes. Curiously, these results have only appeared in a thesis and have not been published generally. Subsequent work did not appear until 1961-2 but since then the volume of results has increased yearly. For the purposes of this discussion only the most important work is quoted in the text and full references are given in the tables.

2.1. $\frac{[MX_4]^{2-}}{[MX_4]^{2-}}$

The distribution and activity of the fundamentals for square-planar $[MX_4]^{2-}$ is as follows.

D _{4h}	1.	2.	3.	4.	5.	6.	7.
	A _{1g}	A _{2u}	B _{1g}	B _{1u}	B _{2g}	E _u	E _u
	R	IR	R	Inact	R	IR	IR

For $[PtCl_4]^{2-}$, both Raman³⁷ and infrared data^{3,5} have been recorded and the assignments are well established, (Table 1). For K₂PtCl₄ the infrared-active fundamentals lie near 325, 190 and 175 cm.⁻¹ for ν (PtCl), δ (PtCl) and π (PtCl) respectively. As the

cation is increased in size, $\nu(\text{PtCl})$ drops to a lower frequency, viz. 316 cm.^{-1} for Cs_2PtCl_4 ⁵. Limited infrared data exist for $[\text{PtBr}_4]^{2-}$. The assignment of $\nu(\text{PtBr})$ at 233 by Adams and Gebbie⁶ has been confirmed³⁵ but those of the bending modes at 135 and 80 cm.^{-1} are more doubtful. No Raman data is available for $[\text{PdX}_4]^{2-}$ but infrared-active modes have been assigned at 332, 191, 168 and 254, 136, 106 cm.^{-1} for K_2PdCl_4 and K_2PdBr_4 respectively³. Durig et. al. have shown that as the cation is changed from K^+ to $[\text{Pd}(\text{NH}_3)_4]^{2+}$, $\nu(\text{PdCl})$ drops from 335 to 324 cm.^{-1} , (Table 2).

2.2. $[\text{MX}_6]^{2-}$.

The distribution and activity of the fundamentals for octahedral $[\text{MX}_6]^{2-}$ is as follows.

Oh	1.	2.	3.	4.	5.	6.
	A_{1g}	E_g	F_{1u}	F_{1u}	F_{2g}	F_{2u}
	R	R	IR	IR	R	Inact.

The anions $[\text{PtX}_6]^{2-}$, (X = Cl, Br) and $[\text{PdCl}_6]^{2-}$ have been fully assigned from Raman⁴² and infrared work⁴¹, (Table 3). The stretching frequencies are

10-20 cm.^{-1} higher than in corresponding M(II) anions, the effect on frequency of increase in oxidation state outweighing that of increase in coordination number.

2.3. Substituted M(II) complexes.

There is no Raman data on platinum or palladium substituted complexes. The infrared data on cis- and trans- $[\text{MX}_2\text{L}_2]$ is considerable though confined to X = Cl, Br, (Tables 4 to 7). For cis- complexes two $\nu(\text{MX})$ have generally been observed and one is found for trans- complexes in accord with theory. A systematic study of cis- and trans-

$[\text{PtX}_2\text{L}_2]$ by Adams et. al. soundly established a relation between the stretching frequency of the platinum-chlorine bond and the nature of the trans- ligand³³. They found that, in cis- $[\text{PtCl}_2\text{L}_2]$ complexes, the average of the $\nu(\text{PtCl})$ frequencies varies from 336 (L = pyridine) to 292 cm.^{-1} (L = PEt_3). If the series trans- $[\text{PtClR}(\text{PEt}_3)_2]$ ^{33, 2}, (Table 7), is included then the lower limit of $\nu(\text{PtCl})$ is extended to 269 cm.^{-1} , (R = H). This wide range of

$\nu(\text{PtCl})$ frequencies (for bromides $\nu(\text{PtBr})$ is in the range 251-184 cm.^{-1}) indicates a marked dependence

of platinum-chlorine bond strength on L when L is trans to chloride. In contrast, for trans- complexes $[\text{PtCl}_2\text{L}_2]$, $\nu(\text{PtCl})$ is insensitive to L occurring at $339 \pm 4 \text{ cm.}^{-1}$. The most important factor determining the platinum-halogen bond strength is the electronegativity of L but there are anomalies which might be attributed to π -bonding in the Pt-L bond. There is a rough inverse correlation between the trans-directing influence of L and $\nu(\text{PtX})$, with the notable exception of $[\text{PtX}_2.\text{COD}]$ in which $\nu(\text{PtX})$ is relatively high although the olefin has a high trans-effect. This accords with the view that there are inductive and mesomeric mechanisms whereby a ligand can exert its trans- effect. trans- Bond weakening is to be associated only with the inductive mechanism, whereas olefins exert their trans- effect mainly by the mesomeric mechanism. This area is further pursued in the discussion in Chapter II. Further work on these complexes has extended the frequency range of $\nu(\text{PtX})$ and provided confirmation of the ligand correlation. (Table 4 and 5). A similar but less marked dependence of $\nu(\text{MCl})$ on a trans- ligand is seen in the published data for Pd(II) complexes, (Table 6). The range of ligand is narrower and no

bromo-complexes have been studied apart from trans- $[\text{PdX}_2(\text{NH}_3)_2]$, (X = Cl, Br, I) for which Hendra and Sadasivan found $\nu(\text{PdBr})$ and $\nu(\text{PdI})$ at 228 and 195 cm^{-1} respectively³⁵.

Data on complexes of the type $[\text{MX}_3\text{L}]^-$ is confined to $\text{K}[\text{PtCl}_3\text{L}]$, (Table 8). The trans- PtCl_2 grouping absorbs consistently at a higher frequency than that of the single Pt-Cl bond trans to L. This is in accord with theories of the trans-effect. Smart³⁹ found a weaker absorption on the low-frequency side of the $\nu(\text{PtCl})$ bands in Zeises' salt, ($\Delta = 10 \text{ cm}^{-1}$), which he attributed to $\nu(\text{Pt}^{37}\text{Cl})$.

In a study of the diethylenetriamine complex, $[\text{Pd}(\text{dien})\text{X}] \text{X}$, Watt and Klett²¹ assigned $\nu(\text{PdX})$ at 333 and 241 cm^{-1} for X = Cl, Br; $\nu(\text{PdI})$ lying below 200 cm^{-1} .

A square-planar MX_2M halogen-bridged system should exhibit two infrared-active frequencies mainly associated with M-X stretching, B_{2u} and B_{3u} . There are a few isolated assignments of these bridge frequencies in platinum and palladium complexes of the type $\text{M}_2\text{X}_4\text{L}_2$, (Table I-1, Chapter I)^{19, 26, 27}. For PtCl_2 which has a structure identical with that

of the $[\text{Ta}_6\text{Cl}_{12}]^{2+}$ ion, the highest absorption at 318 cm.^{-1} was assigned to $\nu(\text{PtCl})_b^{26}$. $(\text{PdCl}_2)_n$ which has a chain structure absorbs at 340 cm.^{-1} ²⁶.

2.4 Substituted complexes of platinum and palladium (IV).

Pd(IV) complexes have not been studied and the small amount of data on Pt(IV) complexes is presented in Table 9. For cis- $[\text{PtX}_4\text{L}_2]$, theory allows four $\nu(\text{PtCl})$ vibrations whilst for the trans- complex one is allowed. Two brief studies^{11, 43} of cis- $[\text{PtCl}_4\text{L}_2]$ were in accord with theory but incomplete in that only three $\nu(\text{PtCl})$ bands were observed, (see Chapter IV). In the only other study of Pt(IV) complexes, Jones¹⁸ assigned $\nu(\text{PtX})$ at 349, 247 and 199 cm.^{-1} for trans- $\text{K}_2[\text{PtX}_2(\text{CN})_4]$, $\text{X} = \text{Cl, Br and I}$ respectively. Generally Pt(IV) -halogen bond stretching vibrations lie at frequencies similar to those found for Pt(II) complexes, although further work is required to elucidate their behaviour with variation of ligand.

2.5 Summary.

Table 10 represents the infrared data discussed in this review expressed in frequency ranges

Table 1.

Frequencies and assignments for $[\text{PtX}_4]^{2-}$ *

	Raman			Infrared			Reference
	ν_1	ν_5	ν_3	ν_6	ν_7	ν_2	
$[\text{PtCl}_4]^{2-}$	335	304	164				37
$\text{R}_2 \text{PtCl}_4$; R = K				325	193	175	5
K				326	194	175	3
Rb				320	190	167	5
Cs				316	185	160	5
$\text{Pt}(\text{NH}_3)_4$				310	198	175	3
$\text{Pd}(\text{NH}_3)_4$				321	188	174	3
pyH.				315			28
$\text{R}_2 \text{PtBr}_4$; R = K				233	135	80	6
K				234			35
pyH.				230			28

* Further work in references 16, 25, 34.

Table 2.

Frequencies and assignments for $[\text{PdX}_4]^{2-}$ *

	ν_6	ν_7	ν_2	Reference
$\text{R}_2 \text{PdCl}_4$; R = K	332	191	168	3
K	335			15
Cs	327			14
NH_4	329			15
MeNH_3	330			15
EtNH_3	329			15
$\text{Pd}(\text{NH}_3)_4$	324			15
$\text{Pt}(\text{NH}_3)_4$	333	224	164	3
K_2PdBr_4	254	136	106	3
	264			35

* Further work in reference 38.

Table 3.

Frequencies and Assignments for $[MX_6]^{2-}$ *

	Cation	Raman			Infrared		Reference
		ν_1	ν_2	ν_5	ν_3	ν_4	
$[PtCl_6]^{2-}$		344	320	162			42
	K				343	182	41
	K				344	186	6
	NEt_4				330		4
$[PtBr_6]^{2-}$		207	190	97			42
	K				240	78	6
	K				244	90	41
$[PtI_6]^{2-}$	K				186	46	6
$[PdCl_6]^{2-}$		317	292	164			42
	K				340	175	41
	K				356		6
	NEt_4				337		4

* Further work in references 11 and 34.

Table 4.

$\nu(\text{PtX})$ frequencies for trans- [PtX₂L₂] (b).

L.	$\nu(\text{PtCl})$	$\nu(\text{PtBr})$	Reference
SEt ₂	342	254	33
SeEt ₂	337	241	33
NH ₃	332	227	33
PhNH ₂	331		44
pY	343	251	33
PMe ₃	326		14
PEt ₃	340	254	33
PPr ₃ ⁿ	339	259	33
PPh ₃	345		23
(a) TPP	344	253	9
AsMe ₃	337		14
AsEt ₃	339	251	33
AsPr ₃ ⁿ	337	245	33

(b) Further work in references 2,7,11,16,22,27,28,35

(a) T PP - triphenylphosphole.

Table 5.

$\nu(\text{PtX})$ frequencies for cis- $[\text{PtX}_2\text{L}_2]$ (b).

L.	$\nu(\text{PtCl})$		$\nu(\text{PtBr})$		Reference
SEt ₂	330	318	254	226	33
(PhSCH ₂ -)	317	313			13
SeEt ₂	333	317			33
(PhSeCH ₂ -)	320	314			13
TeEt ₂	302	282	217	208	33
TePr ⁿ ₂	306	291			33
NH ₃	326		224	221	33
py	343	328	219	211	33
bipy	351	338			36
MeCN	360	345			36
PhCN	356	346			36
PMe ₃	302	288	277		14
PEt ₃	303	281	212	194	33
PPr ⁿ ₃	307	277			33
AsMe ₃	313	293			14
AsEt ₃	314	288			33
AsPr ⁿ ₃	310	286	220		33
SbPr ⁿ ₃	311	281	217		33
COD ^(a)	338	316	230	215	33

(a) COD - 1, 5 cyclooctadiene

(b) Further work in references 7,10,11,16,20,27,28.

Table 6. $\nu(\text{PdCl})$ frequencies for cis- and trans- $[\text{PdCl}_2\text{L}_2]$ (a)

L.	<u>trans-</u> $\nu(\text{PdCl})$	Reference	L.	<u>cis-</u> $\nu(\text{PdCl})$	Reference
SMe ₂	359	14	(MeSCH ₂ -)	315	296
SEt ₂	358	14	(EtSCH ₂ -)	323	310
NH ₃	333	15	NH ₃	327	306
MeNH ₂	341	15	MeNH ₂	317	308
PhNH ₂	334	15	EtNH ₂	317	296
py	358	15	C ₂ H ₄ (NH ₂) ₂	307	296
MeCN	357	36	(Me ₂ NCH ₂ -)	330	322
PhCN	366	36	py	342	333
PEt ₃	355	14	bipy	353	346
PPr ₃	353	14	phen.	353	346
PPh ₃	357	14	PMe ₃	294, 283, 269	14
TPP	355	9	(Ph ₂ PCH ₂ -)	310	286
AsEt ₃	353	14	AsMe ₃	316	299
Et ₂ N ₂ O	362	24	COD	335, 325, 296	14

(a) Further work in references 8, 10, 13, 20, 28, 35, 44.

Table 7.

$\nu(\text{PtX})$ frequencies for trans- $[\text{PtXR}(\text{PEt}_3)_2]$ ³³.

		$\nu(\text{PtCl})$	$\nu(\text{PtBr})$
R =	H	269	184
	Ph	270	184
	Me	274	
	C_6F_5 (a)	310	

(a) Reference 2.

Table 8. $\nu(\text{PtCl})$ frequencies for K $[\text{PtCl}_3\text{L}]$.

		<u>trans</u> Cl-Pt-Cl		<u>trans</u> Cl-Pt-L		Reference
L =	C_2H_4	343	333	308	298	39
	C_2D_4	343		308		39
	C_2H_4	340	331	306		27
	C_3H_6	330		306		32
	C_3D_6	330		306		32
	ol	335 (sh)	330	305		27
	ac ₁	326		312		27
	ac ₂	335 (sh)	325	314		27

ol. = allyl alcohol; ac₁ = $(\text{Me}_2\text{C}(\text{OH})\text{C}\equiv)$;

ac₂ = $(\text{Me}_2\text{C}(\text{OMe})\text{C}\equiv)$.

Table 9.

$\nu(\text{PtX})$ frequencies for some substituted Pt(IV) complexes

	<u>cis</u>	<u>trans</u>	Reference
PtCl_4L_2 ; L = NH_3	350 337 330	341	11
py	352 343 329		43
bipy	361 348 330 290		43
phen	361 348 324		43
diph	345 289 272		43
diars	344 289 270		43
$\text{PtCl}_2(\text{NH}_3)_2(\text{NO}_2)_2$	330 305	353	11
$\text{K}_2 [\text{PtCl}_2(\text{NO}_2)_4]$		333	11
$\text{K}_2 [\text{PtX}_2(\text{CN})_4]$; X = Cl		349	18
Br		247	18
I		199	18
$\text{PtCl}_2(\text{NH}_3)_4$	348		11
$\text{PtCl}_3(\text{NH}_3)_2(\text{NO}_2)$	349 320		11

for the M-X vibrations.

Table 10. Frequency ranges for M-X vibrations.

		<u>Stretching</u>	<u>Bending</u>
M = Pt	X = Cl	360-270	200-160
	Br	260-180	135-80
	I	-	-
M = Pd	X = Cl	365-270	225-165
	Br	-	-
	I	-	-

Only for $\nu(\text{PtX})$, X = Cl, Br and $\nu(\text{PdCl})$ can the data be considered adequate. Frequencies of bending modes are confined to simple complex halides and M-I bond vibrations are almost unknown, so that a frequency range cannot be given for these modes. In addition there are large gaps in the knowledge of M-X vibrations for some structural types. In particular, halogen-bridged complexes of Pt(II) and Pd(II) and substituted Pt(IV) complexes. A major aim of this thesis has been to provide this further information. Thus in Chapter I $[\text{M}_2\text{X}_6]^{2-}$, (M = Pt, Pd; X = Cl, Br, I), systems act as prototypes for terminal and bridged-stretching frequencies

and provide more data on bending modes. In Chapter II this information is used to assign corresponding modes in a range of substituted halogen-bridged $M_2X_4L_2$ complexes and the effect of varying L on these modes is discussed. Finally in Chapter IV, cis- and trans- $[PtX_4L_2]$ complexes are examined in the first systematic study of Pt(IV) complexes. Stretching and bending modes are assigned for $X = Cl, Br$ and I and their sensitivity to L is examined. Finally the number of $\nu(PtX)$ modes observed is shown to be a useful guide to the stereochemistry of these complexes.

3. Vibrational interactions.

As a prologue to the work in this thesis it is relevant at this point to discuss the evidence for applying the concept of group (or localised) vibrations to the skeletal vibrations of complex inorganic systems, e.g. $\nu(MX)$ and $\nu(ML)$ frequencies. A basis for this discussion is the classic work on this subject by Herzberg⁹⁸. In the interpretation of the vibrational spectra of organic molecules the concept of group frequencies is valuable. For example, all molecules containing the $\equiv CH$ bond have normal

frequencies of about 3300 and 700 cm.^{-1} corresponding to the C-H bond-stretching and bond-bending vibrations. This is possible because such vibrations are highly localised and involve few molecular coordinates. In contrast, there are no generally useful correlations for $\nu(\text{C-C})$ because these are skeletal vibrations. For example in a molecule containing $\begin{array}{c} \rightarrow \text{C} - \overset{\text{I}}{\underset{\text{I}}{\text{C}}} - \text{N} \langle \end{array}$ a complex vibration is expected rather than one characteristic of each bond, since the masses as well as the force constants are of about the same magnitude; whereas in a molecule containing $\begin{array}{c} \rightarrow \text{C} - \text{C} \equiv \text{N} \end{array}$, there would be a characteristic group frequency for C-C and C \equiv N.

The metal-ligand vibrations studied in this work are skeletal vibrations and are therefore likely to be sensitive to changes in the complex as a whole. Vibrational interactions are considered so that the problems of interpretation and assignment may be appreciated. A further principle to be considered is that modes of the same symmetry species will interact and perturb one another, the extent of the interaction depending on how close the unperturbed frequencies lie. Thus for linear X-M-X, the two

stretching modes are of different symmetry and will not interact with one another. For X-M-Y such interaction is allowed and will result in 'mixing' of $\nu(\text{M-X})$ and $\nu(\text{M-Y})$, so that in some cases it may not be possible to talk about $\nu(\text{M-X})$ and $\nu(\text{M-Y})$ but rather only about two normal modes involving both types of stretching. In complexes where the force constants of the M-X and M-Y bonds markedly differ, the two modes will correspond closely to $\nu(\text{M-X})$ and $\nu(\text{M-Y})$. For example in trans- $[\text{PtHCl}(\text{PEt}_3)_2]$, $\nu(\text{PtH}) = 2230 \text{ cm.}^{-1}$ and $\nu(\text{PtCl}) = 269 \text{ cm.}^{-1}$. However in a system such as cis- $[\text{PtCl}_2(\text{SMe}_2)_2]$, there must be considerable 'mixing' and it may be meaningless to describe observed bands as $\nu(\text{PtCl})$ or $\nu(\text{PtS})$. The justification for doing so rests upon the fact that these vibrational interactions will be damped out by the large mass of the central metal atom. Comparison of the $\text{SnMe}_{4-n}\text{Cl}_n$, ($n = 0$ to 3), series with the Ge, Si and C analogues shows that the vibrational fundamentals of the R group become 'purer' and less coupled as the mass of the central metal atom is increased. This is because the metal

atom moves less and less during the vibration and the vibration is increasingly the oscillation of the Me group¹⁸⁷. Thus for platinum descriptions such as, $\nu(\text{PtX})$ and $\nu(\text{PtL})$ should be good approximations but for palladium and rhodium they will be less accurate. In particular there may be substantial mixing in the iodo and to a lesser extent the bromo- complexes where the mass of the halogen becomes similar to that of the metal atom. To further investigate these systems full Raman data are required. Along with the infrared results, this data will provide the information for a normal coordinate analysis and a calculation of the potential energy distribution amongst the internal coordinates. The latter being a direct measure of the extent of vibrational interaction.

CHAPTER I

Halogen-bridged anionic complexes of
Pt(II) and Pd(II).

I-1. Introduction

A square-planar bridged system M_2X_2 , (Figure I-1), should exhibit two infrared-active frequencies mainly associated with M-X bond stretching, B_{2u} and B_{3u} in D_{2h} and $2B_u$ in C_{2h} symmetry. No systematic infrared spectral study has been made of

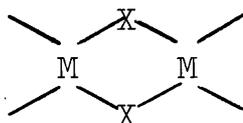


Figure I-1.

these systems. A few isolated assignments^{19, 26, 27} of bridge stretching vibrations do exist for platinum and palladium complexes of the $M_2X_4L_2$ type, (X = Cl, Br; L = Ligand). However in no case were both bridge frequencies assigned, although for $Pd_2Cl_4(C_2H_4)_2$ and the deuterated analogue, Fritz¹⁹ observed them but wrongly assigned the higher one, at 304 cm.^{-1} , to a vibration of the terminal palladium-chlorine bonds. This data is listed in Table I-1; platinumous chloride is included as it has a polymeric structure with platinum atoms linked by bridging chlorine atoms,^{4, 6} and the band observed at 318 cm.^{-1} in its spectrum was assigned²⁶ to a bridge stretching mode.

Assignment of palladium-chlorine bridge stretching vibrations, $\nu(\text{PdCl})_b$, at $360\text{-}340\text{ cm.}^{-1}$ for dimeric π -allylic complexes,^{4,7} and at 354 cm.^{-1} for the mesityl oxide complex^{4,8} are considered to be in error. These values are much higher than those

Compound	$\nu(\text{MX})_t$	$\nu(\text{MX})_b$	Reference
$\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$	352, 347	304 272, 267	19
$\text{Pd}_2\text{Cl}_4(\text{C}_2\text{D}_4)_2$	343	306 270	19
$\text{Pt}_2\text{Cl}_4(\text{PEt}_3)_2$	352	- 265	26
$\text{Pt}_2\text{Br}_4(\text{PEt}_3)_2$	248	209 -	26
$\text{Pt}_2\text{Cl}_4(\text{Py})_2$	349	308 -	27
PtCl_2	-	318 -	26

Table I-1 Data from previous studies of bridged-halogen systems.

found in this study and in neither case was the spectral region studied extended below 300 cm.^{-1} or the halogen sensitivity of the bands confirmed by comparison with the spectra of analogous bromo-complexes.

In this work, the bridged systems were studied in three parts. In this Chapter, the infrared

spectra and vibrational assignments for a series of anions $[M_2X_6]^{2-}$, (M = Pt, Pd ; X = Cl, Br, I.), are discussed. The results obtained for these anions then serve as models for the discussion of substituted halogen-bridged platinum and palladium complexes in Chapter II and rhodium complexes in Chapter III.

I-2. Infrared spectra and vibrational assignment of halogen-bridged anionic complexes of bivalent palladium and platinum.

The complex anions $[M_2X_6]^{2-}$, (M = Pt, Pd; X = Br, I.), were prepared as tetraethylammonium salts, as described previously.⁴⁹ The chloro-palladium complex was prepared in a similar manner with tetraphenylarsonium, tetra-n-butylammonium, and n-cetyltrimethylammonium cations. The $[Pt_2Cl_6]^{2-}$ anion, first isolated by Chatt,⁵⁰ was prepared as the new compound $[AsPh_4]_2[Pt_2Cl_6]$.

An X-ray structural determination carried out on $[NEt_4]_2[Pt_2Br_6]$ ⁴⁹ confirmed that it has a planar binuclear halogen-bridged structure. Within experimental error the bridge was symmetrical and the terminal and bridge bonds were of the same length. A powder photograph of the analogous palladium compound⁴⁹ indicated the same structure.

Thus the reasonable assumption was made that all the compounds examined in this study contained the $[M_2X_6]^{2-}$ anion.

The planar bridged dimeric M_2X_6 , Figure I-2,

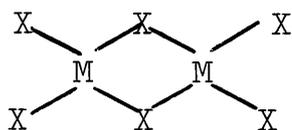


Figure I-2

of point group D_{2h} has 18 fundamental modes of vibration. The system is centrosymmetric and according to selection rules, 9 of the fundamentals are Raman-active ($4A_g + 3B_{1g} + B_{2g} + B_{3g}$), 8 are infrared-active ($2B_{1u} + 3B_{2u} + 3B_{3u}$), and one is inactive in both spectra (A_u). However in the solid state $[NEt_4]_2[Pt_2Br_6]$ belongs to the $P\bar{1}$ space group⁴⁹ and the $[Pt_2Br_6]^{2-}$ anion has site symmetry C_i .⁵¹ Thus the inactive A_u mode, ν_{10} , becomes infrared-active only, Table I-2. In practice it may appear as a weak band or be totally absent from the spectrum. Schematic representations of these modes are given in Figure I-3. For the platinum compounds these representations are good approximations, as vibrational coupling is not expected to be important

Activity	D _{2h}	C _i	Activity
Raman	A _g B _{1g} B _{2g} B _{3g}	A _g	Raman
Inactive	A _u		
Infrared	B _{1u} B _{2u} B _{3u}	A _u	Infrared

Table I-2. Effect of site-symmetry on [Pt₂Br₆]²⁻,
D_{2h} → C_i.⁵³

when the masses of M and X differ considerably. In contrast the bromo- and iodo-palladium compounds may exhibit coupling of vibrations as the masses of M and X are comparable.

The infrared results are given in Table I-3. and the spectra are shown in Figures I-4. to 5. Absorption due to the cations was identified by recording their spectra separately, (Figure I-4).

Fig. I-3.

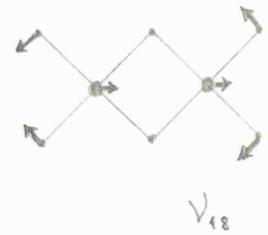
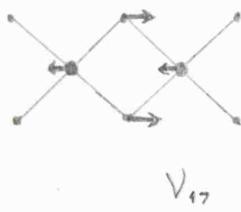
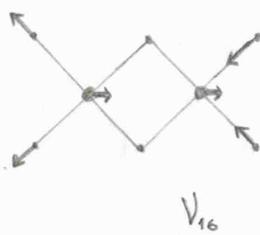
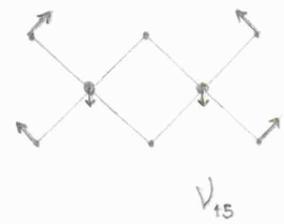
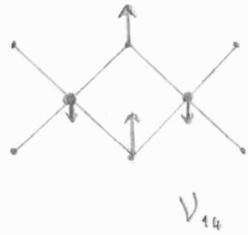
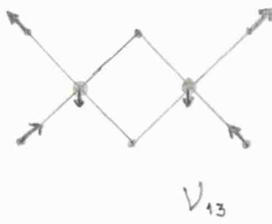
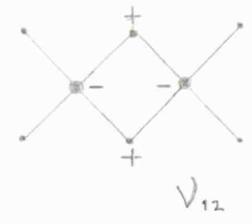
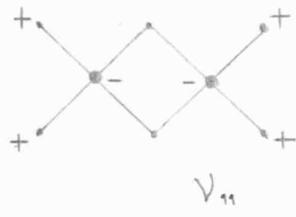
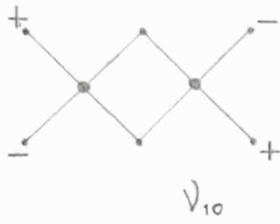
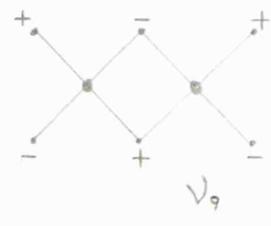
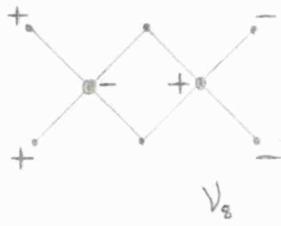
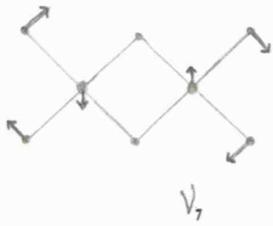
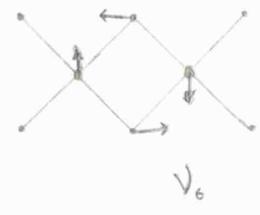
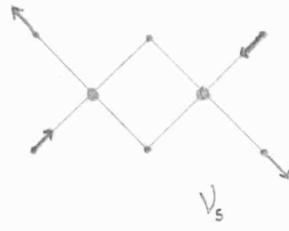
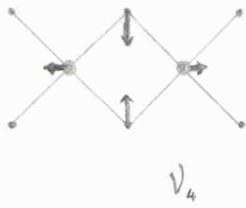
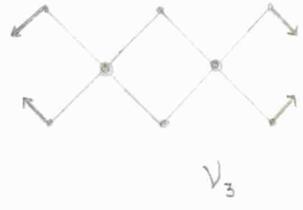
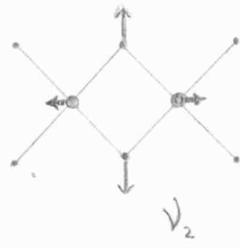


Figure I-3.

Schematic representations of the normal modes of $[M_2X_6]^{2-}$, $(D_{2h})^+$.

Assignment	Symmetry Species	Approximate description of mode
ν_1	Ag	Terminal MX symmetric stretching $\nu(MX)_t$
ν_2	Ag	Symmetric bridge stretching $\nu(MX)_b$
ν_3	Ag	MX ₂ deformation $\delta(MX_2)$
ν_4	Ag	Bridge in-plane bend $\delta(M_2X_2)$
ν_5	B _{1g}	Terminal antisymmetric MX stretching $\nu(MX)_t$
ν_6	B _{1g}	Bridge in-plane bend $\delta(M_2X_2)_b$
ν_7	B _{1g}	MX ₂ rocking $\rho_r(MX_2)$
ν_8	B _{2g}	MX ₂ wagging $\rho_w(MX_2)$
ν_9	B _{3g}	MX ₂ twisting $\rho_t(MX_2)$
ν_{10}	A _u	MX ₂ twisting $\rho_t(MX_2)$
ν_{11}	B _{1u} [†]	MX ₂ wagging $\rho_w(MX_2)$
ν_{12}	B _{1u}	Bridge out-of-plane bend $\pi(M_2X_2)$
ν_{13}	B _{2u}	Terminal MX antisymmetric stretching $\nu(MX)_t$

Figure I-3. (Continued)

Assignment	Symmetry Species	Approximate description of mode
ν_{14}	<u>B_{2u}</u>	Antisymmetric bridge stretching $\nu(\text{MX})_b$
ν_{15}	<u>B_{2u}</u>	MX ₂ rocking $\rho_r(\text{MX}_2)$
ν_{16}	<u>B_{3u}</u>	Terminal MX antisymmetric stretching $\nu(\text{MX})_t$
ν_{17}	<u>B_{3u}</u>	Antisymmetric bridge stretching $\nu(\text{MX})_b$
ν_{18}	<u>B_{3u}</u>	MX ₂ deformation $\delta(\text{MX}_2)$

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+ The bridge lies in the xy plane and the x-axis passes through the line of the two M atoms. The z-axis is perpendicular to the xy plane and passes through the centre point of the bridge.

++ Infrared-active modes are underlined.

The cations are all large and lattice modes will occur at extremely low frequencies and interaction with the vibrations of $[M_2X_6]^{2-}$ will be minimal.

The predicted two terminal and two bridged metal halogen stretching vibrations were observed for all the compounds. The remaining fundamentals, described as terminal MX_2 deformation (δ), wag ($\rho_{\underline{W}}$), and rock ($\rho_{\underline{r}}$), and bridge out-of-plane bend (π), were not all observed. Bands not observed, particularly for the iodo-compounds, are expected to lie below the limit of the spectrometer, (70 cm.^{-1}).

I-3. Platinum compounds.

1. Tetrachloro- μ^1 -dichlorodiplatinum

Selection rules allow eight fundamentals but only six were observed in the spectrum of $[Pt_2Cl_6]^{2-}$. The highest and strongest fundamental in the spectrum, at 352 cm.^{-1} , is assigned to the terminal antisymmetric and symmetric stretching modes, $\nu(PtCl)_t$. The band was broad and occurred in a region of high cation absorption, thus making resolution of the modes difficult. Isotope bands, due to $\nu(Pt^{37}Cl)_t$, could occur as shoulders on the low frequency side of the main absorption and also make resolution difficult. The assignment is

Table I-3a.

Observed frequencies and assignments for $[M_2X_6]^{2-}$.

Assignment	Symmetry Species	Mode	$[Pt_2Cl_6]^{2-}$	$[Pt_2Br_6]^{2-}$	$[Pt_2I_6]^{2-}$
ν_{13}	B _{2u}	$\nu(MX)_t$	352 vs	243 vs	194 s
ν_{16}	B _{3u}	$\nu(MX)_t$		237 vs	179 s
ν_{14}	B _{2u}	$\nu(MX)_b$	315 ms	211 wm	157 m
ν_{17}	B _{3u}	$\nu(MX)_b$	302 m	196 m	144 m
ν_{18}	B _{3u}	$\delta(MX_2)$	186 ms	110 ms	-
ν_{11}	B _{1u}	$\rho_w(MX_2)$	159 ms	85 w	-
ν_{15}	B _{2u}	$\rho_T(MX_2)$	98 wm	(68) ⁺ w	-
ν_{12}	B _{1u}	$\pi(M_2X_2)$	-	-	-

+ Enclosed figures represent tentative assignments.

Table I-3b.

Observed frequencies and assignments for $[\text{Pd}_2\text{X}_6]^{2-}$.

Assign- ment	Symmetry Species	Mode	$\text{M}_2[\text{Pd}_2\text{Cl}_6]$			$[\text{Pd}_2\text{Br}_6]^{2-}$	$[\text{Pd}_2\text{I}_6]^{2-}$
			AsPh ₄	NBu ₄	NMe ₃ Cet.		
ν_{13}	B _{2u}	$\nu(\text{MX})_t$	353 vs	349 vs	339 vs	266 vs	222 vs
ν_{16}	B _{3u}	$\nu(\text{MX})_t$	} 305 m	340 vs	336 vs	262 vs	220 vs
ν_{14}	B _{2u}	$\nu(\text{MX})_b$		302 ms	305 m	192 wm	144 m
ν_{17}	B _{3u}	$\nu(\text{MX})_b$	264 wm	264 m	263 ms	177 m	132 m
ν_{18}	B _{3u}	$\delta(\text{MX}_2)$	186 ms	161 m	160 wm	117 m	-
ν_{11}	B _{1u}	$\rho_w(\text{MX}_2)$	156 s	155 ms	146 m	88 w	-
ν_{15}	B _{2u}	$\rho_T(\text{MX}_2)$	97 w	-	(79) ⁺ w	-	-
ν_{12}	B _{1u}	$\pi(\text{M}_2\text{X}_2)$	-	-	-	-	-

-32-

+ Enclosed figures represent tentative assignments.

Figure I-4

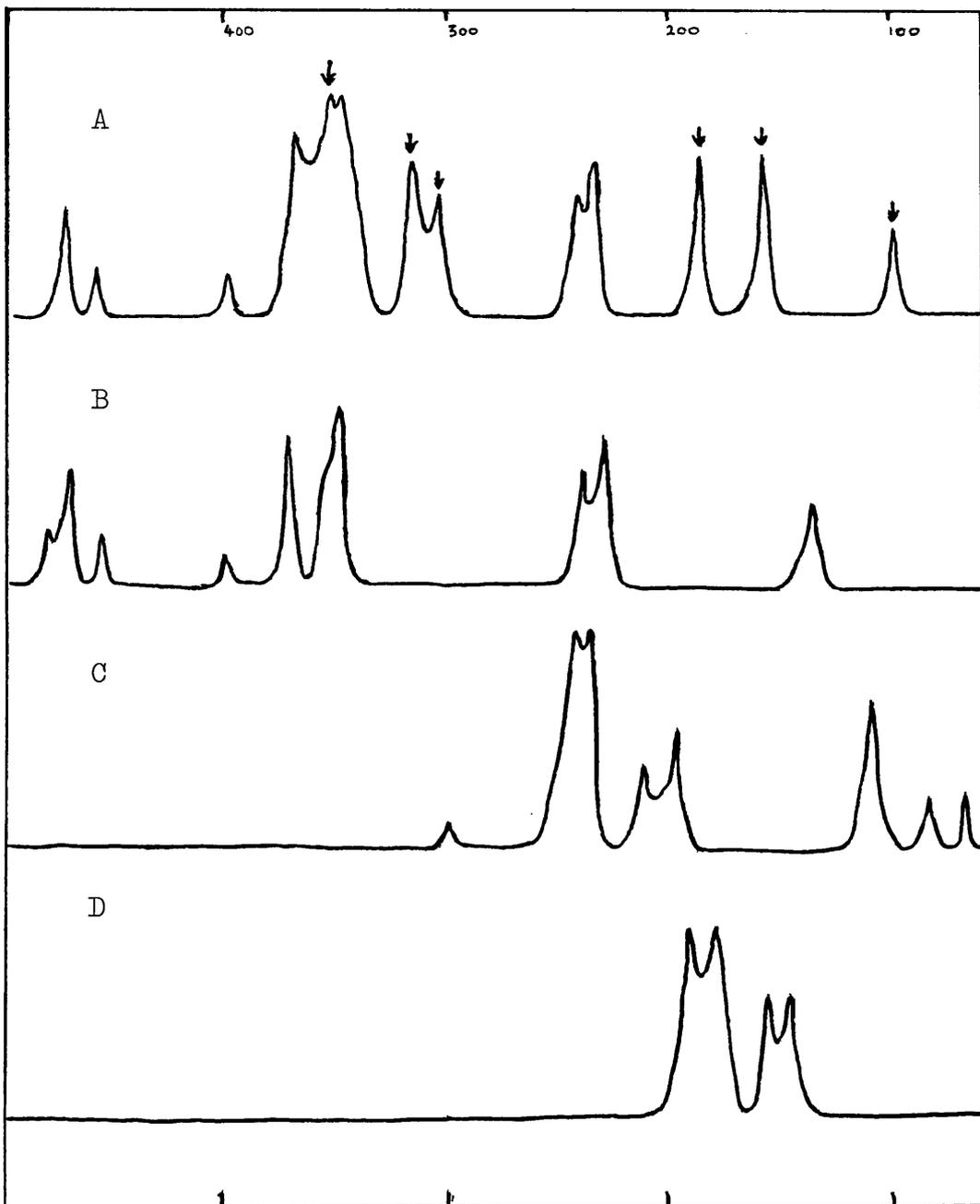


Figure I-4.

Spectra Sketches for $[\text{Pt}_2\text{X}_6]^{2-}$.

- A. - $[\text{AsPh}_4]_2[\text{Pt}_2\text{Cl}_6]$.
- B. - $[\text{AsPh}_4]\text{Cl}$. +
- C. - $[\text{NEt}_4]_2[\text{Pt}_2\text{Br}_6]$
- D. - $[\text{NEt}_4]_2[\text{Pt}_2\text{I}_6]$

+ $[\text{NEt}_4]\text{X}$, (X = Br, I.); $[\text{NBu}_4]\text{Cl}$; and $[\text{NMe}_3\text{cetyl}]\text{Cl}$ showed no absorption in the region $400 - 70 \text{ cm.}^{-1}$

Figure I-5

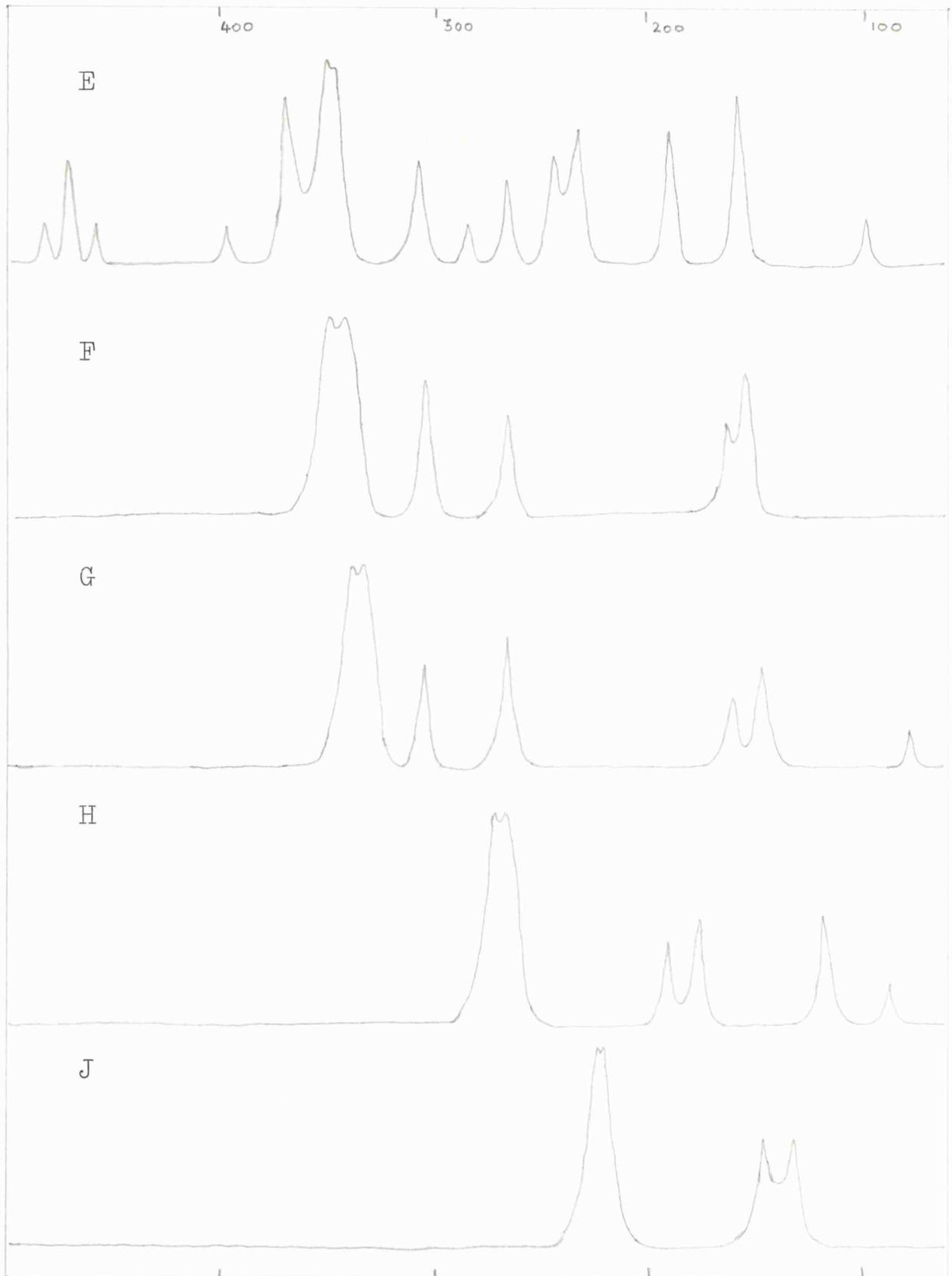


Fig. I-5.

Spectra sketches for $[\text{Pd}_2\text{X}_6]^{2-}$.

- E. - $[\text{AsPh}_4]_2[\text{Pd}_2\text{Cl}_6]$
- F. - $[\text{NBu}_4]_2[\text{Pd}_2\text{Cl}_6]$
- G. - $[\text{NMe}_3\text{cetyl}]_2[\text{Pd}_2\text{Cl}_6]$
- H. - $[\text{NEt}_4]_2[\text{Pd}_2\text{Br}_6]$
- J. - $[\text{NEt}_4]_2[\text{Pd}_2\text{I}_6]$

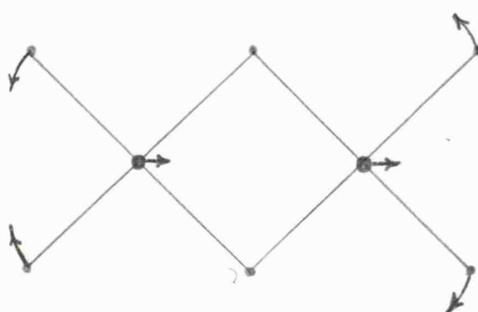
consistent with spectra observed for trans-[PtCl₂L₂] adducts^{14,33} and for [PtCl₆]²⁻.⁶ The bridge stretching vibrations, $\nu(\text{PtCl})_b$, are at 315 and 302 cm.⁻¹. In contrast to Ga₂Cl₆ and Al₂Cl₆, both are lower than the terminal stretching vibrations. Bending vibrations are not expected above 220 cm.⁻¹ and alternative assignment of $\nu(\text{PtCl})_t$ at 315 cm.⁻¹ is not tenable. For [PtCl₄]²⁻, the in-plane bend, $\delta(\text{PtCl}_4)$, is at 194 and the out-of-plane bend, $\pi(\text{PtCl}_4)$, at 175 cm.⁻¹.³ These vibrations are closely related to $\delta(\text{PtCl}_2)$ and $\rho_w(\text{PtCl}_2)$ in [Pt₂Cl₆]²⁻, (Fig. I-6). Therefore the bands at 186 and 159 cm.⁻¹ in [Pt₂Cl₆]²⁻, are assigned to the deformation, ν_{18} , and wag, ν_{11} , respectively. The remaining band at 98 cm.⁻¹ is assigned to $\rho_r(\text{PtCl}_2)$, ν_{15} . The bridge out-of-plane bending mode is expected to lie below 70 cm.⁻¹ and was not observed.

I-3. 2. Tetrabromo- $\mu\mu'$ -dibromodiplatinum.

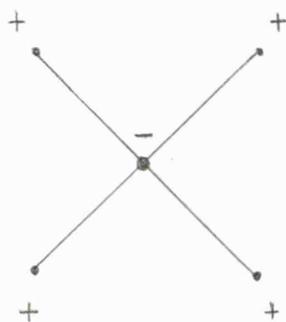
Seven fundamentals were observed for [Pt₂Br₆]²⁻. They show the expected shift to lower frequency when the halogen is changed from chlorine to bromine and all lie below 250 cm.⁻¹. From its position and intensity the weak absorption at 300 cm.⁻¹ cannot be a fundamental. First overtones of B_{nu}



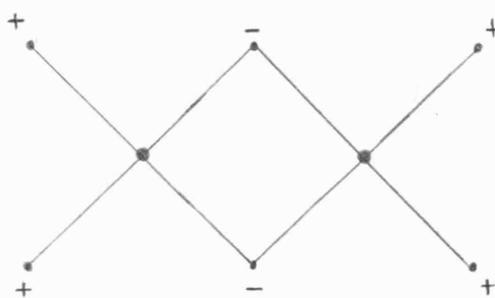
δ (PtCl_4)



δ (PtCl_2)



π (PtCl_4)



ρ_w (PtCl_2)

Fig.I-6. Correlation between bending modes for
 $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}_2\text{Cl}_6]^{2-}$.

vibrations are infrared-inactive and the band is therefore assigned to a combination mode.

Combinations of $A_g + B_u$ or $A_u + B_g$ modes give infrared-active B_u combination modes. Two examples are:-

$$A_{1g} + B_{2u} = B_{3u}$$

$$A_{1u} + B_{3g} = B_{2u}$$

Raman-active only modes are involved in these combinations and lack of Raman data precludes identification of the combination band. The terminal and bridge stretching modes are easily assigned. The bands at 243 and 237 cm.^{-1} are assigned to $\nu(\text{PtBr})_t$. This is consistent with $\nu(\text{PtBr})_6^6$ at 240 cm.^{-1} in $[\text{PtBr}_6]^{2-}$. By comparison with the spectrum of $[\text{Pt}_2\text{Cl}_6]^{2-}$, $\nu(\text{PtBr})_b$ lie at 211 and 196 cm.^{-1} and $\delta(\text{PtBr}_2)$ and $\rho_w(\text{PtBr}_2)$ at 110 and 85 cm.^{-1} respectively. In background spectra polythene has a sharp band at 72 cm.^{-1} . In this spectrum, the band is broad and two maxima were found at 72 and 68 cm.^{-1} . The latter is tentatively assigned to $\rho_r(\text{PtBr}_2)$. The bridge out-of-plane bend should be well below 70 cm.^{-1} and was not observed.

I-3. 3. Tetraiodo- $\mu\mu'$ -diiododiplatinum.

Four bands, lying between 200-140 cm.^{-1} , were observed for $[\text{Pt}_2\text{I}_6]^{2-}$. The assignments closely

follow those made for the chloro- and bromo-anions. The two highest bands at 194 and 179 cm.^{-1} are assigned to $\nu(\text{PtI})_t$ and the lowest at 157 and 144 cm.^{-1} to $\nu(\text{PtI})_b$. The values of the terminal stretching vibrations are more widely separated, $\Delta = 15 \text{ cm.}^{-1}$, than in the bromo-complex, $\Delta = 6 \text{ cm.}^{-1}$, but compare with K_2PtI_6 .⁶ None of the four Pt-I bending vibrations were observed, but trends in the spectra of the chloro- and bromo-compounds and values assigned to $\delta(\text{PtI}_4)$ in $[\text{PtI}_6]^{2-}$ ⁶ and $[\text{PtI}_4]^{2-}$ ^{4,5} suggest they will lie below 70 cm.^{-1} .

I-4. Palladium compounds.

I-4. 1. Tetrachloro- $\mu\mu'$ -dichlorodipalladium.

Spectral results for the $[\text{Pd}_2\text{Cl}_6]^{2-}$ anions are shown in Table I-4. Assignment of the spectra parallels that made for $[\text{Pt}_2\text{Cl}_6]^{2-}$. The $\nu(\text{PdCl})_t$ were observed as doublets at 349, 340 cm.^{-1} and 339, 336 cm.^{-1} for the tetra-n-butylammonium and n-cetyltrimethylammonium complexes, respectively. Strong cation absorption makes assignment of $\nu(\text{PdCl})_t$ at 353 cm.^{-1} tentative for $[\text{AsPh}_4]_2[\text{Pd}_2\text{Cl}_6]$. The expected drop in frequency of $\nu(\text{PdCl})_t$ was observed when $[\text{NBU}_4]^+$ was replaced by $[\text{NMe}_3\text{Cetyl}]^+$. This assignment in the range 355-335 cm.^{-1} is consistent with the spectra observed for K_2PdCl_6 ,^{6,41} K_2PdCl_4 ,^{35,38}

Assignment	Symmetry Species	Mode	M = AsPh ₄	M = NBu ₄	M = NMe ₃ Cetyl
ν_{13}	B _{2u}	$\nu(\text{PdCl})_t$	353 vs	349 vs	339 vs
ν_{16}	B _{3u}	$\nu(\text{PdCl})_t$		340 vs	336 vs
ν_{14}	B _{2u}	$\nu(\text{PdCl})_b$	305 m	302 ms	305 m
ν_{17}	B _{3u}	$\nu(\text{PdCl})_b$	264 wm	264 m	263 ms
ν_{18}	B _{3u}	$\delta(\text{PdCl}_2)$	186 ms	161 m	160 wm
ν_{11}	B _{1u}	$\rho^*(\text{PdCl}_2)$	156 s	155 ms	146 m
ν_{15}	B _{2u}	$\rho^*(\text{PdCl}_2)$	97 w	-	(79) ⁺ w
ν_{12}	B _{1u}	$\pi(\text{Pd}_2\text{Cl}_2)_b$	-	-	-

+ Tentative assignments are enclosed by brackets

Table I-4. Assignments of $M_2[\text{Pd}_2\text{Cl}_6]$ complexes.

and trans- [PdCl₂L₂] adducts.¹⁴ The two fundamentals at 305 and 264 cm.⁻¹ are assigned to $\nu(\text{PdCl})_b$. In contrast to $\nu(\text{PdCl})_t$, these palladium-chlorine stretching vibrations are of weak to medium intensity and in [AsPh₄]₂[Pd₂Cl₆] difficult to detect. The values of the bridge vibrations show cation independence and occur at lower frequencies than the corresponding modes of [Pt₂Cl₆]²⁻. The terminal PdCl₂ deformation ν_{18} , wag ν_{11} , and rock ν_{15} , are assigned at 186, 156, and 97 cm.⁻¹, respectively for [AsPh₄]₂[Pd₂Cl₆]. The bridge bending vibration, $\pi(\text{Pd}_2\text{X}_2)$, is expected to occur below 70 cm.⁻¹ and was not observed.

Assignments of the deformation and wag are consistent with the spectra of Na₂PdCl₄⁴⁵ and K₂PdCl₆⁴¹. Bands at 161, 155 cm.⁻¹ for [NBu₄]₂[Pd₂Cl₆] and at 160, 146 cm.⁻¹ for [NMe₃Cetyl]₂[Pd₂Cl₆] were observed. These are assigned to $\delta(\text{PdCl}_2)$ and $\rho_w(\text{PdCl}_2)$ respectively. A weak band at 79 cm.⁻¹ in the spectrum of the n-cetyltrimethylammonium complex is tentatively assigned to $\rho_+(\text{PdCl}_2)$. No correlation is apparent for these bending frequencies as the cation is changed. Both $\delta(\text{PdCl}_2)$ and $\rho_w(\text{PdCl}_2)$ shift to lower frequencies, but the shift is irregular and of different magnitude for each of

these vibrations.

I-4. 2. Tetrabromo- $\mu\mu'$ -dibromodipalladium.

Six fundamentals were observed for $[\text{Pd}_2\text{Br}_6]^{2-}$. The two highest absorptions at 266 and 262 cm^{-1} are assigned to $\nu(\text{PdBr})_t$. The bridge stretching vibrations occur at 192 and 177 cm^{-1} and $\delta(\text{PdBr}_2)$ and $\rho_w(\text{PdBr}_2)$ occur at 117 and 88 cm^{-1} respectively. There is little data on Pd-Br vibrations, $\nu(\text{PdBr})$ in K_2PdBr_4 is at 264 cm^{-1} ³⁵ and in $[\text{PdBr}(\text{dien})]\text{Br}$ at 241 cm^{-1} ,²¹ but no data on bending modes are available. The bridge stretching modes occur 20 cm^{-1} lower than the analogous $\nu(\text{PtBr})_b$. In contrast all other modes are higher in frequency, $\nu(\text{PdBr})_t$ being 20 cm^{-1} higher than $\nu(\text{PtBr})_t$.

I-4. 3. Tetraiodo- $\mu\mu'$ -diiododipalladium.

Only the four stretching vibrations were observed. As for $[\text{Pt}_2\text{I}_6]^{2-}$, the bending modes are expected to lie below 70 cm^{-1} . A barely resolved doublet at 222, 220 cm^{-1} is assigned to $\nu(\text{PdI})_t$, and $\nu(\text{PdI})_b$ occur at 144 and 132 cm^{-1} . The trends apparent in the bromo- complex are repeated here. The terminal vibrations are 40-20 cm^{-1} higher and the bridge vibrations 12 cm^{-1} lower than the corresponding modes of $[\text{Pt}_2\text{I}_6]^{2-}$. No data on the iodides of

palladium exist , but $\nu(\text{PdI})$ in trans- $[\text{PdI}_2(\text{NH}_3)_2]$ is at 195 cm.^{-1} .³⁵

I-5. Conclusion.

Assignments of the observed vibrations of the anionic species, $[\text{M}_2\text{X}_6]^{2-}$, have been made. The values recorded for the bridge stretching vibrations, $\nu(\text{MX})_b$, are now compiled, (Table I-5), and discussed. Two main conclusions are drawn from this data. For

$[\text{M}_2\text{X}_6]^{2-}$	$\nu(\text{MX})_b$	$\bar{\nu}$ cm.^{-1}
$[\text{Pt}_2\text{Cl}_6]^{2-}$	315 302	44
$[\text{Pt}_2\text{Br}_6]^{2-}$	211 196	36
$[\text{Pt}_2\text{I}_6]^{2-}$	157 144	36
$[\text{Pd}_2\text{Cl}_6]^{2-}$	305 264	73
$[\text{Pd}_2\text{Br}_6]^{2-}$	192 177	79
$[\text{Pd}_2\text{I}_6]^{2-}$	144 132	83

Table I-5. Halogen-bridged stretching vibrations for $[\text{M}_2\text{X}_6]^{2-}$.

a given anion, $[\text{M}_2\text{X}_6]^{2-}$, $\nu(\text{MX})_b$ occur at a lower frequency than $\nu(\text{MX})_t$. Taking mean values for the bridge and terminal stretching frequencies, the shift, $\bar{\nu}$, is $\sim 40 \text{ cm.}^{-1}$ for all the platinum complexes. For palladium complexes, $\bar{\nu}$ is much larger and increases as

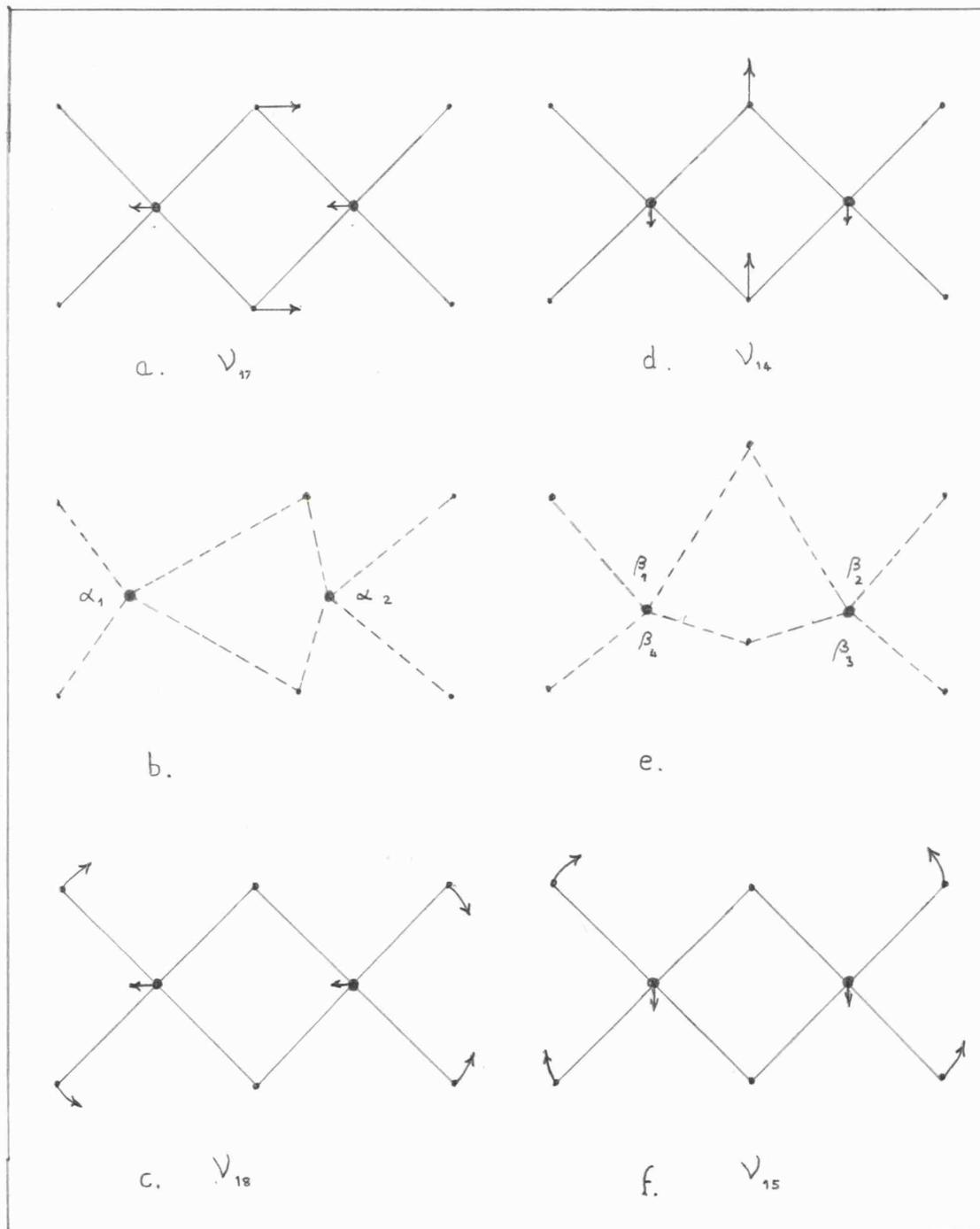
the halogen is changed from Cl, Br to I, (Table I-5). Secondly, whilst $\nu(\text{PdX})_t$ is at a higher frequency than $\nu(\text{PtX})_t$, the reverse is true for the bridge vibrations. Several effects are occurring simultaneously;

(a) the closed-ring nature of the bridge framework requires that $\nu(\text{MX})_b$ involves movement of the four atoms M_2X_2 , (Fig. I-1). The large mass of M causes the vibration to occur at a lower frequency than the more isolated $\nu(\text{MX})_t$.

(b) The B_{3u} bridge stretching vibration, (ν_{17}), is represented in Fig. I-7a. The atoms carry out a simple harmonic motion, from the equilibrium position, in the directions indicated by the arrows. Inspection of Fig. I-7b, which represents ν_{17} at maximum amplitude, shows that the vibration involves deformation of the angles $\alpha_{1,2}$ as well as the predominant bridge-bond stretching. Comparison with ν_{18} , the deformation of terminal MX_2 bonds, (Fig. I-7c), confirms this. Both ν_{17} and ν_{18} are of B_{3u} symmetry and thus coupling could take place between the two modes causing a lowering of $\nu(\text{MX})_b$ from the region expected for M-X stretching vibrations. A similar analysis of ν_{14} , (Fig. I-7. d-f), indicates probable coupling of the

Fig. I-7.

Coupling between bridge stretching and
terminal bending modes for $[M_2X_6]^{2-}$.



bridge stretching vibration (B_{2u}) with the B_{2u} in-plane rock, ν_{15} . The $\rho(MX_2)$ occurs at a much lower frequency than $\delta(MX_2)$ and its coupling with $\nu(MX)_b$ would be smaller. Consequently, the higher bridge frequency is tentatively assigned to the B_{2u} mode.

(c) Effect (b) is stronger for the palladium anions. The large mass of the platinum atom relative to the halogen atoms reduces coupling of vibrations but the mass of the palladium atom is comparable to that of bromine and iodine and coupling becomes much more important. On mass considerations, $\nu(PdX)$ should occur at a higher frequency than $\nu(PtX)$. The higher Pt-X bond strength would reverse this order. For $\nu(MX)_t$, the balance of the forces is such that $\nu(PdX)_t > \nu(PtX)_t$. For bridge vibrations, the greater amount of coupling with the bending modes in $[Pd_2X_6]^{2-}$ causes $\nu(PtX)_b > \nu(PdX)_b$.

CHAPTER II

Substituted halogen-bridged complexes
of Pt(II) and Pd(II).

II-1. Introduction.

The complexes studied were of general formula $M_2X_4L_2$, ($M = Pt, Pd$; $X = Cl, Br, I$ and $L = PR_3, AsR_3, SR_2, SeR_2, TeR_2, C_2H_4, C_3H_6$ and p-toluidine). Planar halogen-bridged complexes of this type can theoretically exist in three isomeric forms, (Fig. II-1), viz., the unsymmetric form, (a), and the cis- and trans- symmetric forms, (b and c). No evidence for the unsymmetric form exists.

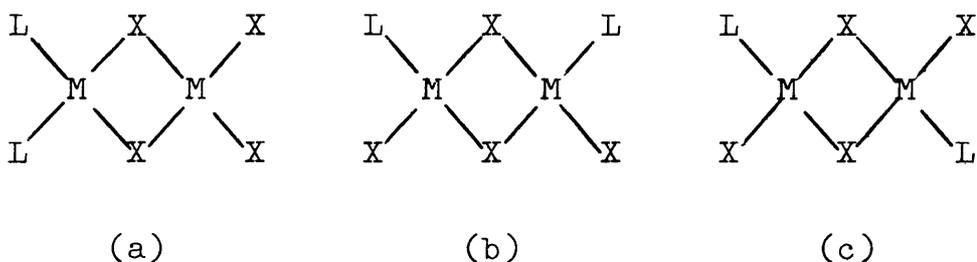


Fig. II-1. Isomeric forms of $M_2X_4L_2$.

Chatt and Mann⁵⁴, using chelating phosphines, arsines and sulphides failed to prepare a complex of this configuration and the chemical reactions of the bridged complexes may be explained assuming either the cis- or trans- structure⁵⁴. The predicted dipole moments⁵⁵, (in Debye units, D.), of the structures are; unsymmetric form = 12-14 D; cis- form = 7-8 D; and

trans- form = nil. Measurements made in benzene solution on bridged complexes ⁵⁵, ⁵⁶, indicate an equilibrium between the cis- and trans- isomers. For $\text{Pt}_2\text{Cl}_4 (\text{P Pr}_3^{\text{n}})_2$ ⁵⁵, the equilibrium mixture need contain only c.a. 2% cis- isomer to account for the observed dipole moment of 1.6 D.

X-ray investigations of $\text{Pd}_2 \text{Br}_4 (\text{AsMe}_3)_2$ ⁵⁷, $\text{Pd}_2\text{Cl}_4 (\text{C}_2\text{H}_4)_2$ ⁵⁸, $\text{Pd}_2 \text{Cl}_4 (\text{styrene})_2$ ⁵⁹, and $\text{Pt}_2\text{Cl}_4 (\text{P Pr}_3^{\text{n}})_2$ ⁶⁰ show that in the solid state, only the planar halogen-bridged trans- symmetrical structure is found. Similar studies of $[\text{Pt Cl (OMe) (dicyclopentadiene)}]_2$ ⁶¹ and $[\text{Au Br Et}_2]_2$ ⁶² also indicate a planar halogen-bridged system. In $\text{Pd}_2 \text{Br}_4 (\text{As Me}_3)_2$, the bridge and terminal Pd-Br bonds are of the same length, but in $\text{Pd}_2\text{Cl}_4 (\text{styrene})_2$, the terminal Pd-Cl bond length is 2.27 Å and the bridge Pd-Cl bond lengths 2.32 and 2.41 Å. The longer bridge bond is trans- to the coordinated double bond.

The thio-bridged system, $\text{M}_2 (\text{SEt})_2$, is sufficiently stable to allow isolation of both the cis- and trans- isomers of $[\text{Pt Cl}_2 (\text{SEt})_2 (\text{P Pr}_3^{\text{n}})_2]$ and, unlike chloro- bridged systems, it is not cleaved by reaction with p-toluidine or bipyridyl ⁶³. The stability of halogen-bridged systems increases as the halogen is

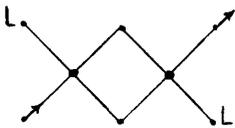
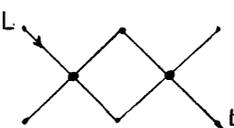
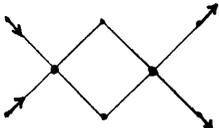
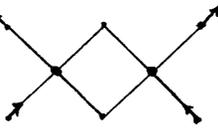
changed from Cl to Br to I. An amine will only split the iodo-bridge with difficulty and the resulting product, trans - $[MI_2.am.L.]$, tends to reform into the original bridge complex, $M_2I_4L_2$ ⁶⁴. By analogy with thio-bridged complexes, it may be possible for an iodo-bridged complex to exist as a cis- and trans- isomeric mixture in the solid state.

In this infrared spectral study the complexes were examined as solids. Assuming the trans- configuration (C_{2h}) and treating the ligands, (L), as point masses, $M_2X_4L_2$ has eighteen skeletal normal vibrations, (7 A_g + 2 B_{2g} + 3 A_u + 6 B_u). Nine are infrared-active only, (3 A_u + 6 B_u), and nine are Raman-active only, (7 A_g + 2 B_g). Direct comparison between the normal vibrations of $[M_2X_6]^{2-}$, (D_{2h}), and $M_2X_4L_2$, (C_{2h}), may be made. The change in symmetry species of the modes as the symmetry is lowered from D_{2h} to C_{2h} is shown in Table II-1. Schematic representations of the normal modes of $M_2X_4L_2$ are not given. They are essentially similar to those of the M_2X_6 system previously discussed, (Chapter I). For example, representations of the terminal metal-ligand and metal-halogen vibrations of $M_2X_4L_2$ are derived from those of M_2X_6 as in Fig. II-2. Approximate designations of the nine infrared fundamentals, predicted

Table II-1. Correlation table for $D_{2h} \rightarrow C_{2h}$ symmetry.⁵³

$M_2X_6 (D_{2h})$		$M_2X_4L_2 (C_{2h})$	
Activity	Symmetry Species	Symmetry Species	Activity
Raman	A_g	A_g	Raman
	B_{1g}	A_g	
	B_{2g}	B_g	
	B_{3g}	B_g	
Inactive	A_u	A_u	Infrared
Infrared	B_{1u}	A_u	
	B_{2u}	B_u	
	B_{3u}	B_u	

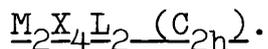
Fig. II-2. Relationship between the normal modes of $M_2X_4L_2$ and M_2X_6 .

 <p>(a): $\vee(MX)_t, B_u$</p>	 <p>(b): $\vee(ML)_t, B_u$</p>	$M_2X_4L_2$
 <p>(c): $\vee(MX_2)_t, B_{3u}$</p>	 <p>(d): $\vee(MX_2)_t, B_{2u}$</p>	M_2X_6
$a + b = c;$		$a - b = d.$

by theory, are given in Table II-2.

Frequency	Symmetry species	Approximate description of mode
ν_{10}, ν_{11}	2Bu	Bridge metal-halogen stretch, $\nu(\text{MX})_b$.
ν_{12}	Bu	Terminal metal-halogen stretch, $\nu(\text{MX})_t$.
ν_{13}	Bu	Metal-ligand stretch, $\nu(\text{ML})$.
ν_{14}	Au	Bridge out-of-plane bend, $\pi(\text{M}_2\text{X}_2)$.
ν_{15}	Bu	Terminal metal-halogen in-plane bend, $\delta(\text{MX})$.
ν_{16}	Bu	Metal-ligand in-plane bend, $\delta(\text{ML})$.
ν_{17}	Au	Terminal metal-halogen out-of-plane bend, $\pi(\text{MX})$.
ν_{18}	Au	Metal-ligand out-of-plane bend, $\pi(\text{ML})$.

Table II-2. Infrared-active normal vibrations of



Coupling may take place between metal-halogen and metal-ligand vibrations of the same symmetry species. If this occurs distinction between metal-halogen and metal-ligand vibrations will be meaningless and the bands observed will be considered as arising from vibrations of the whole molecule. The heavy mass

of the platinum atom, and to a lesser extent the palladium atom, should tend to localise the vibrations and reduce this coupling effect.

The metal-halogen modes are assigned by their halogen sensitivity and by comparison with the data obtained for $[M_2X_6]^{2-}$ systems, (Chapter I). Metal-ligand modes are assigned by comparison with free ligand spectra and other data from Chapter V. Finally, the assignment and discussion of internal ligand modes in the complexes and the free ligand are deferred until Chapter V.

II-2. Platinum (II) complexes.

The assignments of $Pt_2X_4L_2$ systems are shown in Tables II-3. to II-4. and the spectra sketched in Figs. II-3. to II-7. Definite assignments are made of $\nu(PtX)_t$ and $\nu(PtX)_b$ and in some cases of $\nu(PtL)$.

II-21. Chloro-complexes.

The chloro-complexes, $Pt_2Cl_4L_2$, have the greatest range of ligand, L, and are considered first, in detail. When $L = PEt_3$, PPr_3^n , $AsEt_3$, $AsPr_3^n$, or C_2H_4 , bromo- and iodo- analogues exist for all but the ethylene complex, (bromo- only), and assignment is straightforward. Assignments of metal-ligand modes

Fig. II-3.

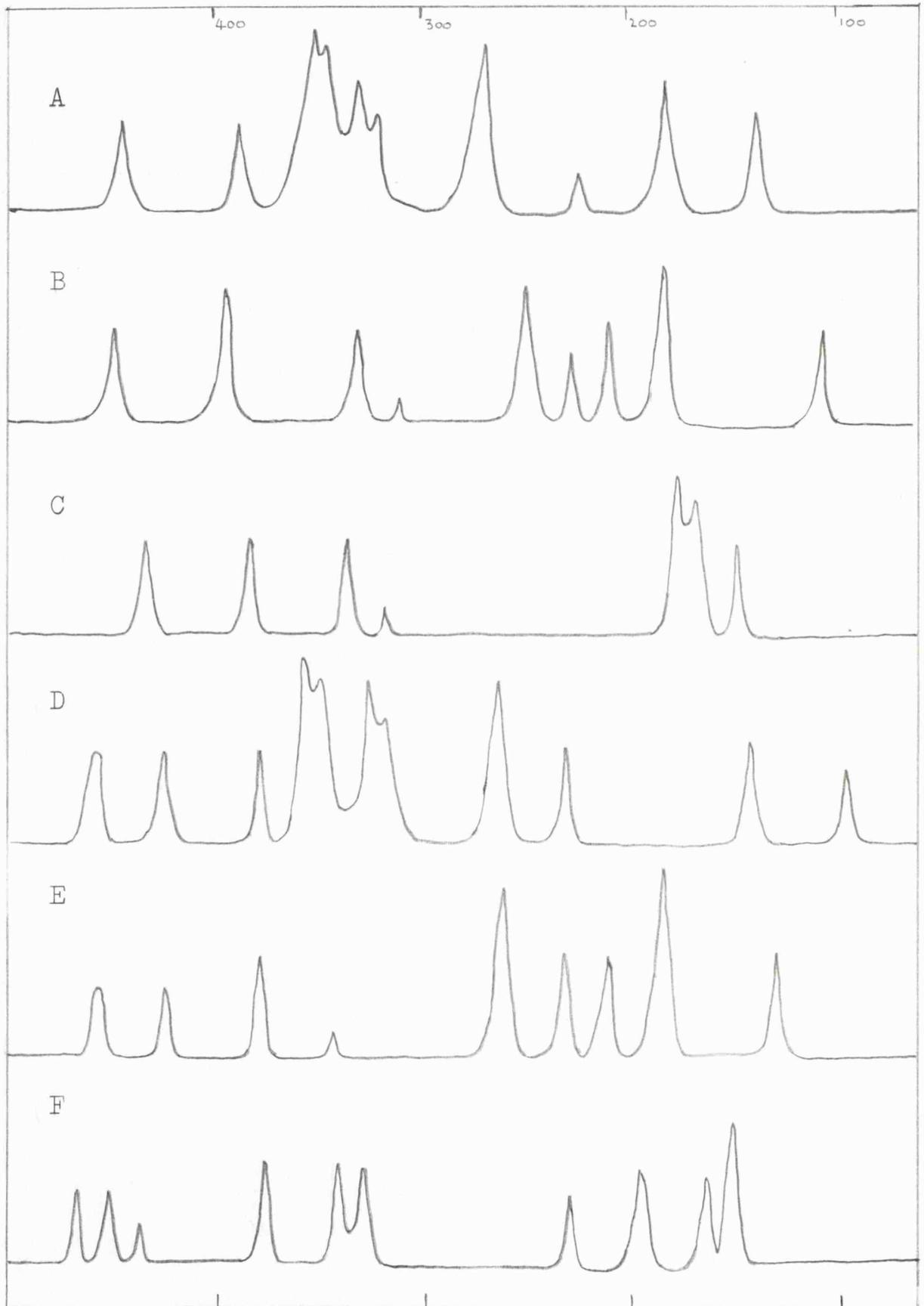


Fig. II-3. (facing page).

Spectra sketches of $Pt_2X_4L_2$.

- A. $Pt_2Cl_4 (PEt_3)_2$.
- B. $Pt_2Br_4 (PEt_3)_2$.
- C. $Pt_2I_4 (PEt_3)_2$.
- D. $Pt_2Cl_4 (P Pr_3^n)_2$.
- E. $Pt_2Br_4 (P Pr_3^n)_2$.
- F. $Pt_2I_4 (P Pr_3^n)_2$.

Fig. II-4.

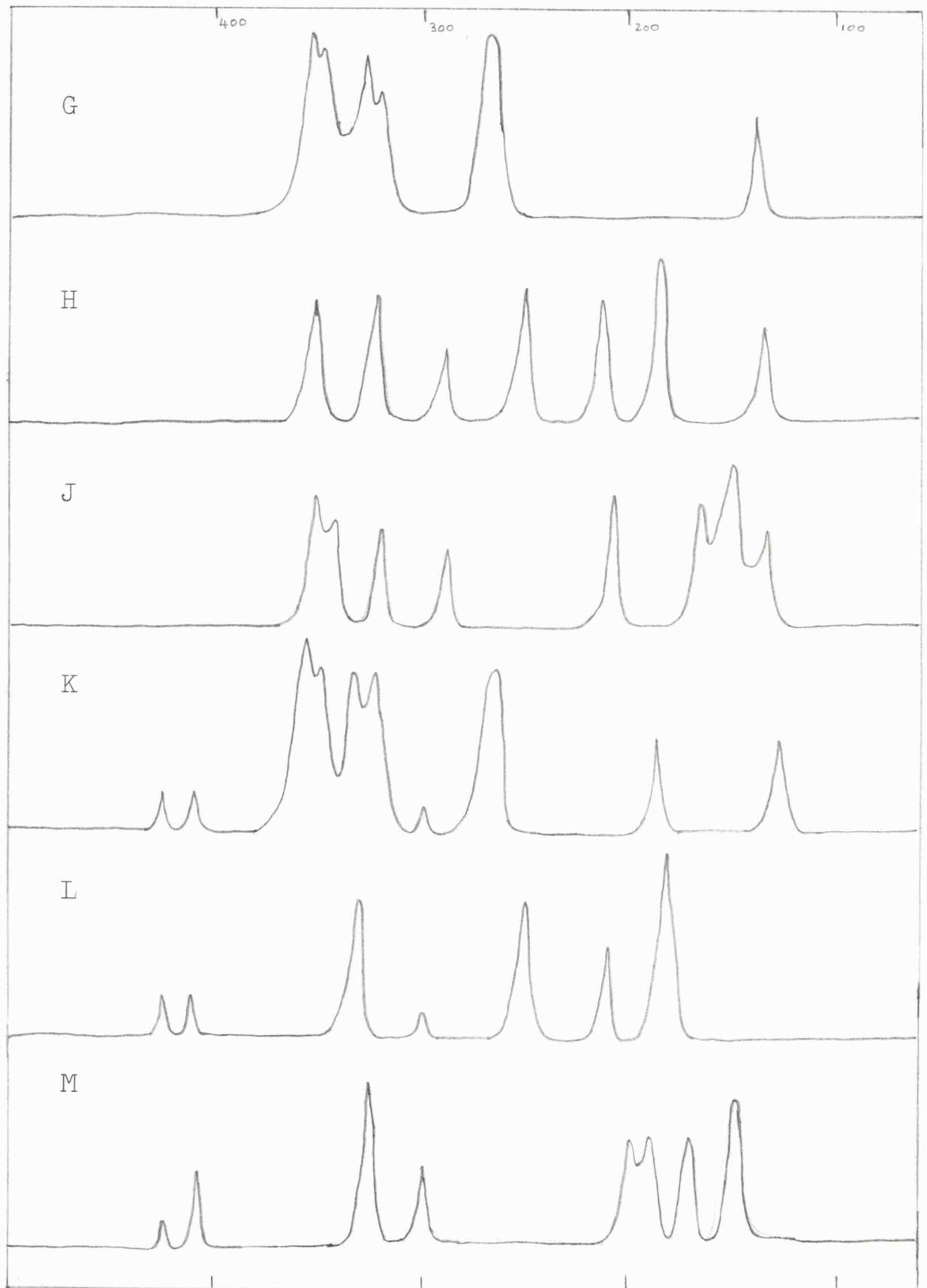


Fig. II-4. (facing page).

Spectra sketches of $Pt_2X_4L_2$.

- G. $Pt_2Cl_4 (AsEt_3)_2$.
- H. $Pt_2Br_4 (AsEt_3)_2$.
- J. $Pt_2I_4 (AsEt_3)_2$.
- K. $Pt_2Cl_4 (AsPr_3^n)_2$.
- L. $Pt_2Br_4 (AsPr_3^n)_2$.
- M. $Pt_2I_4 (AsPr_3^n)_2$.

Fig. II-5.

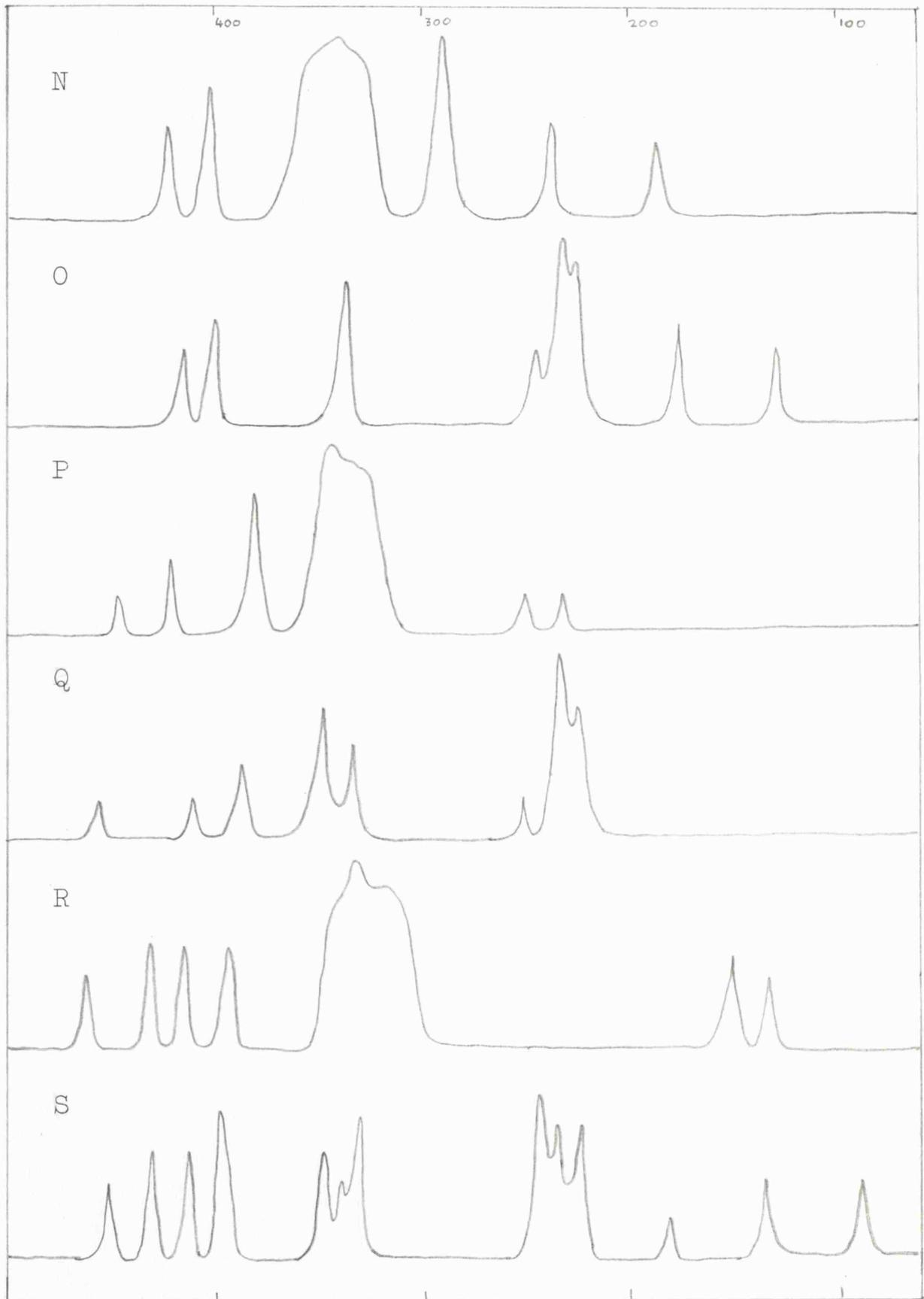


Fig. II-5. (facing page).

Spectra sketches of $\text{Pt}_2\text{X}_4\text{L}_2$.

- N. Pt_2Cl_4 $(\text{S Et}_2)_2$.
- O. Pt_2Br_4 $(\text{S Et}_2)_2$.
- P. Pt_2Cl_4 $(\text{S Pr}_2^{\text{n}})_2$.
- Q. Pt_2Br_4 $(\text{S Pr}_2^{\text{n}})_2$.
- R. Pt_2Cl_4 $(\text{S Bu}_2^{\text{n}})_2$.
- S. Pt_2Br_4 $(\text{S Bu}_2^{\text{n}})_2$.

Fig. II-6

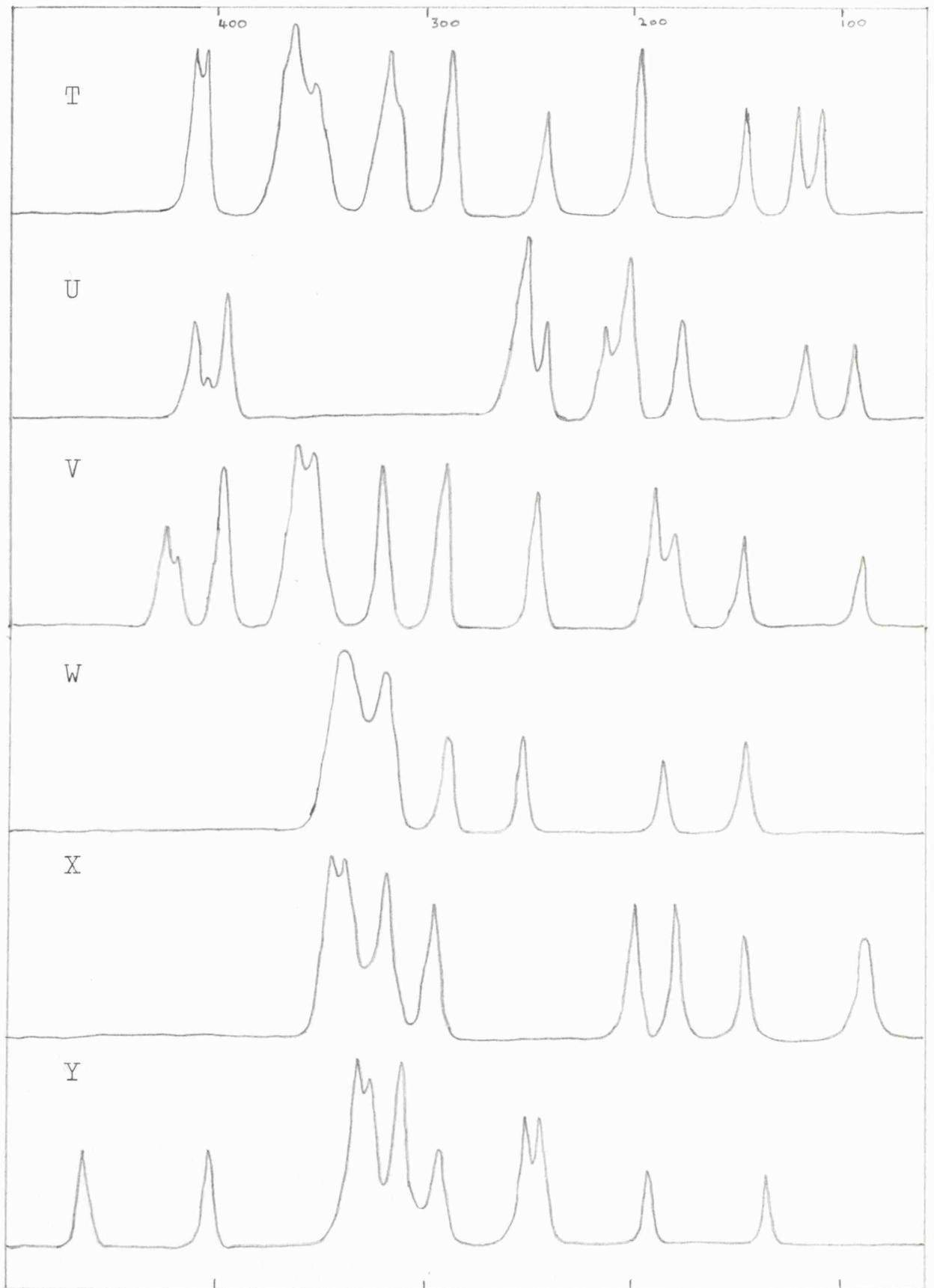


Fig. II-6. (facing page).

Spectra sketches of $\text{Pt}_2\text{X}_4\text{L}_2$.

- T. $\text{Pt}_2\text{Cl}_4 (\text{C}_2\text{H}_4)_2$.
- U. $\text{Pt}_2\text{Br}_4 (\text{C}_2\text{H}_4)_2$.
- V. $\text{Pt}_2\text{Cl}_4 (\text{C}_3\text{H}_6)_2$.
- W. $\text{Pt}_2\text{Cl}_4 (\text{Te Pr}_2^{\text{n}})_2$.
- X. $\text{Pt}_2\text{Cl}_4 (\text{Te Et}_2)_2$.
- Y. $\text{Pt}_2\text{Cl}_4 (\text{p-toluidine})_2$.

Fig. II-7.

Spectra sketches of $Pt_2X_4L_2$.

- Z. $Pt_2Cl_4 (PCl_3)_2$.
- AA. $Pt_2Cl_4 [P(OEt)_3]_2$.
- BB. $Pt_2I_4 (PPh_3)_2$.

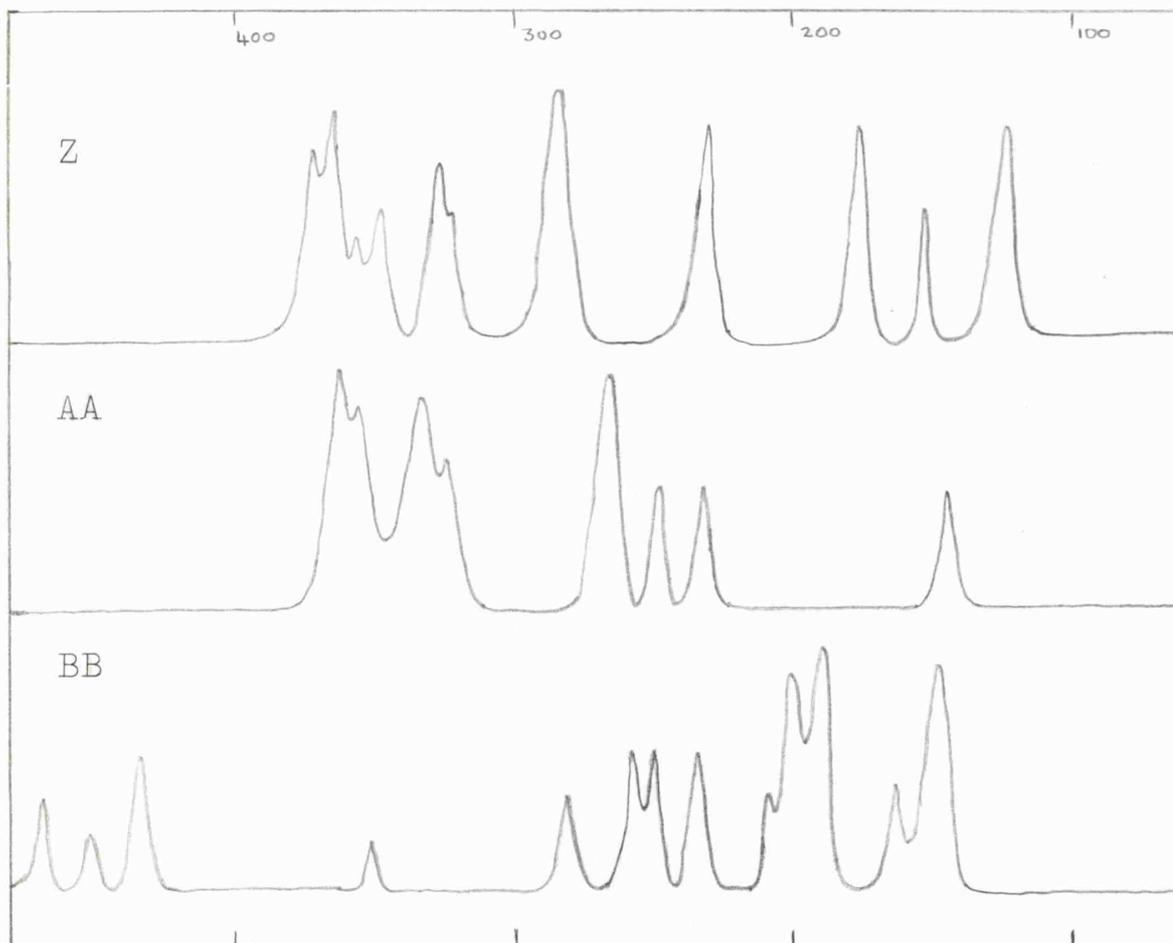


Table II-3 (contd.)

Frequencies and Assignments of complexes $\text{Pt}_2\text{Cl}_4\text{L}_2$.

	C_2H_4	C_3H_6	TeEt_2	TePr_3^n	$\text{P}(\text{OEt})_3$	PCl_3	P^- toluidine
$\nu(\text{PtL})$	411 (s) 406 (s)	424 (m) 420 (sh)			361*	346 (m)	249 (ms) 241 (ms)
$\nu(\text{PtCl})_t$	362 (vs) 354 (ms)	361 (vs) 354 (vs)	344 (vs) 337 (vs)	340 (vs, as)	361 (vs) 354 (sh)	365 (s)	330 (vs) 322 (s)
$\nu(\text{PtCl})_b$	318 (s) 311 (sh) 287 (s)	320 (s) 291 (s)	316 (s) 296 (ms)	319 (s) 290 (m)	325 (m) 264 (vs, b)	328 (ms) 319 (sh) 286 (vs, b)	312 (vs) 291 (m)
Other bands	369 (sh) 241 (m) 196 (s) 146 (m) 122 (m) 112 (m)	397 (s) 246 (ms) 189 (ms) 180 (m) 146 (m) 93 (wm)	197 (ms) 177 (ms) 144 (m) 88 (m, b)	254 (m) 185 (wm) 146 (m)	333 (s, b) 248 (m) 232 (m) 143 (m)	373 (ms) 355 (wm) 232 (s) 176 (s) 154 (m) 124 (s)	461 (m) 402 (m) 190 (wm) 137 (wm)

* Masked by $\nu(\text{PtCl})_t$

Table II-4.

Frequencies and Assignments of complexes $Pt_2X_4L_2$, (X = Br, I.).

	PEt_3	PPr_3^n	$AsEt_3$	$AsPr_3^n$	C_2H_4	SEt_2	SPr_2^n	SBu_2^n
$\nu(PtL)$	449 (m)	456 (wm, b)	320 (ms)	332 (ms)	409 (m) 404 (w) 398 (ms)	338 (ms)		
$\nu(PtBr)_t$	249 (ms)	260 (s)	249 (ms)	251 (ms)	253 (vs)	234 (vs)	235 (vs)	242 (s)
$\nu(PtBr)_b$	210 (m) 184 (s)	210 (m) 183 (vs)	209 (ms) 182 (s)	210 (m) 181 (vs)	213 (m) 207 (sh) 204 (s)	228 (s)	222 (ms)	224 (ms)
Other bands	394 (ms) 332 (m) 314 (vw) 226 (wm) 107 (m)	424 (wm) 377 (m) 342 (vw) 231 (m) 129 (m)	351 (ms) 288 (wm) 134 (m)	424 (w) 413 (w) 300 (vw)	243 (m) 177 (m) 117 (wm) 95 (wm)	417 (wm) 400 (m) 245 (wm) 178 (m) 129 (wm)	455 (w) 411 (w) 391 (wm) 347 (ms) 333 (m) 249 (w)	452 (wm) 428 (m) 414 (m) 397 (ms) 346 (m) 338 (wm) 334 (ms) 236 (ms) 183 (w) 137 (wm) 93 (wm)

Table II-4 (contd.).

Frequencies and Assignments of complexes $\text{Pt}_2\text{X}_4\text{L}_2$, (X = Br, I.).

	PEt_3	PPr_3^n	AsEt_3	AsPr_3^n	PPh_3	PPh_3 contd.
$\nu(\text{PtL})$	433 (m)	466 (wm) 453 (wm)	319 (m)	325 (s)	433 (m)	
$\nu(\text{PtI})_t$	177 (s)	198 (m)	205 (ms)	198 (m)	200 (s)	
$\nu(\text{PtI})_b$	167 (ms) 149 (m)	164 (m) 150 (ms)	164 (ms) 149 (s)	169 (m) 149 (ms)	164 (wm) 149 (s)	
Other bands	382 (m) 336 (m) 319 (vw)	437 (w) 375 (m) 341 (m) 328 (m) 231 (wm)	349 (ms) 340 (sh) 286 (wm) 134 (m)	424 (vw) 408 (wm) 300 (wm) 188 (m)	467 (wm) 450 (w) 350 (w) 280 (wm) 257 (m)	248 (m) 234 (m) 207 (wm) 193 (vs)

follow similar assignments made in Chapter V. Bromo- analogues of $\text{Pt}_2\text{Cl}_4\text{L}_2$, ($\text{L} = \text{PCl}_3$, $\text{P}(\text{OEt})_3$, C_3H_6 , TeEt_2 , TePr_2^{n} and p-toluidine), were not prepared and in these complexes assignment of $\nu(\text{PtCl})$ is more tentative. In this work no other complexes containing these ligands were studied and therefore the spectra are considered in detail here.

II-2.11 . Bis-(trichlorophosphine) dichloro- $\mu\mu'$ -dichlorodiplatinum; $\text{Pt}_2\text{Cl}_4(\text{PCl}_3)_2$.

Trichlorophosphine, PCl_3 , is pyramidal, (C_{3v}), and has four infrared-active fundamentals ($2 \text{A}_1 + 2\text{E}$), described in Table II-5.

Symmetry species	Description	Frequency cm^{-1} .
A_1	$\nu(\text{PCl}_3)_s$	507
A_1	$\delta(\text{PCl}_3)$	260
E	$\nu(\text{PCl}_3)_{as}$	494
E	$\delta(\text{PCl}_3)$	189

Table II-5. Infrared-active modes of PCl_3 ⁶⁵.

The system Pt-PCl₃, arising from coordination to platinum, is tetrahedral and has six infrared-active fundamentals, viz. $\nu(\text{PCl}_3)$ (A₁ + E);

$\delta(\text{PCl}_3)$ (A₁ + E); $\nu(\text{Pt-PCl}_3)$ (A₁); and $\rho(\text{PCl}_3)$ (E). Data for tetrahedral OPCl₃⁶⁶ and SPCl₃⁶⁷ indicate the position and expected shifts in frequency of these modes and were used as a basis for the tentative assignment of Pt₂Cl₄(PCl₃)₂,

Table II-6.

Symmetry species	Description of mode	OPCl ₃ ⁽⁶⁶⁾	SPCl ₃ ⁽⁶⁷⁾	Pt ₂ Cl ₄ (PCl ₃) ₂
A ₁	$\nu(\text{PCl}_3)$	486	435	373 (ms)
Bu	$\nu(\text{Pt-PCl}_3)$			346 (m)
A ₁	$\delta(\text{PCl}_3)$	267	250	232 (s)
E	$\nu(\text{PCl}_3)$	581	542	
E	$\delta(\text{PCl}_3)$	337	250	232 (s)
E	$\rho(\text{PCl}_3)$	193	167	154 (m)
Bu	$\nu(\text{Pt-Cl})_t$			365 (s)
Bu	$\nu(\text{Pt-Cl})_b$			328(ms) 319(sh)
				286 (vs,b)
Other bands				355 (wm)
				176 (s)
				124 (s)

Table II-6. Assignment of Pt₂Cl₄(PCl₃)₂.

From the seven bands lying between 373-286 cm.^{-1} , $\nu(\text{PtCl})_t$ and the higher $\nu(\text{PtCl})_b$ are assigned at 365 and 328 cm.^{-1} respectively. The basis of the assignment being the intensity and position of the bands. The very strong and broad band at 286 cm.^{-1} is characteristic and assigned to the lower $\nu(\text{PtCl})_b$. One of the remaining bands in this group must be $\nu(\text{PtP})$ and it is tentatively assigned at 346 cm.^{-1} . The highest band in the spectrum at 373 cm.^{-1} is assigned to $\nu(\text{PCl}_3)$. The unassigned bands at 176 and 124 cm.^{-1} are probably associated with platinum-halogen and platinum-phosphorus bending modes.

II-2.12. Bis-(triethylphosphite) dichloro- μ' -dichlorodiplatinum; $\text{Pt}_2\text{Cl}_4[\text{P}(\text{OEt})_3]_2$.

Bands at 333, 248 and 232 cm.^{-1} are assigned to internal modes of triethylphosphite. The corresponding bands in the Raman spectrum of free triethylphosphite are at 315 (4), 248 (1) and 213 (2) cm.^{-1} respectively, figures in parentheses indicating Raman intensity.⁶⁸ The assignments of $\nu(\text{PtCl})_t$ at 361 and $\nu(\text{PtCl})_b$ at 325 and 264 cm.^{-1} are fairly certain due to the simplicity of the spectrum. No band remains

in the spectrum which can be assigned to $\nu(\text{PtP})$, but the evidence from the spectrum of $\text{Pd}_2\text{Br}_4 [\text{P}(\text{OEt})_3]_2$ is that $\nu(\text{PdP})$ is at 354 cm.^{-1} . In $\text{Pt}_2\text{Cl}_4 [\text{P}(\text{OEt})_3]_2$, $\nu(\text{PtP})$ is probably masked by the very intense $\nu(\text{PtCl})_t$ at 361 cm.^{-1} . The remaining band at 143 cm.^{-1} is probably a platinum-phosphorus or -chlorine bend.

II-2.13. Bis- (propylene) dichloro- μ' - dichloro-
diplatinum; $\text{Pt}_2\text{Cl}_4(\text{C}_3\text{H}_6)_2$.

Two bands occur below 500 cm.^{-1} in the spectrum of propylene^{69, 70}. The C-C-C bend is at 428 cm.^{-1} and the C-CH₃ torsion at 177 cm.^{-1} . The corresponding bands in the spectrum of $\text{Pt}_2\text{Cl}_4(\text{C}_3\text{H}_6)_2$ are at 397 and 180 cm.^{-1} respectively. The remaining spectrum is very similar to $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$, $\nu(\text{PtCl})_t$ is at 361, 354, $\nu(\text{PtCl})_b$ at 320, 291 and $\nu(\text{Pt-C}_2\text{H}_4)$ at 424, 420 cm.^{-1} . The four bands observed below 250 cm.^{-1} are assigned to Pt-Cl bending modes and to vibrations of the PtC_2 skeleton. The latter arise as follows; a linear molecule, such as ethylene or propylene, has three translations and two rotations which involve no relative displacement of the atoms and are thus spectroscopically inactive. On coordination, the free rotations and translations become vibrations of the PtC_2 skeleton and

may become infrared- or Raman-active. These modes are discussed fully for ethylene in Chapter V.

II-2.14. Bis-(diethyltelluride) dichloro- $\mu\mu'$ -
dichloro-diplatinum; $\text{Pt}_2\text{Cl}_4(\text{TeEt}_2)_2$.

The infrared spectrum of diethyltelluride has no absorption bands between 500-250 cm.^{-1} ⁷¹. The bands observed in this region for $\text{Pt}_2\text{Cl}_4(\text{TeEt}_2)_2$, are attributed to $\nu(\text{PtCl})$ or $\nu(\text{PtTe})$. In compounds of the type ZnL , ($\text{L} = \text{S}, \text{Se}, \text{and Te}$), the lattice frequencies, $\nu(\text{ZnL})$, are found at 310, 215 and 190 cm.^{-1} respectively ⁷². In dialkylsulphide complexes of Pt(II), $\nu(\text{PtS})$ is found between 350-300 cm.^{-1} , (Chapter V), and by analogy, $\nu(\text{PtTe})$ is not expected to occur above 250 cm.^{-1} . Thus bands observed at 344, 337 and 316, 296 cm.^{-1} in the spectrum of the complex are assigned to $\nu(\text{PtCl})_t$ and $\nu(\text{PtCl})_b$ respectively. The remaining low frequency bands were observed at 197, 177, 144 and 88 cm.^{-1} . Pt-Cl bending modes, $\nu(\text{PtTe})$ and $\delta(\text{TeC}_2)$ should occur in this region but no unambiguous assignment can be made. Comparison with ZnTe ⁷² suggests that $\nu(\text{PtTe})$ may lie at 197 or 177 cm.^{-1} .

II-2.15. Bis-(di-n-propyltelluride) dichloro- μ' -
dichlorodiplatinum; $Pt_2Cl_4(TEPr_2^n)_2$.

No infrared spectral data on di-n-propyltelluride were available. Above 300 cm.^{-1} , the spectrum of $Pt_2Cl_4(TEPr_2^n)_2$ closely resembles the ethyl analogue and by comparison, $\nu(PtCl)_t$ is assigned at 340 cm.^{-1} and $\nu(PtCl)_b$ at 319 and 290 cm.^{-1} .

II-2.16. Bis-(dialkylsulphide) dichloro- μ' -
dichlorodiplatinum; $Pt_2Cl_4(SR_2)_2$.

The spectra of $Pt_2Cl_4(SR_2)_2$, (R = Et, Pr^n , and Bu^n), are difficult to interpret. The broad absorption patterns observed for all three complexes in the region $360\text{--}300\text{ cm.}^{-1}$ are attributed to the Bu modes, $\nu(PtS)$, $\nu(PtCl)_t$ and $\nu(PtCl)_b$, and to internal modes of the ligand. Thus $\nu(PtCl)$ and $\nu(PtS)$ are assigned to a range of frequency rather than a precise frequency in each complex. An exception is $Pt_2Cl_4(SET_2)_2$ which has a strong absorption at 291 cm.^{-1} , separate from the broad band, and assigned to the lower $\nu(PtCl)_b$. In $Pt_2Cl_4(SR_2)_2$, these ranges are $365\text{--}325\text{ cm.}^{-1}$ with maximum at 347 cm.^{-1} , $360\text{--}310\text{ cm.}^{-1}$ with maximum at 346 cm.^{-1} , and $360\text{--}300\text{ cm.}^{-1}$

with maximum at 344 cm.^{-1} , when $R = \text{Et}$, Pr^n , and Bu^n respectively. The position of these broad regions of absorption means that $\nu(\text{PtCl})_b$ have high frequencies ($>290 \text{ cm.}^{-1}$), comparable to $\nu(\text{PtCl})_b$ in $[\text{Pt}_2\text{Cl}_6]^{2-}$ and higher than found in the other complexes studied. It is possible to consider these modes as being coupled as $\nu(\text{PtCl})$ and $\nu(\text{PtS})$ are of B_u symmetry, and absorb in the same region. In the corresponding bromo-complexes, $\nu(\text{PtS})$ and $\nu(\text{PtBr})$ are separated by approx. 100 cm.^{-1} and are assigned to distinct frequencies.

II-2.17. Bis-(p-toluidine) dichloro- μ' -dichloro-diplatinum; $\text{Pt}_2\text{Cl}_4(\text{p-toluidine})_2$.

p-toluidine has not previously been studied in the far-infrared and interpretation of the complex spectrum is tentative. The medium intensity bands at 461 and 402 cm.^{-1} are too high to be associated with $\nu(\text{PtCl})$, but may be the X-sensitive γ -mode of the substituted benzenes, $\text{C}_6\text{H}_5\text{X}^{78}$. Only three other bands occur above 300 cm.^{-1} and are assigned to $\nu(\text{PtCl})$.

$\nu(\text{PtCl})_t$ is at 330 and 322 cm.^{-1} , the latter being the familiar isotope band. Both these bands are of very strong intensity and the strongest bands in the

spectrum. This feature is common to all the chloro-complexes. The higher $\nu(\text{PtCl})_b$ is at 312 cm.^{-1} but the lower $\nu(\text{PtCl})_b$ could be either at 291 or in the region of 250 cm.^{-1} . The former assignment is preferred as the latter would be very low and the bands are an, uncharacteristically, sharp doublet at 249 and 241 cm.^{-1} . These bands are tentatively assigned to $\nu(\text{PtN})$, in line with similar assignments of $\nu(\text{PtN})$ in pyridine complexes discussed in Chapters IV and V.

II-2.18. Summary of data on $\nu(\text{PtCl})$ in $\text{Pt}_2\text{Cl}_4\text{L}_2$ complexes.

Terminal platinum-chlorine stretching vibrations, $\nu(\text{PtCl})_t$, lie in the range $365\text{-}330 \text{ cm.}^{-1}$. The corresponding mode in $[\text{Pt}_2\text{Cl}_6]^{2-}$ is at 349 cm.^{-1} . The range of values is greater than was found for $\nu(\text{PtCl})$ in trans- $[\text{PtCl}_2\text{L}_2]^{33}$, indicating a greater ligand sensitivity. When $\text{L} = p\text{-toluidine}$, dialkylsulphide, and dialkyltelluride, $\nu(\text{PtCl})_t$ has its lowest values, ($350\text{-}330 \text{ cm.}^{-1}$). On changing L to trialkylphosphine and arsine, $\nu(\text{PtCl})_t$ rises to $357\text{-}350 \text{ cm.}^{-1}$ and for $\text{L} = \text{PCl}_3$, P(OEt)_3 and olefins, it lies between $365\text{-}361 \text{ cm.}^{-1}$. The latter values are

the highest recorded for Pt(II)-Cl stretching vibrations, (see Introduction). Nine of the chloro-complexes have a well resolved strong band on the low frequency side of $\nu(\text{PtCl})_t$, which is assigned to $\nu(\text{Pt}^{37}\text{Cl})_t$. The observed isotopic splitting, ($\Delta = 7-8 \text{ cm.}^{-1}$), is in agreement with calculations made using the increased mass of the isotopic chlorine atom and assuming the Pt-Cl bond force constant was unaltered, (Appendix).

As predicted by theory, two bridge stretching modes, $\nu(\text{PtCl})_b$, were observed for the complexes, falling in the ranges 320 ± 8 and $296-263 \text{ cm.}^{-1}$.

The higher frequency $\nu(\text{PtCl})_b$ is comparable to $\nu(\text{PtCl})_b$ in $[\text{Pt}_2\text{Cl}_6]^{2-}$ at 315 cm.^{-1} . However, the lower $\nu(\text{PtCl})_b$ shows a wide variation and is strongly dependent upon the nature of the ligand, L.

It is characteristic of both the terminal and bridge Pt-Cl bond vibrations in these complexes, that they are the strongest bands in each spectrum.

II-2.2. Bromo-complexes.

In the complexes, $\text{Pt}_2\text{Br}_4\text{L}_2$, $\nu(\text{PtBr})_t$ lies in the range $260-234 \text{ cm.}^{-1}$ and $\nu(\text{PtBr})_b$ in the ranges $213-209$ and $207-181 \text{ cm.}^{-1}$, with the exception

of the sulphide complexes for which $\nu(\text{PtBr})$ are between 230-220 cm^{-1} . These values compare with those found for $[\text{Pt}_2\text{Br}_6]^{2-}$ at 243, 237, 211 and 196 cm^{-1} and with the general frequency range associated with $\nu(\text{PtBr})$, (Introduction). For the bridge complexes $\nu(\text{PtBr})$ generally follows the same trends observed for $\nu(\text{PtCl})$ but minor differences do exist. For $\text{Pt}_2\text{Br}_4\text{L}_2$, ($\text{L} = \text{PR}_3, \text{AsR}_3$), $\nu(\text{PtBr})_t$ lies in the narrow range 251-249 cm^{-1} except for $\text{L} = \text{PPr}_3^n$ when it has the value 260 cm^{-1} . The cause of this high frequency is unlikely to be interaction as no other band in the spectrum shows an unexpected shift. Furthermore, the chloro- and iodo- analogues do not behave similarly. In a study of a series of compounds, trans- $[\text{PtBr}_2\text{L}_2]^{33}$, the highest $\nu(\text{PtBr})$ at 259 cm^{-1} was observed when $\text{L} = \text{PPr}_3^n$.

For $\text{Pt}_2\text{Br}_4(\text{SR}_2)_2$, ($\text{R} = \text{Et}, \text{Pr}^n, \text{and Bu}^n$), only one bridge mode was observed in the range 228-222 cm^{-1} . This is very close to $\nu(\text{PtBr})_t$ at 242-234 cm^{-1} and considerably higher than the

$\nu(\text{PtBr})_b$ observed for other complexes. No halogen-sensitive bands were observed in the spectra between 220-180 cm^{-1} and therefore the lower bridge modes

are not assigned. $\text{Pt}_2\text{Br}_4(\text{SBU}_2^n)_2$ has three medium-strong bands at 242, 236 and 222 cm^{-1} , which can be assigned to $\nu(\text{PtBr})_t$ and $\nu(\text{PtBr})_b$ respectively.

However the corresponding chloro-complex has a weak band at 236 cm^{-1} and definite assignment is only made for the highest and the lowest bands.

This small difference between the frequencies of

$\nu(\text{PtBr})_t$ and $\nu(\text{PtBr})_b$ was also found for the corresponding modes in $\text{Pt}_2\text{Cl}_4(\text{SR}_2)_2$.

II-2.3. Iodo-complexes.

Only five phosphine and arsine iodo-complexes were examined. The values found for $\nu(\text{PtI})_t$ are consistent at $201 \pm 4 \text{ cm}^{-1}$ and compare with $\nu(\text{PtI})_t$ in $[\text{Pt}_2\text{I}_6]^{2-}$ at 194 and 179 cm^{-1} . The complex, $\text{Pt}_2\text{I}_4(\text{PEt}_3)_2$, is an exception. No band was observed in the spectrum of this complex between 300-180 cm^{-1} and $\nu(\text{PtI})_t$ is tentatively assigned to the highest halogen-sensitive mode at 177 cm^{-1} . This assignment is inconsistent with the close relationship observed between the frequencies of the $\nu(\text{PtI})$ in all the arsine and phosphine complexes studied. No structural deviation in the complex is apparent from the values assigned to the internal ligand modes although $\nu(\text{PtP})$,

at 433 cm.^{-1} , is approximately 15 cm.^{-1} lower than is expected from correlation with the chloro- and bromo- analogues.

The bridge modes, $\nu(\text{PtI})_b$, show little ligand sensitivity and occur in the ranges 169-164 and $150\text{-}149 \text{ cm.}^{-1}$. In contrast to the chloro- and bromo- analogues, $\nu(\text{PtI})_b$ is higher in the substituted complexes than in $[\text{Pt}_2\text{I}_6]^{2-}$, (157 and 144 cm.^{-1}). It is known^{64,73}, (Section II-1), that the iodo-bridge is much stronger than the chloro- and bromo- bridges in $\text{Pt}_2\text{X}_4(\text{PPr}_3^n)_2$, ($\text{X} = \text{Cl}, \text{Br}$ and I), but this does not explain why $\nu(\text{PtI})_b$ is higher when $\text{L} = \text{PPr}_3^n$ than when $\text{L} = \text{I}$. A more detailed discussion is developed in the next section.

II-2.4. Effect of ligand, L, upon $\nu(\text{PtX})$, (X = Cl, Br, and I).

Where comparable complexes were studied, similar trends are found for both chloro- and bromo-complexes. Conclusions drawn from discussion of the chloro-complexes can, therefore, be extended to the bromo-complexes. Dissimilarities between the two series are discussed. The restricted range of ligands in the iodo-complexes precludes discussion of general

trends, For this discussion, the $[\text{Pt}_2\text{X}_6]^{2-}$ complexes are included and considered as substituted complexes $\text{Pt}_2\text{X}_4\text{L}_2$, (L = Cl, Br and I).

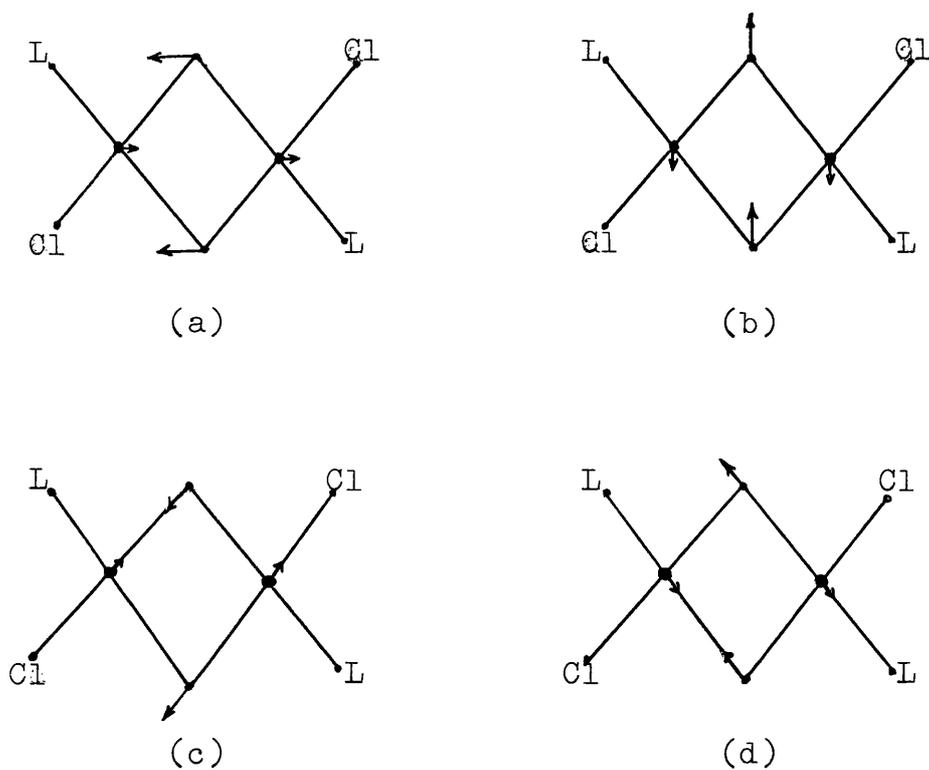
II-2.41. Bridge stretching vibrations, $\nu(\text{PtX})_b$.

The observed values of $\nu(\text{PtCl})_b$ show that the higher $\nu(\text{PtCl})_b$ is relatively ligand insensitive, having the values $320 \pm 8 \text{ cm.}^{-1}$. The lower $\nu(\text{PtCl})_b$, however, shows a marked ligand sensitivity and occurs in the range 296 to 262 cm.^{-1} . The bridge modes are depicted schematically in Fig. II-8, (a and b). In these figures, neither mode predominantly involves compression or extension along the bridge Pt-Cl bonds trans- to terminal Pt-Cl or Pt-L bonds. If the arrows, representing the direction of motion of the atoms, are rotated through 45° in an anti-clockwise direction then two further representations of the bridge modes are obtained, Fig. II-8, (c and d). Modes c and d involve mainly compression and extension along the bridge bonds trans- to the terminal Pt-Cl and Pt-L bonds respectively. The actual vibrations are considered to be linear combinations (a + c) and (b + d). The empirically observed frequencies of the two $\nu(\text{PtCl})_b$ are explained assuming modes c and d

predominate in their respective combinations. The former is relatively ligand insensitive and related to the higher bridge mode and the latter is ligand sensitive and related to the lower bridge mode.

Fig. II-8.

Schematic representations of $\nu(\text{PtCl})_b$.



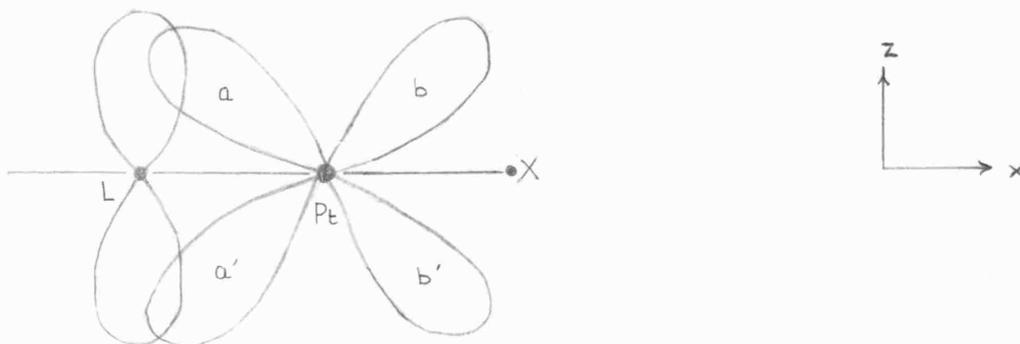
The ligands, L, in order of decreasing frequency of the lower $\nu(\text{PtCl})_b$, Table II-3, are;

Cl \rangle SR₂ \sim TeEt₂ \rangle TePr₂ⁿ \sim p-toluidine \sim C₃H₆ \rangle
 C₂H₄ \rangle PCl₃ \gg PEt₃ \rangle P(OEt)₃ \rangle AsEt₃ \sim PPr₃ⁿ
 \sim AsPr₃ⁿ. The sulphide complexes are anomalous, in that the lower bridge mode has not been definitely assigned but evidence suggests that it would occupy a high position in the above sequence. From this order, several conclusions are drawn. The higher the electronegativity of the donor atom of the ligand, L, then the higher the frequency of $\nu(\text{PtCl})_b$. Thus withdrawal of electron density from the platinum atom increases the strength of the trans- Pt-Cl bridge bond. This is true for donor atoms S, Cl, Te and N. Phosphines and arsines are exceptions in that they are electronegative and have low frequency $\nu(\text{PtCl})_b$. Phosphorus and arsenic are strong donors to platinum and inductive electron release in the σ -coordinate bond causes an increase in the electron density on the platinum atom. For phosphines and arsines this trans- effect predominates over the electronegative effect of the donor atoms and the trans-Pt-Cl bond is weakened and a low frequency for $\nu(\text{PtCl})_b$ is observed. In contrast,

olefin complexes have high frequency ν (PtCl)_b and olefins also have a high trans- effect. However, the mechanism of the trans- effect, in this case, is mesomeric rather than inductive. Olefins are strongly π -bonded and their high trans- effect is due to electron withdrawal from platinum via π -coordinate bonds. This mesomeric effect will cause a trans-bond strengthening due to the reduction of electron density on the platinum atom when Cl is the trans-bonded atom, as it is only weakly π -bonded to

Figure II-9.

Pt \rightarrow L $d\pi$ - $p\pi$ bonding.



platinum. Thus $\nu(\text{PtCl})_b$ in olefin complexes is at a high frequency. The trans- bond would be weakened if the trans- ligand formed sufficiently strong π - bonds with platinum, e.g. another olefin ⁷⁴. Fig. II-9 shows ligand, L, bound to platinum by $p\pi - d\pi$, π - bonding. The d_{xz} orbital stretches right across the platinum atom and so electron withdrawal into regions of π - bond aa' will reduce electron density in bb' in trans- positions to aa' . If ligand X in trans- position to L has an unfilled π -type orbital capable of π - bonding with bb' it enters into direct competition with L for d electrons. The strength of π - bonding at X is considerably reduced from what it would be if L were a ligand with little or no double bonding properties. Thus strong double bonding of platinum to L leads to weak double bonding to X in trans- position. When L is olefin and X the bridge Cl atom then as π - bonding in the Pt-Cl bond is very weak ^{79, 80}, Pt-Cl bond strength and the $\nu(\text{PtCl})_b$ frequency are not lowered a significant amount. The strong σ - donation of phosphorus to platinum is reduced in $\text{Pt}_2\text{Cl}_4(\text{PCl}_3)_2$ due to the electronegative Cl atoms on the PCl_3 ligand, This reduction in electron

density on the platinum atom and strengthening of the trans- Pt-Cl bridge bond results in a $\nu(\text{PtCl})_b$ at 286 cm.^{-1} , comparable to that found in $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$.

In $\text{Pt}_2\text{Br}_4\text{L}_2$ the same general order of ligands is found. In contrast to the corresponding chloro-complexes, $\nu(\text{PtBr})_b$ is higher when $\text{L} = \text{C}_2\text{H}_4$ than when $\text{L} = \text{Br}$. Bromine is less electronegative than chlorine and will weaken the trans- Pt-Br bridge bond in $[\text{Pt}_2\text{Br}_6]^{2-}$ relative to the same bond in the ethylene complex. The high value of $\nu(\text{PtBr})_b$ in $\text{Pt}_2\text{Br}_4(\text{C}_2\text{H}_4)_2$, (204 cm.^{-1}), suggests that there is little or no Pt-Br π -bonding in the bromo-complexes.

In the iodo-complexes, $[\text{Pt}_2\text{I}_6]^{2-}$ has the lowest frequency recorded for $\nu(\text{PtI})_b$. This is in contrast to the chloro-complexes, in which the highest $\nu(\text{PtCl})_b$ is found in $[\text{Pt}_2\text{Cl}_6]^{2-}$. The two possible reasons for this are; firstly the lower electronegativity of iodine compared with chlorine and secondly Pt-I π -bonding being significant and resulting in a weaker bridge bond in $[\text{Pt}_2\text{I}_6]^{2-}$ than in $\text{Pt}_2\text{I}_4\text{L}_2$, ($\text{L} = \text{AsR}_3, \text{PR}_3$).

Summarising, the main factors affecting $\nu(\text{PtX})_b$, ($\text{X} = \text{Cl}, \text{Br}$), are the electronegativity of L, with

the trans- effect, except when it is inductive and high, playing a minor role. With the exception of the tellurides, a similar order of ligands was found for $\nu(\text{PtX})$ in cis- $[\text{PtX}_2\text{L}_2]$, (X = Cl, Br)³³. Only in the iodo-complexes does π -bonding between platinum and the halogen, (X), become important enough to influence bond strengths and the frequencies of the Pt-X bond vibrations.

II-2.42. Terminal stretching vibrations, $\nu(\text{PtX})_t$.

As the ligand, L, is changed in $\text{Pt}_2\text{Cl}_4\text{L}_2$, $\nu(\text{PtCl})_t$ shows a gradual shift from 365 to 332 cm.^{-1} . From the highest to lowest $\nu(\text{PtCl})_t$, the ligands, L, fall in the order; PCl_3 , C_2H_4 , $\text{C}_3\text{H}_6 \sim \text{P(OEt)}_3$, $\text{PPr}_3^n \sim \text{AsPr}_3^n$, PEt_3 , AsEt_3 , Cl, $\text{SR}_2 \sim \text{TeEt}_2$, TePr_2^n , p-toluidine. Where comparable, $\nu(\text{PtBr})_t$ fall in the same order and discussion is confined to $\nu(\text{PtCl})_t$.

Although the Pt-Cl terminal bond is cis- to the Pt-L bond, $\nu(\text{PtCl})_t$ show a significant ligand dependence, unlike the higher bridge Pt-Cl mode ($320 \pm 8 \text{ cm.}^{-1}$) or $\nu(\text{PtCl})$ in trans- $[\text{PtCl}_2\text{L}_2]$, ($337 \pm 6 \text{ cm.}^{-1}$)³³. Strong π -bonding ligands, such as olefins and PCl_3 , have the highest and electronegative ligands, such as SR_2 and p-toluidine, the lowest

$\nu(\text{PtCl})_t$. Ligand influence on the terminal Pt-Cl bond occurs in more than one way. Pt-L π -bonding will not affect the π -bonding strength of the cis-Pt-Cl bond but the accompanying withdrawal of electron density from the platinum atom will strengthen the cis-Pt-Cl σ -bond. In addition, electron withdrawal or release in the L \rightarrow Pt σ -bond will strengthen or weaken, respectively the cis-Pt-Cl σ -bond. The former, but not the latter, effect does show some correlation with the observed order of ligands. However it is difficult to accept the explanation, as the magnitude expected for this secondary electrostatic effect is small and unlikely to be decisive. Further, there is no correlation between $\nu(\text{PtCl})_t$ and either of the $\nu(\text{PtCl})_b$ which would indicate coupling between the terminal and bridge modes.

A more extensive study, covering a wider range of ligands, is required to establish the factors which influence $\nu(\text{PtCl})_t$ in the bridge complexes, $\text{Pt}_2\text{Cl}_4\text{L}_2$.

II-2.5. Platinum-ligand stretching vibrations, $\nu(\text{PtL})$.

$\nu(\text{PtL})$ for the complexes $\text{Pt}_2\text{X}_4\text{L}_2$, when L = phosphines, arsines and olefins, are assigned definitely. The complexity of the sulphide spectra allows assignment

of $\nu(\text{PtS})$ only in $\text{Pt}_2\text{Br}_4(\text{SEt}_2)_2$. The spectra of the ligands and bromo-analogues of $\text{Pt}_2\text{Cl}_4\text{L}_2$, (L = dialkyltelluride and p-toluidine), were not obtained and assignment of $\nu(\text{PtL})$ in these complexes is uncertain.

As predicted by theory for $\text{Pt}_2\text{X}_4\text{L}_2$ (C_{2h}), only one

$\nu(\text{PtL})$ was observed for the complexes where definite assignments are made. The exception is $\text{Pt}_2\text{I}_4(\text{PPr}_3^n)_2$; a doublet was observed at 466, 453 cm^{-1} and is assigned to $\nu(\text{PtP})$. Splitting of the ligand bands in this spectrum was also observed. This is probably due to lattice effects or to deviations from idealised C_{2h} symmetry.

The method of assignment and general discussion of $\nu(\text{PtL})$ is in Chapter V. The interesting series of phosphorus donor atom ligands show a wide variation of

$\nu(\text{PtP})$ and Pt-P bond strengths and for this reason are discussed in this section.

II-2.51. Platinum- phosphorus stretching vibrations,
 $\nu(\text{PtP})$.

In $\text{Pt}_2\text{X}_4(\text{PEt}_3)_2$, $\nu(\text{PtP})$ is at 445, 449 and 433 cm^{-1} for X = Cl, Br and I respectively. The corresponding mode for trans- $[\text{PtX}_2(\text{PEt}_3)_2]$, (Chapter V), is between 420-400 cm^{-1} . Thus assuming the Pt-P

σ -bond strength is unaltered in both the monomeric and bridged complexes, the higher $\nu(\text{PtP})$ is associated with the greater Pt-P π -bonding found in the bridged complexes by N.M.R. studies⁷⁵. Two bands are observed in the platinum-phosphorus stretching region in the spectra of tri-n-propylphosphine complexes. Comparison with trans- $[\text{PtX}_2(\text{PPr}_3^n)_2]$ ³³ shows that the lower band is unshifted but the upper band is shifted to a higher frequency, ($\Delta = 10\text{-}20 \text{ cm.}^{-1}$), in the bridged complexes. Thus the latter at 459 (Cl), 456 (Br), and 466, 453 cm.^{-1} (I) are assigned to $\nu(\text{PtP})$ by analogy with the triethylphosphine complexes.

In $\text{Pt}_2\text{Cl}_4\text{L}_2$, (L = PCl_3 , P(OEt)_3), the electronegative chloro- and ethoxy- groups attached to phosphorus reduce the σ -donor but increase the π -acceptor ability of phosphorus. The former is Pt-P bond weakening and the latter bond strengthening. The overall Pt-P bond strength and position of $\nu(\text{PtP})$ are decided by the balance of the two effects. Considerable Pt-P bond weakening appears to take place when L changes from PEt_3 to PCl_3 and P(OEt)_3 . $\nu(\text{PtP})$ is assigned at 445, 346 and $\sim 360 \text{ cm.}^{-1}$ respectively, showing a drop of 100 and 85 cm.^{-1} .

Greenwood et. al.^{76, 77} have assigned both $\nu(\text{Ga-PPh}_3)$ and $\nu(\text{Ga-PR}_3)$, (R = Me and Et), in a similar region of the spectrum, (370-325 cm.^{-1}). By analogy $\nu(\text{Pt-PPh}_3)$ in $\text{Pt}_2\text{I}_4(\text{PPh}_3)_2$, will lie above 400 cm.^{-1} . By comparison with data from other triphenylphosphine complexes, (Chapter V), $\nu(\text{PtP})$ is assigned at 433 cm.^{-1} and the band at 467 cm.^{-1} to the \underline{t} - mode⁷⁸ of the substituted benzene ring.

Variation of the total mass of PX_3 , (X = Cl, Et, Pr^n , Ph and OEt), has no corresponding effect on $\nu(\text{PtP})$. However the nature of X and its effect on Pt-P bond strength causes large shifts of $\nu(\text{PtP})$ over the range 470-340 cm.^{-1} .

II-2.6. Terminal bending vibrations.

Theory shows that the system $\text{Pt}_2\text{X}_4\text{L}_2$ (C_{2h}) has four terminal bending vibrations approximately described as $\sigma(\text{PtX})$, $\delta(\text{PtL})$, $\pi(\text{PtX})$ and $\pi(\text{PtL})$. Thus in a system with little coupling between the ligand, L, and halogen, X, modes, four low frequency bands are predicted. However in contrast to the stretching modes, no definite assignments are made of platinum-ligand or platinum-halogen bending vibrations. The halogen sensitive bands in the spectra below

200 cm.^{-1} show little correlation with assignments made in $[\text{Pt}_2\text{X}_6]^{2-}$ systems. In closely related complexes, such as $\text{Pt}_2\text{Cl}_4\text{L}_2$, ($\text{L} = \text{PEt}_3, \text{PPr}_3^{\text{n}}$), the spectra below 200 cm.^{-1} are so dissimilar that consistent interpretation of the low frequency bands is not possible. The spectra of the complexes $\text{Pt}_2\text{X}_4\text{L}_2$, ($\text{L} = \text{PEt}_3, \text{PPr}_3^{\text{n}}$, and AsEt_3), illustrate these difficulties.

II-2.61. $\text{Pt}_2\text{X}_4(\text{PEt}_3)_2$; ($\text{X} = \text{Cl}, \text{Br}$ and I).

By comparison with $[\text{Pt}_2\text{X}_6]^{2-}$, ($\text{X} = \text{Cl}, \text{Br}$), the halogen sensitive bands at 189 and 139 cm.^{-1} in the chloro-complex and at 107 cm.^{-1} in the bromo-complex may be assigned to $\delta(\text{PtCl})$, $\pi(\text{PtCl})$ and $\delta(\text{PtBr})$ respectively. As in $[\text{Pt}_2\text{I}_6]^{2-}$, no platinum-iodine bending modes were observed and are expected to lie below 70 cm.^{-1} . The absence of further bands below 200 cm.^{-1} precludes assignment of platinum-ligand bending modes.

II-2.62. $\text{Pt}_2\text{X}_4(\text{PPr}_3^{\text{n}})_2$, ($\text{X} = \text{Cl}, \text{Br}$ and I).

For these complexes, the low frequency bands are at 142 and 95 cm.^{-1} , ($\text{X} = \text{Cl}$), and at 129 cm.^{-1} , ($\text{X} = \text{Br}$). These bands show no correlation with assignments made of $[\text{Pt}_2\text{X}_6]^{2-}$ or $\text{Pt}_2\text{X}_4(\text{PEt}_3)_2$,

(Section II-2.61). Thus, although halogen sensitive, the bands do not occur in the region of the spectrum associated with platinum-halogen bending vibrations. A possible explanation is that coupling with Pt-P bending modes is taking place and that $\nu(\text{PtPcl})$ is at 142 cm.^{-1} and $\nu(\text{PtPBr})$ at 129 cm.^{-1} . However the evidence in $[\text{Pt}(\text{PEt}_3)_4]^{2+}$, (Chapter V), is that Pt-P bending modes occur in the range $200\text{-}180 \text{ cm.}^{-1}$ and thus $\nu(\text{PtPcl})$ at 142 cm.^{-1} is $50\text{-}40 \text{ cm.}^{-1}$ lower than would be expected.

II-2.63. $\text{Pt}_2\text{X}_4(\text{AsEt}_3)_2$, (X = Cl, Br and I).

In each complex, (X = Cl, Br and I), assignment of the single halogen insensitive band at $137 \pm 3 \text{ cm.}^{-1}$ to $\nu(\text{PtAs})$ compares with assignments made for other triethylarsine complexes, (Chapter V). No other bands below 200 cm.^{-1} are observed and thus Pt-X bending vibrations are absent from these spectra.

The conflicting evidence and lack of consistency in the data means that no definite assignments of platinum-ligand or platinum-halogen bending modes are made. Thus the limitations of an empirical analysis are evident and further work on a complete vibrational analysis of these systems with force

constant calculations is required, This knowledge could then be used to explain the results obtained from these spectra below 200 cm.^{-1} .

II-3. Palladium (II) complexes.

The spectra of the complexes $\text{Pd}_2\text{X}_4\text{L}_2$ are sketched in Figs. II-10 to II-13 and assignments made are in Tables II-7 and II-8. Definite assignments of $\nu(\text{PdX})_t$, $\nu(\text{PdX})_b$ and in some cases of $\nu(\text{PdL})$ are made. The spectra are discussed in the same manner as the platinum complexes and a comparison between $\nu(\text{PdX})$ and $\nu(\text{PtX})$ is made.

II-3.1. Chloro-complexes.

The complexes, $\text{Pd}_2\text{Cl}_4\text{L}_2$, ($\text{L} = \text{PEt}_3$, PPr_3^n , AsEt_3 , AsPr_3^n , PPh_3 and P(OEt)_3), are assigned by comparison with the corresponding bromo- and in some cases the iodo- complexes. When $\text{L} = \text{SeEt}_2$, SePr_2^n , SEt_2 and SPr_2^n , only chloro-complexes were examined and assignments of these complexes are discussed fully. The ligand spectra of the selenide complexes are also discussed as the complexes are unique in this work.

Fig. II-10.

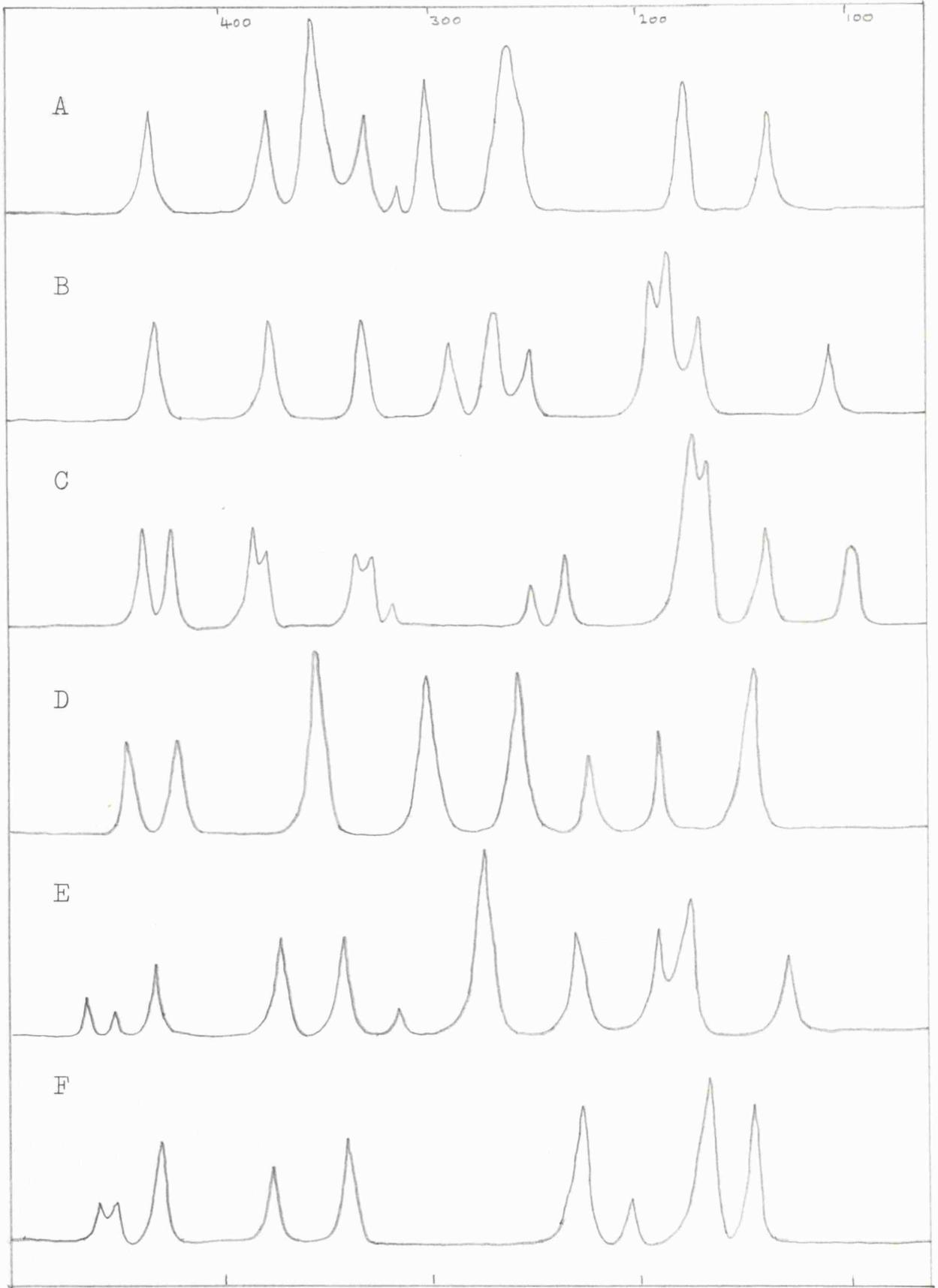


Fig. II-10 (facing page).

Spectra sketches of Pd₂X₄L₂.

- A. Pd₂Cl₄ (PEt₃)₂.
- B. Pd₂Br₄ (PEt₃)₂.
- C. Pd₂I₄ (PEt₃)₂.
- D. Pd₂Cl₄ (PPr₃ⁿ)₂.
- E. Pd₂Br₄ (PPr₃ⁿ)₂.
- F. Pd₂I₄ (PPr₃ⁿ)₂.

Fig. II-11.

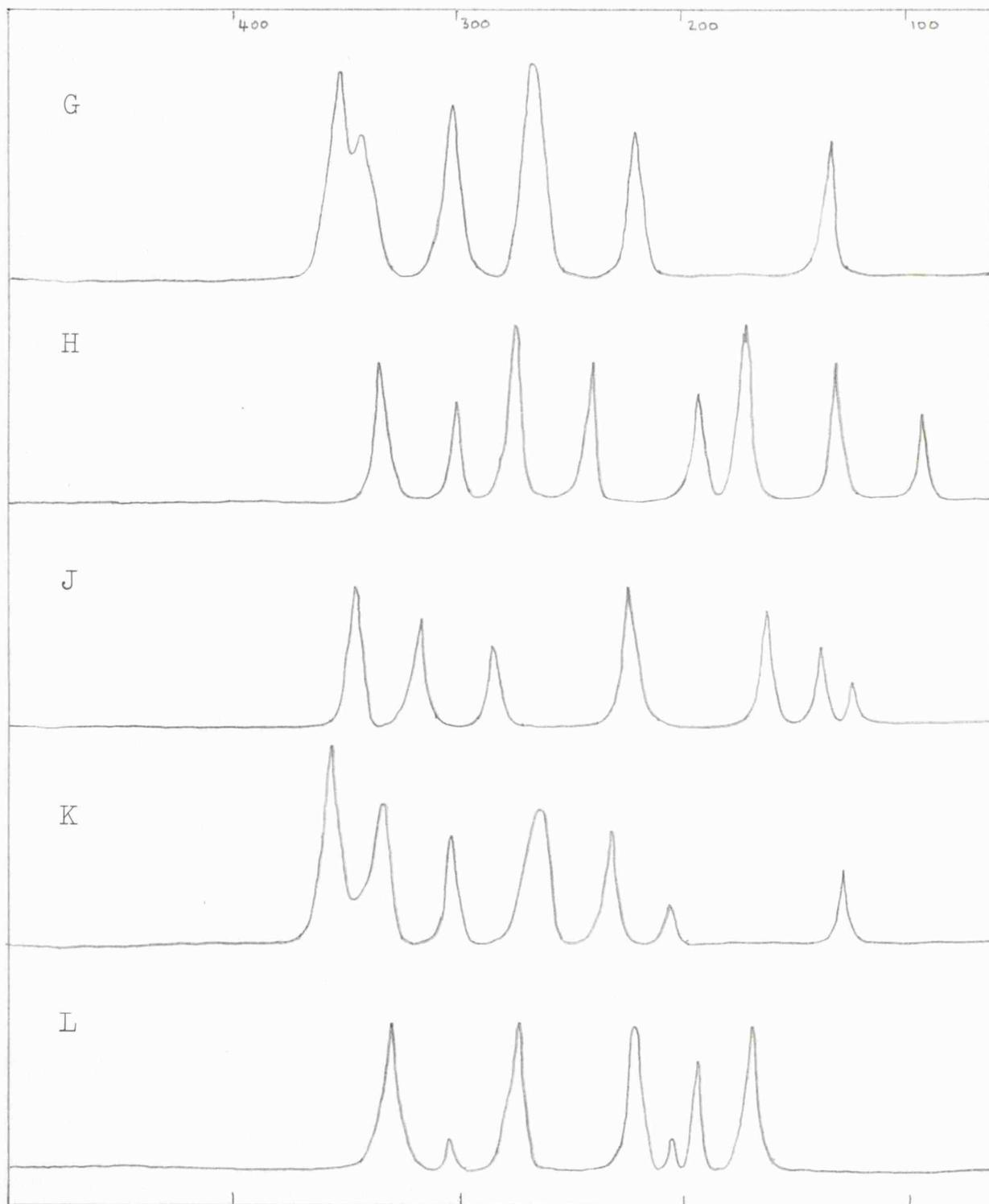


Fig. II-11. (facing page)

Spectra sketches of Pd₂X₄I₂.

- G. Pd₂Cl₄ (AsEt₃)₂.
- H. Pd₂Br₄ (AsEt₃)₂.
- J. Pd₂I₄ (AsEt₃)₂.
- K. Pd₂Cl₄ (AsPr₃ⁿ)₂.
- L. Pd₂Br₄ (AsPr₃ⁿ)₂.

Fig. II-12.

Spectra sketches of $\text{Pd}_2\text{X}_4\text{L}_2$

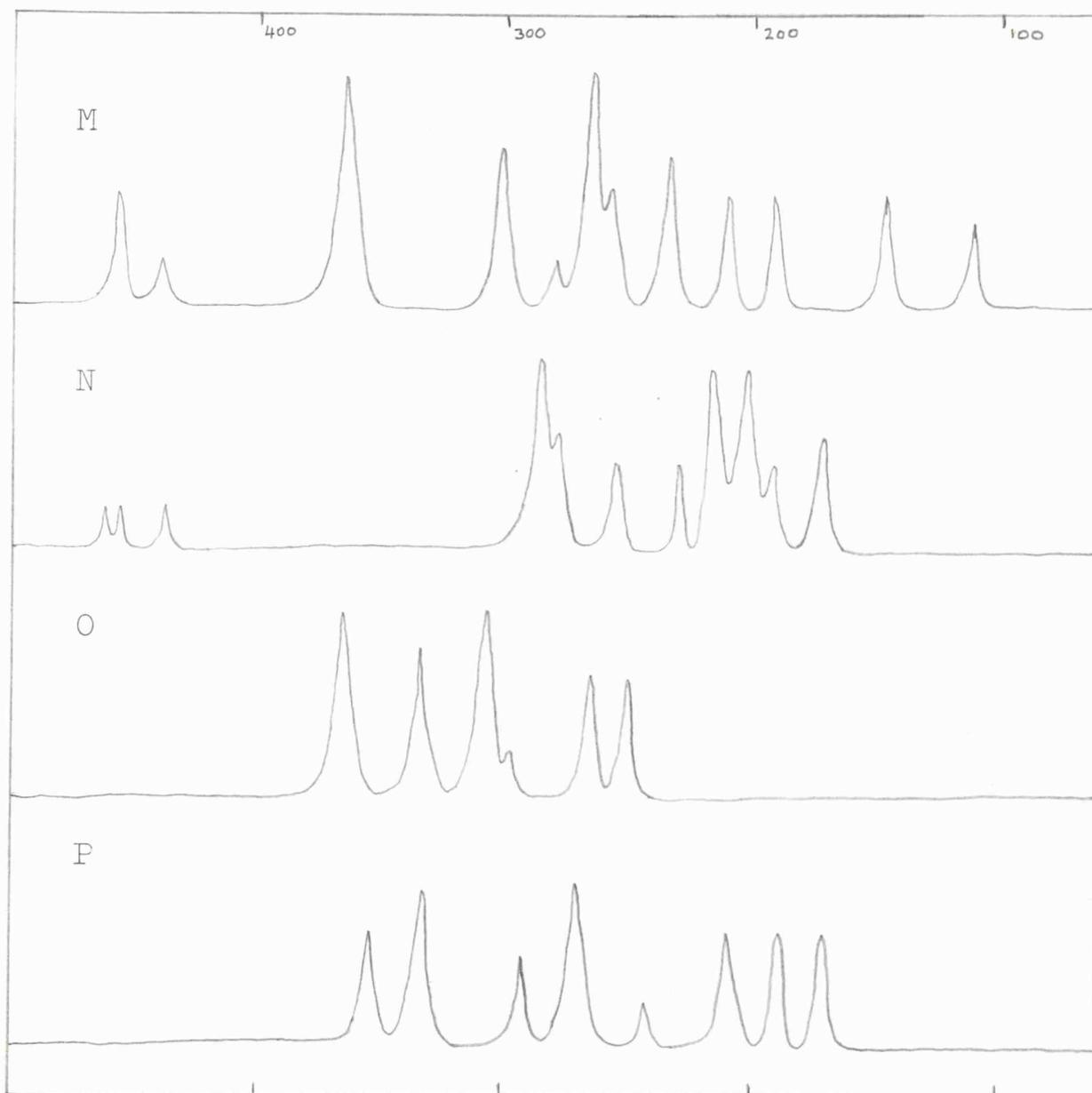
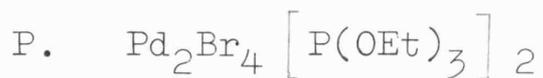
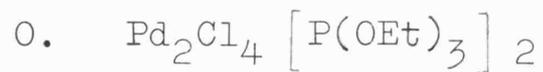
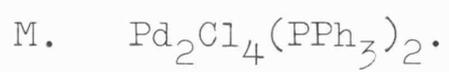


Fig. II-13.

Spectra sketches of Pd₂X₄L₂

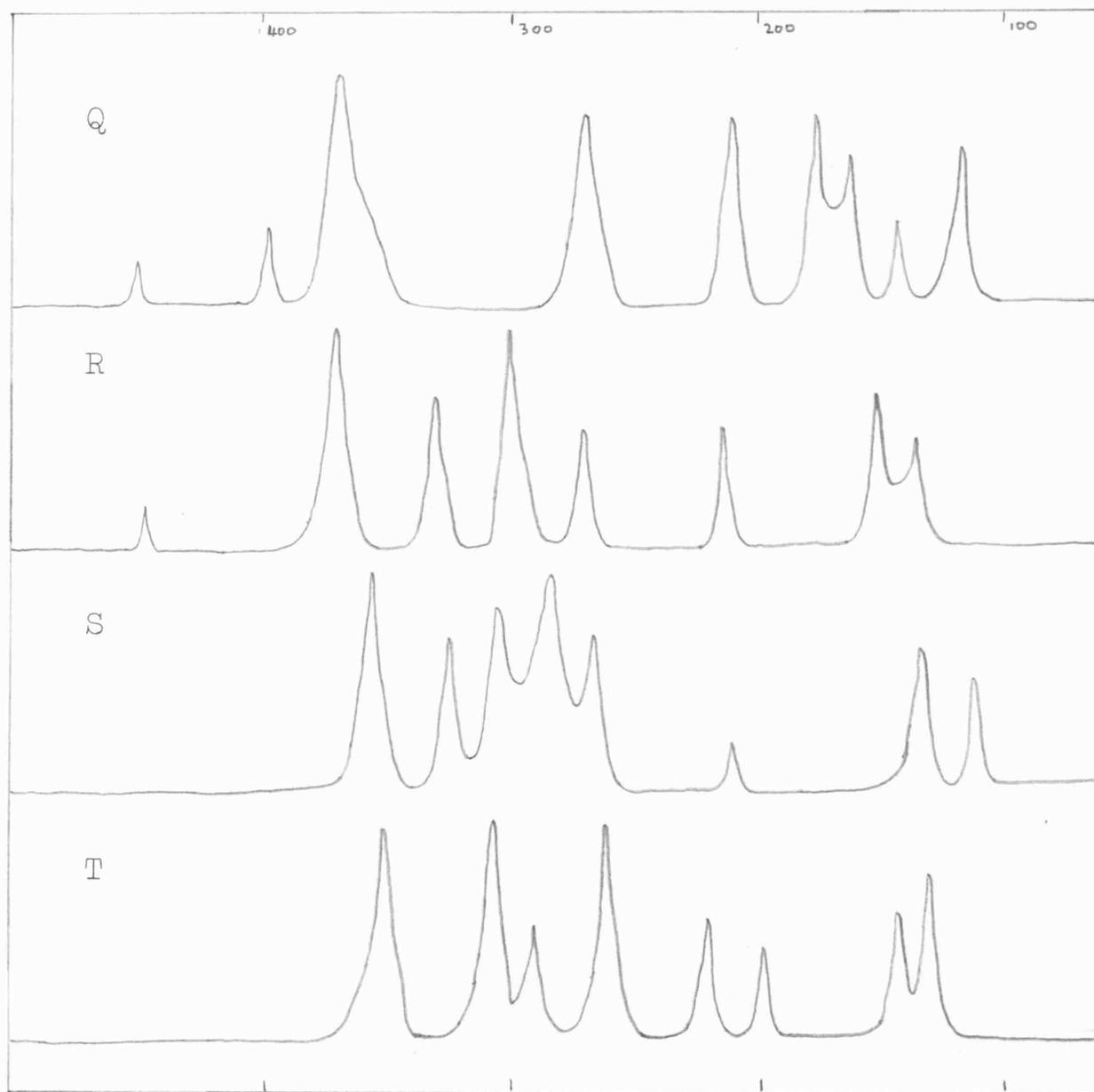
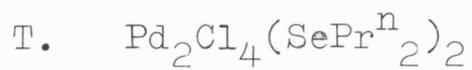
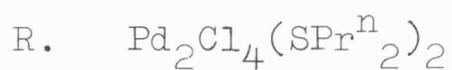
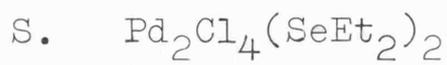
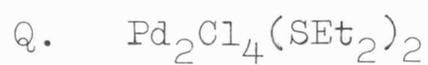


Table II-7. Frequencies and assignments of $\text{Pd}_2\text{Cl}_4\text{L}_2$.

	νEt_3	PPr_3^n	AsEt_3	AsPr_3^n	SEt_2	SPr_2^n
$\nu(\text{PdL})$	435 (m)	444 (m)	342 (ms)	332 (ms)		327 (ms)
$\nu(\text{PdCl})_t$	357 (vs)	356 (vs)	354 (vs)	358 (vs)	366 (vs,as)	366 (vs)
$\nu(\text{PdCl})_b$	302 (ms)	301 (s)	301 (s)	302 (m)		298 (vs)
	263 (s,b)	259 (s)	264 (vs,b)	261 (ms,b)	266 (s)	271 (m)
Other bands	378 (m)	421 (m)	220 (ms)	232 (m)	452 (w)	448 (w)
	331 (m)	224 (wm)	134 (ms)	206 (w)	398 (wm)	214 (m)
	317 (vw)	191 (m)		127 (wm)	212 (s)	149 (ms)
	176 (ms)	144 (s)			176 (s)	137 (m)
	139 (m)				164 (ms)	
					144 (wm)	
					116 (ms)	

Table II-7. (contd.).

	P(OEt) ₃	SeEt ₂	SePr ₂	PPh ₃
$\nu(\text{PdL})$	364*	282 (vs)	290 (m)	438 (w)
$\nu(\text{PdCl})_t$	364 (s)	357 (vs)	353 (vs)	363 (vs)
$\nu(\text{PdCl})_b$	305 (s) 266 (m)	303 (s) 264 (ms)	306 (vs) 261 (vs)	300 (ms) 264 (vs)
Other bands	333 (ms) 298 (w) 249 (m)	322 (ms) 211 (w) 134 (ms) 110 (m)	220 (wm) 198 (wm) 142 (m) 129 (ms)	457 (m) 278 (w) 255 (m) 233 (ms) 208 (wm) 190 (m) 144 (m) 110 (wm)

* Masked by $\nu(\text{PdCl})_t$

Table II-8. Frequencies and assignments of $\text{Pd}_2\text{X}_4\text{L}_2$, (X = Br, I).

	ν_{Et_3}	$\nu_{\text{Pr}_3}^{\text{n}}$	$\nu_{\text{Et}_3}^{\text{As}}$	$\nu_{\text{Pr}_3}^{\text{As}}$	$\nu_{\text{Et}_3}^{\text{P(OEt)}}$	$\nu_{\text{Ph}_3}^{\text{P}}$
$\nu(\text{PdL})$	431 (m)	464 (w) 453 (vw)	335 (ms)	328 (ms)	354 (m)	438 (w)
$\nu(\text{PdBr})_{\text{t}}$	268 (m)	277 (vs)	273 (s)	271 (ms)	272 (ms)	284 (s)
$\nu(\text{PdBr})_{\text{b}}$	194 (ms) 185 (s)	190 (m) 178 (ms)	193 (m) 171 (s)	192 (m) 166 (ms)	189 (m) 173 (m)	191 (wm) 169 (m)
Other bands	376 (m) 330 (m) 289 (wm) 253 (wm) 168 (m) 107 (wm)	434 (wm) 374 (m) 342 (m) 316 (vw) 230 (m) 128 (wm)	301 (m) 239 (ms) 132 (ms) 95 (wm)	301 (vw) 220 (ms) 202 (vw)	332 (ms) 293 (wm) 244 (w) 212 (m)	461 (w) 457 (w) 278 (m) 254 (wm) 228 (wm) 218 (s) 200 (s)

Table II-8. (contd.).

	PPr_3^{a}	AsEt_3	PEt_3	PEt_3 contd.
$\nu(\text{PdL})$	458 (w) 451 (w)	346 (ms) 316 (m)	438 (m) 423 (m)	
$\nu(\text{PdI})_{\text{t}}$	225 (ms)	222 (ms)	173 (vs) 166 (s)	
$\nu(\text{PdI})_{\text{b}}$	165 (s) 142 (ms)	161 (m) 139 (wm)	139 (m) 98 (wm, b)	
Other bands	427 (m) 373 (wm) 339 (m) 200 (w)	283 (wm) 124 (w)	384 (m) 379 (wm) 335 (wm) 325 (wm) 319 (vw)	251 (w) 237 (wm)

II-3.11. Bis- (diethylselenide) dichloro- $\mu\mu'$ -
dichlorodipalladium; Pd₂Cl₄(SeEt₂)

The infrared spectrum of diethyleselelide has not been examined, but the related dimethylselenide⁷¹ has no bands between 500-250 cm.⁻¹. Diethylselenide is expected to have only one additional band in this region due to $\delta(\text{CCSe})$. The spectrum of the complex has five bands between 500-250 cm.⁻¹, which are therefore assigned to $\nu(\text{PdCl})_t$, $\nu(\text{PdCl})_b$, $\nu(\text{PdSe})$ and $\delta(\text{CCSe})$. Bands at 357, 303 and 264 cm.⁻¹ are assigned to $\nu(\text{PdCl})_t$ and $\nu(\text{PdCl})_b$ respectively. They are all strong bands and compare closely with other assignments of $\nu(\text{PdCl})$, (Table II-7). The band at 282 cm.⁻¹ is assigned to $\nu(\text{PdSe})$. This compares with previous assignments in the region 315-240 cm.⁻¹ 81, 82 and a band at 290 cm.⁻¹ which is similarly assigned in the n- propyl analogue. The remaining band at 322 cm.⁻¹ is assigned to the $\delta(\text{CCSe})$ mode of diethylselenide. Evidence for the assignment to an internal mode of the ligand is that a comparable band is not found in the n- propyl analogue above 220 cm.⁻¹. This shift in frequency is the result of the increase in the number of carbon atoms in going

from diethyl- to di-n-propylselenide. The three remaining bands in the spectrum at 211, 134 and 110 cm.^{-1} are unassigned

II-3.12. Bis-(di-n-propylselenide) dichloro- μ' -dichlorodipalladium; $\text{Pd}_2\text{Cl}_4(\text{SePr}_2^{\text{n}})_2$.

The bands at 353, 306 and 261 cm.^{-1} are assigned to $\nu(\text{PdCl})_{\text{t}}$ and $\nu(\text{PdCl})_{\text{b}}$ respectively. The bands are all of very strong intensity and the frequencies are close to those of the corresponding modes in $\text{Pd}_2\text{Cl}_4(\text{SeEt}_2)_2$. $\nu(\text{PdSe})$ is assigned at 290 cm.^{-1} but insufficient evidence is available to assign the low frequency bands at 220, 198, 142 and 129 cm.^{-1} .

II-3.13. Bis-(diethylsulphide) dichloro- μ' -dichlorodipalladium; $\text{Pd}_2\text{Cl}_4(\text{SEt}_2)_2$.

A feature of this spectrum is the absence of any band which could be described as the higher $\nu(\text{PdCl})_{\text{b}}$. A very strong absorption at 366 cm.^{-1} , assigned to $\nu(\text{PdCl})_{\text{t}}$, is asymmetric on the low frequency side. This asymmetry may mask $\nu(\text{PdS})$ but is probably too high, ($> 320 \text{ cm.}^{-1}$), to be associated with $\nu(\text{PdCl})_{\text{b}}$. The lower $\nu(\text{PdCl})_{\text{b}}$ is assigned to a strong band at 266 cm.^{-1} . The bands

below 200 cm.^{-1} follow the pattern observed in $[\text{Pd}_2\text{Cl}_6]^{2-}$, (Chapter I), and other diethylsulphide complexes, (Chapter V). The tentative assignments, $\delta(\text{PdCl})$ at 176 or 164, $\pi(\text{PdCl})$ at 144 and $\delta(\text{PdS})$ at 116 cm.^{-1} are made. The remaining bands are associated with internal modes of diethylsulphide.

II-3.14. Bis-(di-*n*-propylsulphide) dichloro- μ' -dichlorodipalladium; $\text{Pd}_2\text{Cl}_4(\text{SPr}_2^{\text{n}})_2$.

The very intense band at 366 cm.^{-1} is assigned to $\nu(\text{PdCl})_{\text{t}}$ and by comparison with the spectrum of $\text{Pt}_2\text{Cl}_4(\text{SPr}_2^{\text{n}})_2$, $\nu(\text{PdCl})_{\text{b}}$ are assigned at 298 and 271 cm.^{-1} in a region free from ligand absorption. The assignment of $\nu(\text{PdS})$ at 327 cm.^{-1} is tentative as di-*n*-propylsulphide has absorption bands in this region.

II-3.15. Summary of data on $\nu(\text{PdCl})$ in $\text{Pd}_2\text{Cl}_4\text{L}_2$ complexes.

As predicted by theory, three $\nu(\text{PdCl})$ were observed in $\text{Pd}_2\text{Cl}_4\text{L}_2$. $\nu(\text{PdCl})_{\text{t}}$ lie in the range $359 \pm 7 \text{ cm.}^{-1}$ and the two bridge modes, $\nu(\text{PdCl})_{\text{b}}$, in the ranges 302 ± 4 and $265 \pm 6 \text{ cm.}^{-1}$. The values of $\nu(\text{PdCl})$ found in $[\text{AsPh}_4]_2 [\text{Pd}_2\text{Cl}_6]$ fall

within these ranges, occurring at 353, 305 and 264 cm.^{-1} respectively. As for $\nu(\text{PtCl})$, all $\nu(\text{PdCl})$ are intense absorptions but they do not exhibit the isotopic splitting observed in $\text{Pt}_2\text{Cl}_4\text{L}_2$ complexes. Calculations show that a significant $\nu(\text{Pd}^{35}\text{Cl})$, $\nu(\text{Pd}^{37}\text{Cl})$ splitting is possible for palladium but empirically it has only been observed for the heavier elements, gold¹⁴ and platinum.

II-3.2. Bromo-complexes.

The predicted number of $\nu(\text{PdBr})$ were observed for all $\text{Pd}_2\text{Br}_4\text{L}_2$ complexes. $\nu(\text{PdBr})_t$ lie in the range $276 \pm 8 \text{ cm.}^{-1}$ and $\nu(\text{PdBr})_b$ in the range 191 ± 3 and $176 \pm 10 \text{ cm.}^{-1}$. The corresponding modes in $[\text{Pd}_2\text{Br}_6]^{2-}$ are at 266, 192 and 177 cm.^{-1} respectively. The range of ligand, L, is restricted to phosphines and arsines but the lower bridge mode, $\nu(\text{PdBr})_b$ has a range of 20 cm.^{-1} . In the corresponding $\text{Pt}_2\text{Br}_4\text{L}_2$ complexes, the range was 4 cm.^{-1} and the lower $\nu(\text{PdX})_b$, (X = Cl and I), were also observed over a narrow frequency range, 266-259 and 142-139 cm.^{-1} respectively.

II-3.3. Iodo-complexes.

The complexes $\text{Pd}_2\text{I}_4\text{L}_2$, ($\text{L} = \text{PEt}_3, \text{PPr}_3^{\text{n}}$ and AsEt_3), were studied. When $\text{L} = \text{PPr}_3^{\text{n}}$ and AsEt_3 , $\nu(\text{PdI})_{\text{b}}$ are at 165, 142 and 161, 139 cm^{-1} respectively and are significantly higher than the corresponding modes in $[\text{Pd}_2\text{I}_6]^{2-}$, at 144 and 132 cm^{-1} . The assignments of $\nu(\text{PdI})_{\text{t}}$ at 225 cm^{-1} (PPr_3^{n}) and 222 cm^{-1} (AsEt_3) are tentative. Both complexes have ligand absorption at similar frequencies and the assignments are based upon the enhanced intensity of the bands, comparison with $[\text{Pd}_2\text{I}_6]^{2-}$ and the absence of any other absorption between 280-170 cm^{-1} . The spectrum of $\text{Pd}_2\text{I}_4(\text{PEt}_3)_2$ cannot be explained in terms of the trans- structure ($\text{C}_{2\text{h}}$). Three bands which appear in the corresponding chloro- and bromo- complexes appear to have split in the iodo-complex, Table II-7. The remaining bands in the spectrum, which are not internal modes of the ligand, are at 173, 166 139 and 98 cm^{-1} . One of this group is possibly $\nu(\text{PdI})_{\text{t}}$ and the remainder will be Pd-I bond vibrations. However, the frequencies are not comparable with previous assignments of $\nu(\text{PdI})_{\text{t}}$ or $\nu(\text{PdI})_{\text{b}}$. The unusual spectrum of $\text{Pd}_2\text{I}_4(\text{PEt}_3)_2$

Table II-7.

Splitting of halogen insensitive bands in Pd₂I₄(PEt₃)₂.

Pd ₂ X ₄ (PEt ₃) ₂ X =	ν(PdP)	Internal modes of PEt ₃	
Cl.	435	378	331
Br.	431	376	330
I.	438, 423	384, 374	335, 325.

suggests some deviation from idealised C_{2h} symmetry.

The possible cis- structure, (D_{2h}), would require two ν(PdP) and four ν(PdI)_b but not a splitting of internal modes of the ligand.

II-3.4. Effect of ligand, L, upon ν(PdX),

X = Cl, Br and I.

The chloro-complexes, Pd₂Cl₄L₂, have the widest range of ligands, L, and are considered in detail. ν(PdX), X = Br and I, are discussed only when their behaviour differs significantly from ν(PdCl).

II-3.41. Bridge stretching vibrations, $\nu(\text{PdCl})_b$.

The higher bridge mode, $\nu(\text{PdCl})_b$, was observed in the narrow range $302 \pm 4 \text{ cm.}^{-1}$, and shows the ligand insensitivity observed for the corresponding mode in the $\text{Pt}_2\text{Cl}_4\text{L}_2$ complexes.

The lower $\nu(\text{PdCl})_b$ was observed in the range $265 \pm 6 \text{ cm.}^{-1}$ and the ligand sensitivity of this mode is much reduced in comparison with the corresponding mode in $\text{Pt}_2\text{Cl}_4\text{L}_2$. In $\text{Pt}_2\text{Cl}_4\text{L}_2$, when L = alkylphosphine or arsine, $\nu(\text{PtCl})_b$ is 40 cm.^{-1} below that found for $[\text{Pt}_2\text{Cl}_6]^{2-}$. In the palladium complexes, no corresponding drop in frequency was observed. Thus palladium (II) does not show the trans- effect as strongly as platinum (II). In addition, π -bonding between the metal and ligand, which affects bridge-bond strength, is much more important in platinum than in palladium complexes. Thus in platinum, the 5d orbitals have energy levels close to the 6s or 6p orbitals. The vacant $6p_z$ orbital of platinum, by hybridisation with the $5d_{xz}$ orbital produces π -type orbitals especially favourable for dative π -bond formation.

X-ray structural evidence of M-X bond lengths

in the bridge system M_2X_2 , ($M = Pt, Pd$), has already been discussed. The complex $[Et_4N]_2 [Pt_2Br_6]$ has a completely symmetrical bridge with equal Pt-Br bond lengths, whereas $Pd_2Cl_4(styrene)_2$ has unequal bridge-bond lengths. With the discussion in Section II-2.41. on ligand influence on the frequencies of $\nu(PtCl)_b$ and the 30-40 $cm.^{-1}$ difference between the higher and lower $\nu(PdCl)_b$, it would be of interest to have more detailed and modern structural evidence on these complexes. It is probable that the trends observed in the infrared frequencies of the bridge modes would be reflected in unsymmetrical bridge systems M_2X_2 , ($M = Pt, Pd$), with unequal and varying M-X bond lengths.

II-3.42. Terminal stretching vibrations, $\nu(PdCl)_t$.

$\nu(PdCl)_t$, occurring in the range $359 \pm 7 cm.^{-1}$ are relatively insensitive to the nature of the ligand, L. In $Pt_2Cl_4L_2$, the corresponding mode $\nu(PtCl)_t$ has a much wider range of frequency, (365-330 $cm.^{-1}$).

Comparing the frequencies of $\nu(PdX)$ and $\nu(PtX)$ for the same ligand, L, then in both $[M_2X_6]^{2-}$ and $M_2X_4L_2$, ($M = Pd, Pt$; $X = Cl, Br$ and I), $\nu(PdX)_t$

$\nu(\text{PtX})_t$ and $\nu(\text{PdX})_b < \nu(\text{PtX})_b$.

II-3.5. Palladium-ligand stretching vibrations,
 $\nu(\text{PdL})$.

The method of assignment and general discussion of $\nu(\text{PdL})$ are in chapter V. $\nu(\text{PdL})$ are assigned definitely for the complexes $\text{Pd}_2\text{X}_4\text{L}_2$, ($\text{L} = \text{PR}_3$ and AsR_3). The assignments of $\nu(\text{PdS})$ and $\nu(\text{PdSe})$ are tentative, (Section II-3.11 and II-3.12). The single $\nu(\text{PdL})$ observed in the chloro-complexes is split into a doublet in five corresponding bromo- and iodo-complexes, ($\text{L} = \text{PEt}_3$, PPr_3^n and AsEt_3). The internal modes of the ligand also doubled up and possible explanations of this phenomenon are lattice effects or some deviation from idealised C_{2h} symmetry. The frequencies of $\nu(\text{PdL})$ and $\nu(\text{PtL})$ are very similar and the discussion of $\nu(\text{PtP})$ in Section II-2.5 is relevant to $\nu(\text{PdP})$. Thus $\nu(\text{PdP})$ was found in the range $465\text{--}350 \text{ cm.}^{-1}$ compared with $\nu(\text{PtP})$ at $470\text{--}340 \text{ cm.}^{-1}$.

II-3.6. Terminal bending vibrations.

No definite assignments of these modes are made. The spectra of $\text{Pd}_2\text{X}_4\text{L}_2$ closely resemble those

of the corresponding platinum complexes in the spectral region below 200 cm.^{-1} , where bending vibrations should occur. As before, tentative assignments of some bands can be made but no assignments remain consistent over a series of complexes. Thus the discussion of the bending vibrations of platinum complexes, Section II-2.6, is equally relevant to the palladium analogues.

Footnote to Section II-3.41.

Subsequent to this work, two complexes $[\text{Pt}_2\text{X}_2(\text{PBu}_3^n)_4] [\text{BCl}_4]_2$, ($\text{X} = \text{Cl}, \text{Br}$),²⁰⁹ were examined in the far-infrared. As predicted by theory for planar $\text{Pt}_2\text{X}_2\text{L}_4$, (D_{2h}), two $\nu(\text{PtX})_b$ were observed at 325, 312 and 209, 200 cm.^{-1} for $\text{X} = \text{Cl}$ and Br respectively. The terminal ligands exert an equal influence on the bridge system and as expected the frequencies of the two $\nu(\text{PtX})_b$ in each complex are very close together. It is concluded that a symmetrical Pt_2X_2 bridge system is present in these complexes.

CHAPTER III.

Substituted halogen-bridged complexes

of Rh (I)

III-1. Introduction.

The complexes studied are of the types $Rh_2X_2L_4$ and $Rh_2X_2D_2$, (X = Cl, Br and I; L = monodentate and D = bidentate ligand). The monodentate ligands are carbon monoxide and ethylene and the bidentate ligands, cycloocta-1, 5-diene (COD), dicyclopentadiene (dCPD) and bicyclo [2, 2, 1] hepta-2, 5-diene (norbornadiene-NBD). This range of ligands is narrow because phosphines and arsines preferentially form monomeric complexes⁸³; thus

$$Rh_2Cl_2(CO)_4 + 2 COD \rightarrow Rh_2Cl_2(COD)_2 + 4CO. \text{ but}$$
$$Rh_2Cl_2(CO)_4 + 4 PR_3 \rightarrow 2 [RhCl(CO)(PR_3)_2] + 2CO.$$

The frequencies of $\nu(RhX)_b$ in the planar halogen-bridged anions $[Rh_2X_2(SnX_3)_4]^{4-}$, (X = Cl, Br), (Chapter VI), are included in the discussion on $\nu(RhX)_b$ for comparative purposes.

Detailed X-ray structural studies of $Rh_2Cl_2(COD)_2$ ⁸⁴ and $Rh_2Cl_2(CO)_4$ ⁸⁵ exist. In the cycloocta-1, 5-diene complex, Fig. III-1., a given rhodium atom was bonded only to two chlorine atoms and to two double-bond centres of a COD ring, ("boat" configuration). Within the limits of the study the four double-bond centres, two rhodiums and

two chlorines in a given molecule were coplanar. The rhodium atom having a square-planar configuration. The structure of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ was significantly different, Fig. III-2, the rhodium atoms being in an octahedral configuration. Two essentially planar $\text{Rh}(\text{CO})_2\text{Cl}$ groups intersect at an angle of 124° . The resulting dimers were linked by weak rhodium-rhodium bonds, (3.31 Å), to form infinite chains. To explain the diamagnetism of the compound, in the solid state, a second, so called "bent" Rh-Rh bond was postulated. This results from overlap of d^2sp^3 hybridised σ -type orbitals at an angle approximately equal to 56° . In solution the weak Rh-Rh bonds break to give dimeric molecules. No definite structural data exist for the remaining rhodium complexes studied.

The infrared-active modes of the two structures are described in Table III-1 (D_{2h}) and Table III-2 (C_{2v}). Thus theory shows that in square-planar $\text{Rh}_2\text{X}_2\text{L}_4$ (D_{2h}), two $\nu(\text{RhX})_b$ (B_{2u} and B_{3u}), corresponding to the bridge modes in Chapters I and II, are infrared-active. In the "bent" $\text{Rh}_2\text{X}_2\text{L}_4$ (C_{2v}), the symmetry is lowered and three $\nu(\text{RhX})_b$ ($A_1 + B_1 + B_2$), are infrared-active. The A_1 mode corresponds to the Raman-active only A_g

Fig. III-1. Structure of $\text{Rh}_2\text{Cl}_2(\text{COD})_2$ ⁸⁴.

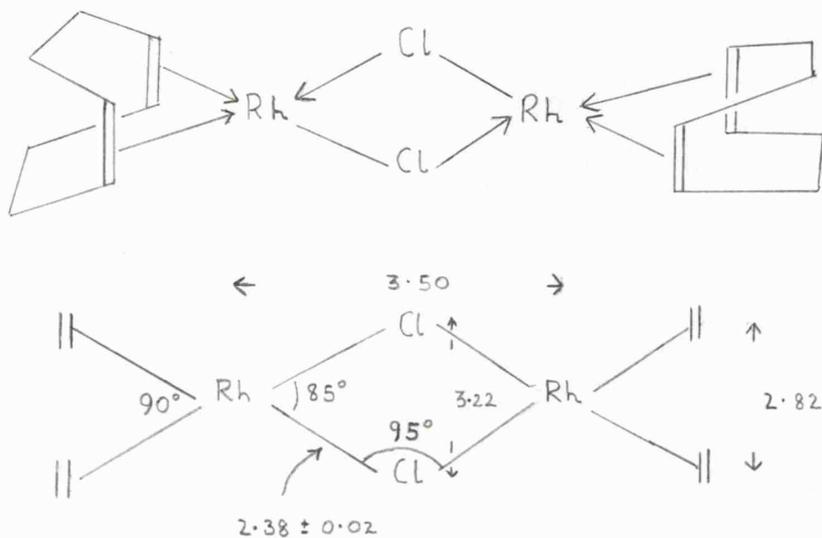
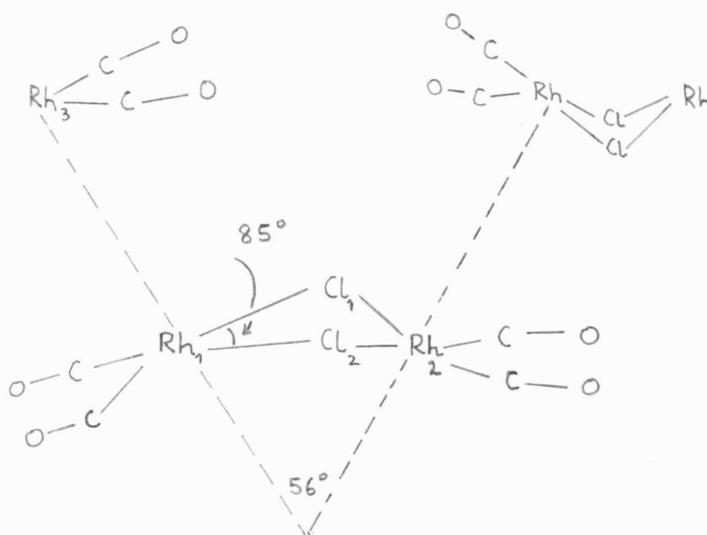


Fig. III-2. Structure of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ ⁸⁵.



Rh_1Rh_2	=	3.12
Rh_1Rh_3	=	3.31
Rh_2Cl_1	=	2.38
Rh_2Cl_2	=	2.33

All bond lengths in Angstroms (Å)

mode in D_{2h} symmetry. Using $Rh_2Cl_2(COD)_2$ and $Rh_2Cl_2(CO)_4$ as proven examples of D_{2h} and C_{2v} symmetry, respectively, the number of $\nu(RhX)_b$ observed in the spectrum of each complex should enable structural designations to be made.

The infrared spectra of $Rh_2Cl_2D_2$, (D = COD and NBD), have been examined^{86, 87} above 600 cm.^{-1} and $Rh_2Cl_2(CO)_4$ ⁹⁰ above 400 cm.^{-1} , but no far-infrared spectra have been recorded. To establish the frequency range of Rh-X stretching vibrations, a series of rhodium (III) complexes $[Rh(en)_2X_2]Y$, (X = Cl, Br and I; Y = ClO_4^- , NO_3^- , I^- ; en = ethylenediamine), kindly donated by Dr. Poë, were examined.⁸⁹ The results, (Table III-3), show $\nu(RhCl)$ at 350-310, $\nu(RhBr)$ at 225-195 and $\nu(RhI)$ at $\sim 180\text{ cm.}^{-1}$. Recent investigations of Rh(III) complexes⁹¹⁻⁹³ and $RhCl_3 \cdot 3H_2O$ ⁹⁴ confirm these assignments. The single infrared study of a rhodium (I) complex⁹⁵ gave $\nu(RhCl)$ at 320 and 290 cm.^{-1} in cis- $[RhCl_2(CO)_2]^-$. Thus terminal $\nu(MX)$, (M = Pt, Pd and Rh), have comparable frequencies, and extending the comparison to $\nu(MX)_b$, $\nu(RhX)_b$ should lie in the ranges 300-250 (Cl), 210-170 (Br), and $170-130\text{ cm.}^{-1}$ (I).

Table III-1. Infrared-active modes of $\text{Rh}_2\text{X}_2\text{L}_4$ (D_{2h})

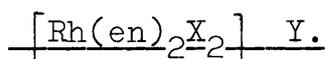
Mode	Symmetry species	Approximate description of mode.	
ν_{11}	B_{1u}	Rhodium-ligand out-of-plane wag,	$\rho_w(\text{RhL}_2)$.
ν_{12}	B_{1u}	Bridge rhodium-halogen out-of-plane bend,	$\pi(\text{Rh}_2\text{X}_2)$.
ν_{13}	B_{2u}	Rhodium-ligand stretch,	$\nu(\text{RhL})$.
ν_{14}	B_{2u}	Bridge rhodium-halogen stretch,	$\nu(\text{RhX})_b$.
ν_{15}	B_{2u}	Rhodium-ligand in-plane rock,	$\rho_f(\text{RhL}_2)$.
ν_{16}	B_{3u}	Rhodium-ligand stretch,	$\nu(\text{RhL})$.
ν_{17}	B_{3u}	Bridge rhodium-halogen stretch,	$\nu(\text{RhX})_b$.
ν_{18}	B_{3u}	Rhodium-ligand in-plane bend,	$\sigma(\text{RhL}_2)$.

Table III-2. Infrared-active modes of $\text{Rh}_2\text{X}_2\text{L}_4$ (C_{2v}).

Mode	Symmetry species	Approximate description of mode.	
ν_1	A ₁	Rhodium-ligand stretch,	$\nu(\text{RhL})$.
ν_2	A ₁	Bridge rhodium-halogen stretch,	$\nu(\text{RhX})_b$.
ν_3	A ₁	Rhodium-ligand in-plane bend,	$\delta(\text{RhL}_2)$.
ν_4	A ₁	Bridge rhodium-halogen in-plane bend,	$\delta(\text{Rh}_2\text{X}_2)$.
ν_5	A ₁	Bridge rhodium-halogen out-of-plane bend,	$\pi(\text{Rh}_2\text{X}_2)$.
ν_6	A ₁	Rhodium-ligand out-of-plane wag,	$\rho_w(\text{RhL}_2)$.
ν_{11}	B ₁	Rhodium-ligand stretch,	$\nu(\text{RhL})$.
ν_{12}	B ₁	Bridge rhodium-halogen stretch,	$\nu(\text{RhX})_b$.
ν_{13}	B ₁	Rhodium-ligand in-plane bend,	$\delta(\text{RhL}_2)$.
ν_{14}	B ₁	Rhodium-ligand out-of-plane wag,	$\rho_w(\text{RhL}_2)$.
ν_{15}	B ₂	Rhodium-ligand stretch,	$\nu(\text{RhL})$.
ν_{16}	B ₂	Bridge rhodium-halogen stretch,	$\nu(\text{RhX})_b$.
ν_{17}	B ₂	Rhodium-ligand in-plane rock,	$\rho_r(\text{RhL}_2)$.
ν_{18}	B ₂	Rhodium-ligand out-of-plane twist,	$\rho_t(\text{RhL}_2)$.

* For a bent molecule (C_{2v}), with a $\text{C}_2(z)$ axis, then in-plane represents motion along the xy-axis and 'out-of-plane' motion along the z-axis.

Table III-3 Assignment of $\nu(\text{RhX})$ in



Complex	$\nu(\text{RhCl})$	$\nu(\text{RhBr})$	$\nu(\text{RhI})$
$\left[\text{Rh}(\text{en})_2 \text{Cl}_2 \right] \text{NO}_3$	347		
$\left[\text{Rh}(\text{en})_2 \text{Cl}_2 \right] \text{ClO}_4$	343		
$\left[\text{Rh}(\text{en})_2 \text{Br}_2 \right] \text{ClO}_4$		223	
$\left[\text{Rh}(\text{en})_2 \text{I}_2 \right] \text{I}$			178
$\left[\text{Rh}(\text{en})_2 \text{ClBr} \right] \text{ClO}_4$	333	213	
$\left[\text{Rh}(\text{en})_2 \text{ClI} \right] \text{ClO}_4$	311		
$\left[\text{Rh}(\text{en})_2 \text{BrI} \right] \text{ClO}_4$		196	

III-2. Results and Discussion.

The spectra of the complexes are sketched in Figs. III-3 and III-4 and the frequencies and assignments are listed in Table III-4. $\nu(\text{RhX})_b$ are identified in all complexes but a complete assignment is not always attempted. The lack of infrared data on the free ligands make the assignments of $\nu(\text{RhL})$ tentative in the diene complexes but the assignments made for $\text{Rh}_2\text{X}_2\text{L}_4$, ($\text{L} = \text{CO}, \text{C}_2\text{H}_4$), are more certain.

Fig. III-3.

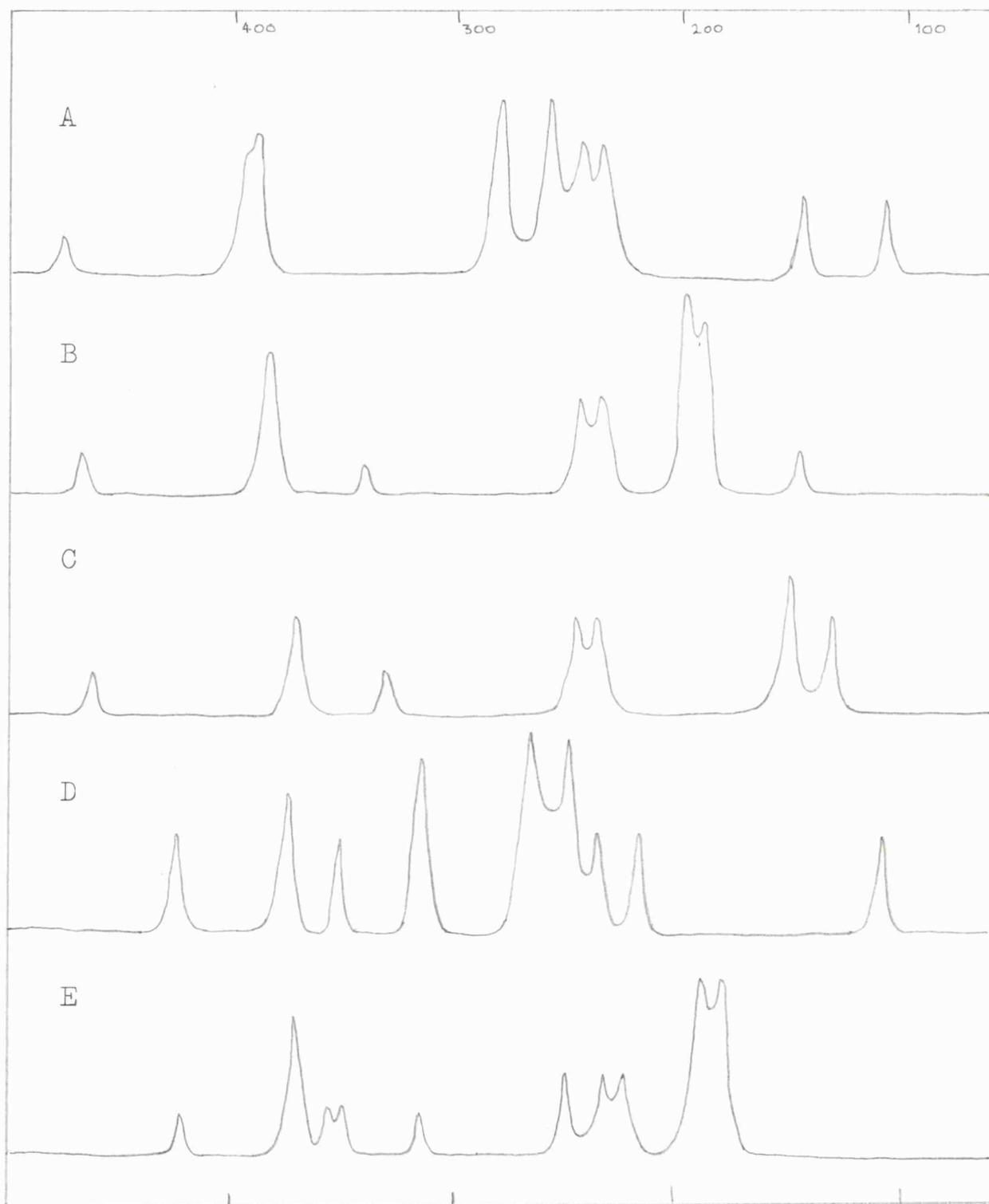


Fig. III-3

Spectra sketches of $\text{Rh}_2\text{X}_2\text{D}_2$.

- A. Rh_2Cl_2 $(\text{COD})_2$.
- B. Rh_2Br_2 $(\text{COD})_2$.
- C. Rh_2I_2 $(\text{COD})_2$.
- D. Rh_2Cl_2 $(\text{dCPD})_2$.
- E. Rh_2Br_2 $(\text{dCPD})_2$.

Fig. III-4.

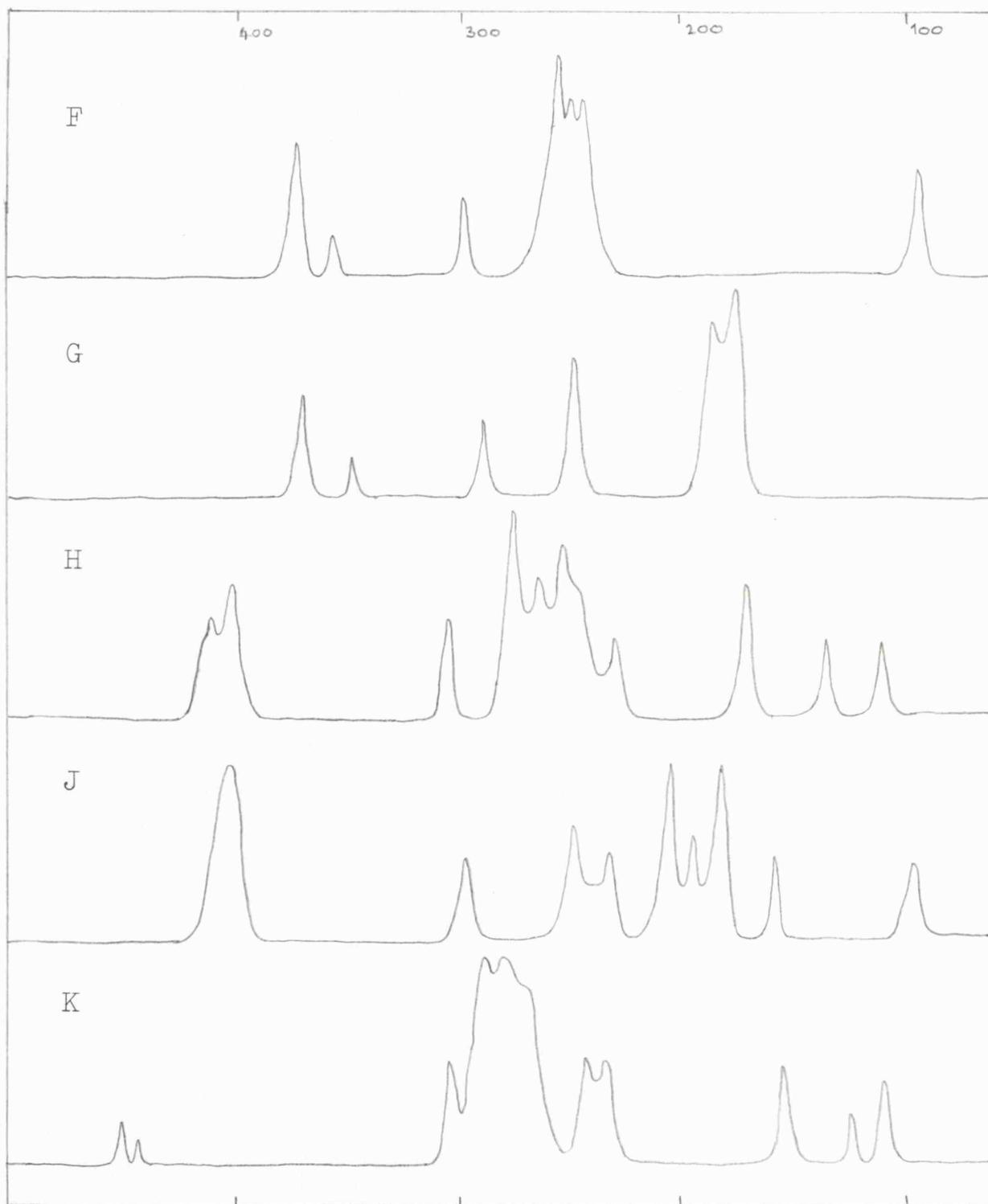


Fig. III-4.

Spectra sketches of $\text{Rh}_2\text{X}_2\text{D}_2$ and $\text{Rh}_2\text{X}_2\text{L}_4$.

- F. $\text{Rh}_2\text{Cl}_2 \quad (\text{NBD})_2$.
- G. $\text{Rh}_2\text{Br}_2 \quad (\text{NBD})_2$.
- H. $\text{Rh}_2\text{Cl}_2 \quad (\text{C}_2\text{H}_4)_4$.
- J. $\text{Rh}_2\text{Br}_2 \quad (\text{C}_2\text{H}_4)_4$.
- K. $\text{Rh}_2\text{Cl}_2 \quad (\text{CO})_4$.

Table III-4a Frequencies and assignments of $\text{Rh}_2\text{X}_2\text{D}_2$ (D_{2h}).

Mode	Symmetry species	Rh_2X_2 (COD) $_2$		Rh_2X_2 (dCPD) $_2$		Rh_2X_2 (NBD) $_2$		
		X = Cl	X = Br	X = I	X = Cl	X = Br	X = Cl	X = Br
$\nu(\text{RhL})$	$B_{2u} + B_{2u}$	397 (sh)	382 (ms)	371 (m)				
		388 (ms)						
$\nu(\text{RhX})_b$	$B_{2u} + B_{2u}$	281 (s)	195 (vs)	151 (ms)	266 (vs)	187 (s)	257 (vs)	186 (s)
		260 (s)	184 (s)	131 (m)	250 (vs)	177 (s)	245 (s)	178 (vs)
Other bands		477 (w)	472 (w)	464 (w)	425 (m)	424 (w)	373 (ms)	370 (m)
		245 (ms)	341 (vw)	334 (w)	376 (ms)	371 (ms)	359 (w)	348 (w)
		237 (ms)	244 (m)	244 (m)	354 (m)	354 (w)	298 (wm)	290 (wm)
		142 (wm)	235 (m)	232 (m)	317 (s)	350 (w)	252 (s)	248 (ms)
		111 (wm)	146 (w)		239 (m)	315 (w)	98 (m)	
			219 (m)	251 (wm)				
			110 (m)	233 (wm)				
				221 (wm)				

Table III-4b. Frequencies and assignments of $\text{Rh}_2\text{X}_2\text{L}_4$ (C_{2v}).

Mode	Symmetry species	$\text{Rh}_2\text{Cl}_2(\text{CO})_4$	Rh_2X_2 (C_2H_4) ₄	
			X = Cl	X = Br
$\nu(\text{RhX})_b$	$A_1 + B_1 + B_2$	288 (vs)	276 (vs)	205 (s)
		280 (vs, b)	262 (ms)	194 (m)
		269 (sh)	252 (s)	183 (s)
$\nu(\text{RhL}_2)$	$A_1 + B_1 + B_2$	450 (w)	417 (sh)	403 (s, vb)
		444 (vw)	412 (m)	
			403 (ms, b)	
$\delta(\text{Rh}_2\text{X}_2)$	A_1	122 (w)	137 (wm)	
$\delta(\text{RhL}_2)$	$A_1 + B_1$	242 (m)	248 (sh)	248 (m)
		237 (m)	229 (wm)	232 (wm)
		303 (m)	304 (m)	298 (wm)
$\rho_t(\text{RhL}_2)$	B_2	156 (m)	171 (ms)	159 (wm)
		110 (wm)	112 (wm)	98 (wm, b)

III-2.1. Bis (cycloocta-1, 5-diene)- $\mu\mu'$ -
dihalogenodirrhodium; $\text{Rh}_2\text{X}_2(\text{COD})_2$,
(X = Cl, Br, I).

$\nu(\text{RhX})_b$ are assigned to two bands in the spectrum of each complex, which shift to a lower frequency as the halogen is changed from Cl to Br to I. The bands are at 281, 260 (Cl); 195, 184 (Br); and 151, 131 cm^{-1} (I). The two $\nu(\text{RhCl})_b$ satisfy theory for $\text{Rh}_2\text{Cl}_2(\text{COD})_2$, (D_{2h}), and the assignments made of $\nu(\text{RhBr})_b$ and $\nu(\text{RhI})_b$ suggest that the bromo- and iodo-analogues are isostructural with the chloro-complex. All other bands remain sensibly constant in each of the spectra and are rhodium-ligand or internal ligand modes. Cycloocta-1, 5-diene adopts the cis-, cis- configuration in $\text{Rh}_2\text{Cl}_2(\text{COD})_2$ ⁸⁴. The band at 470 cm^{-1} in the infrared⁹⁶ and Raman⁹⁷ spectrum of this form of the free ligand was observed at 477, 472 and 464 cm^{-1} in the chloro-, bromo- and iodo-complexes respectively. The far-infrared was not examined and no bands were observed in the Raman spectrum below 400 cm^{-1} . Therefore although infrared-active only modes of the free ligand may occur below 400 cm^{-1} , the majority of halogen insensitive bands observed in

the spectra of the complexes are associated with skeletal vibrations. By comparison with $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$, the bands observed between $400\text{-}370\text{ cm.}^{-1}$ in $\text{Rh}_2\text{X}_2(\text{COD})_2$ are tentatively assigned to rhodium-COD stretching vibrations. The frequencies fall in the sequence Cl, Br, I, indicating a decreasing rhodium-ligand bond strength. Similarly, Chatt⁸⁷ concluded that the instability of $\text{Rh}_2\text{I}_2(\text{COD})_2$, relative to the chloro- and bromo-analogues, was not due to weakness at the bridge but at the rhodium-diene bonds. One band at 111 cm.^{-1} in the chloro-complex is not found in the other complexes but is too high to be assigned to $\nu(\text{Rh}_2\text{X}_2)$.

III-2.2. Bis(dicyclopentadiene)- $\mu\mu'$ -dihalogenodirrhodium; $\text{Rh}_2\text{X}_2(\text{dCPD})_2$, (X = Cl, Br).

The spectra of $\text{Rh}_2\text{X}_2(\text{dCPD})_2$ compare closely with those of the cycloocta-1, 5-diene complexes. Bands observed at 266, 250 and 187, 177 cm.^{-1} are assigned to $\nu(\text{RhCl})_b$ and $\nu(\text{RhBr})_b$, respectively, and $\text{Rh}_2\text{X}_2(\text{dCPD})_2$ are considered to have a planar bridge structure, (D_{2h}). No spectral data exist for the free ligand and assignment of the remaining bands

is not attempted. The position and intensity of these bands are comparable in both the complexes, except for a strong band at 317 cm.^{-1} in the chloro-complex which appears only weakly at 315 cm.^{-1} in the bromo-analogue.

III-2.3. Bis(norbornadiene)- $\mu\mu'$ -dihalogeno-dirhodium; $\text{Rh}_2\text{X}_2(\text{NBD})_2$, (X = Cl, Br).

Two bridge stretching modes, consistent with a planar bridge structure, are assigned in each complex.

$\nu(\text{RhCl})_b$ lie at 257 and 245 cm.^{-1} and $\nu(\text{RhBr})$ at 186 and 178 cm.^{-1} . Assignment of the lower $\nu(\text{RhCl})_b$ is not certain. Ligand or rhodium-ligand absorption at 248 cm.^{-1} (X = Br) is either at 252 or 245 cm.^{-1} (X = Cl). The other halogen insensitive bands shift to a slightly lower frequency on replacing Cl by Br and on this basis, the band at 245 cm.^{-1} is assigned to $\nu(\text{RhCl})_b$ and the bands at 252 cm.^{-1} in the chloro- and at 248 cm.^{-1} in the bromo-complex are considered comparable.

III-2.4. Tetrakis-(carbon monoxide)- $\mu\mu'$ -dichloro-dirhodium; $\text{Rh}_2\text{Cl}_2(\text{CO})_4$.

Three broad, very strong bands at 288 , 280 and

269 (sh) cm.^{-1} are assigned to $\nu(\text{RhCl})_b$ and are in agreement with the established "bent" bridge structure⁸⁵. All other bands in the spectrum are of weak to medium intensity and associated with skeletal modes of the $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ framework.

By comparison with $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ the weak band at 122 cm.^{-1} is assigned to $\pi(\text{Rh}_2\text{X}_2)$. This "in-plane" bend, A_1 , is Raman-active only in planar Rh_2X_2 systems. $\nu(\text{RhC}_2)$ is at 450, 444 cm.^{-1} and the Rh-C bending modes below 300 cm.^{-1} . Without the corresponding bromide it is not possible to assign the bending modes. Formal designation as in Table III-2 may be meaningless, the modes involving complex vibrations of the whole molecule.

III-2.5. Tetrakis-(ethylene)- $\mu\mu'$ -dihalogeno-dirhodium; $\text{Rh}_2\text{X}_2(\text{C}_2\text{H}_4)_4$, X = Cl, Br.

Three bands at 276, 262 and 252 cm.^{-1} in the chloro-complex which shift to 205, 194 and 183 cm.^{-1} in the bromo-complex are assigned to $\nu(\text{RhX})_b$. This is consistent with the "bent" bridge structure of rhodium carbonylchloride. In each complex, the outer $\nu(\text{RhX})_b$ are of strong intensity and the centre $\nu(\text{RhX})_b$ of medium intensity. The latter at 262 (X = Cl) and 194 cm.^{-1} (X = Br) may be symmetric

$\nu(\text{RhX})_b$, A_1 . Ethylene has no absorption below 800 cm.^{-1} ⁹⁸ and the remaining bands in the spectra are skeletal vibrations. Little is known of these modes and only $\nu(\text{RhC}_2)$ is assigned definitely near 400 cm.^{-1} . One band in $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ at 137 cm.^{-1} is not found in the bromo-complex and is assigned to the bridge 'in-plane' bend, $\delta(\text{Rh}_2\text{Cl}_2)$.

III-3. Conclusions.

There is a clear distinction in the far-infrared spectra of these complexes between the planar and "bent" bridge structures. The diene complexes, where $L = \text{COD}$, dCPD and NBD , all have two $\nu(\text{RhX})_b$ consistent with planar D_{2h} symmetry and $\text{Rh}_2\text{X}_2\text{L}_4$, $L = \text{CO}$, C_2H_4 , three $\nu(\text{RhX})_b$ consistent with "bent" C_{2v} symmetry. The bridge structure, C_{2v} , shows two further distinctions; firstly the spectra have a greater number of absorption bands reflecting the drop in symmetry from D_{2h} to C_{2v} and secondly, the bridge bending mode $\delta(\text{Rh}_2\text{Cl}_2)$ was observed, as required by theory.

$\nu(\text{RhX})$ are the strongest bands in the spectra and in consequence easily recognised. Their

frequency ranges are 289-245 and 205-176 cm.^{-1} for $X = \text{Cl}, \text{Br}$ respectively; these values are significantly lower than the corresponding vibrations of platinum and palladium. In a particular complex, the maximum separation between bridge frequencies is 24 cm.^{-1} compared with 60 cm.^{-1} in $\text{Pt}_2\text{X}_4\text{L}_2$. This reflects the symmetry of the Rh_2X_2 system influenced equally by the four donor ligands. Taking the mean of the

$\nu(\text{RhCl})_b$ frequencies, then the ligand sequence is;

$[\text{SnCl}_3]^- \sim \text{CO} > \text{COD} > \text{C}_2\text{H}_4 > \text{dCPD} > \text{NBD}$. The sequence for $\nu(\text{RhBr})$ is substantially the same except that

$[\text{SnBr}_3]^-$ is below ethylene. This difference in relative order is because bromine is less electro-negative than chlorine and consequently $[\text{SnBr}_3]^-$ has a higher inductive trans- effect than $[\text{SnCl}_3]^-$. Apart from $[\text{SnX}_3]^-$, the sequence reflects the π -bonding ability of the ligands and cannot be discussed in terms which enable direct comparison with the sequence of ligands in $\text{M}_2\text{X}_4\text{L}_2$, (Chapter II). For diene complexes, the significant drop in frequency for

$\nu(\text{RhX})_b$ as L is changed from COD to dCPD to NBD is unexpected in such closely related ligands. It is possible that the conformation adopted, for example,

by norbornadiene in $\text{Rh}_2\text{X}_2(\text{NBD})_2$ does not allow maximum overlap between rhodium hybrid orbitals and the π -electron density in the diene; this would weaken the trans - Rh-X bridge bonds and lower $\nu(\text{RhX})$ relative to the other diene and olefin complexes.

The most complete assignments of Rh-L vibrations are made for L = CO and C_2H_4 . Too little is known of ligand spectra to make similar assignments for the diene complexes. However $\nu(\text{Rh-COD})$ was found at 400-370 cm^{-1} and all the diene complexes have bands in the ranges 400-320 and 255-220 cm^{-1} . The former range may well be associated with $\nu(\text{Rh-L})$.

CHAPTER IV.

cis and trans- [PtX₄L₂].

IV-1. Introduction.

Study of halogen-bridged Pt(II) systems, (Chapters I and II), has shown that platinum-halogen stretching vibrations, $\nu(\text{PtX})$, can occur over the wide frequency range $365\text{--}260\text{ cm.}^{-1}$. Far-infrared spectra, to 70 cm.^{-1} , of twentyone octahedral cis- and trans- $[\text{PtX}_4\text{L}_2]$ complexes have now been recorded for comparison with Pt(II) systems. Empirical analyses of the spectra have been attempted, including assignment of platinum-halogen bending and platinum-ligand vibrations.

Complexes were prepared with ammonia, pyridine, dimethylsulphide, triethylphosphine and triethylarsine as the donating ligand. Generally both isomers were prepared by halogen oxidation of the corresponding Pt(II) complex.

IV-1.1. Theory.

For trans- $[\text{PtX}_4\text{L}_2]$, D_{2h} symmetry, (i.e. treating L as a monatomic group), the distribution of normal modes is $2A_{1g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$. Fig. IV-1 gives approximate schematic representations of these normal modes. Eight are infrared-active, $(2A_{2u} + 3E_u)$, and in terms of internal coordinates may

be described as in Table IV-1.

A similar treatment for cis- $[\text{PtX}_4\text{L}_2]$, C_{2v} symmetry shows $6A_1 + 2A_2 + 4B_1 + 3B_2$ as normal modes, (Fig. IV-2). All but the A_2 modes are infrared-active and are described in Table IV-2. The description of these modes is reasonable for the stretching modes but may be over-simplified for the bending modes, as all the latter involve changes in X-Pt-L angles. However it is reasonable to expect that in some cases the Pt-L or Pt-X contribution dominates.

There is the possibility, for both cis- and trans- forms, of interaction between vibrations of the same symmetry and some examples of this have been encountered.

The above treatment assumes that L may be regarded as a monatomic ligand. This is a reasonable assumption, as no evidence was found of splitting of degenerate modes or infrared-activity of otherwise inactive modes, for the metal-ligand vibrations. In addition to the PtX_4L_2 part of the spectrum there are also bands due to internal modes of the ligands and to $\nu(\text{PtLA})$, where A is the atom bonded to the donor

Fig. IV-1. Schematic representations of the normal modes of trans- $[\text{PtX}_4\text{L}_2]$.

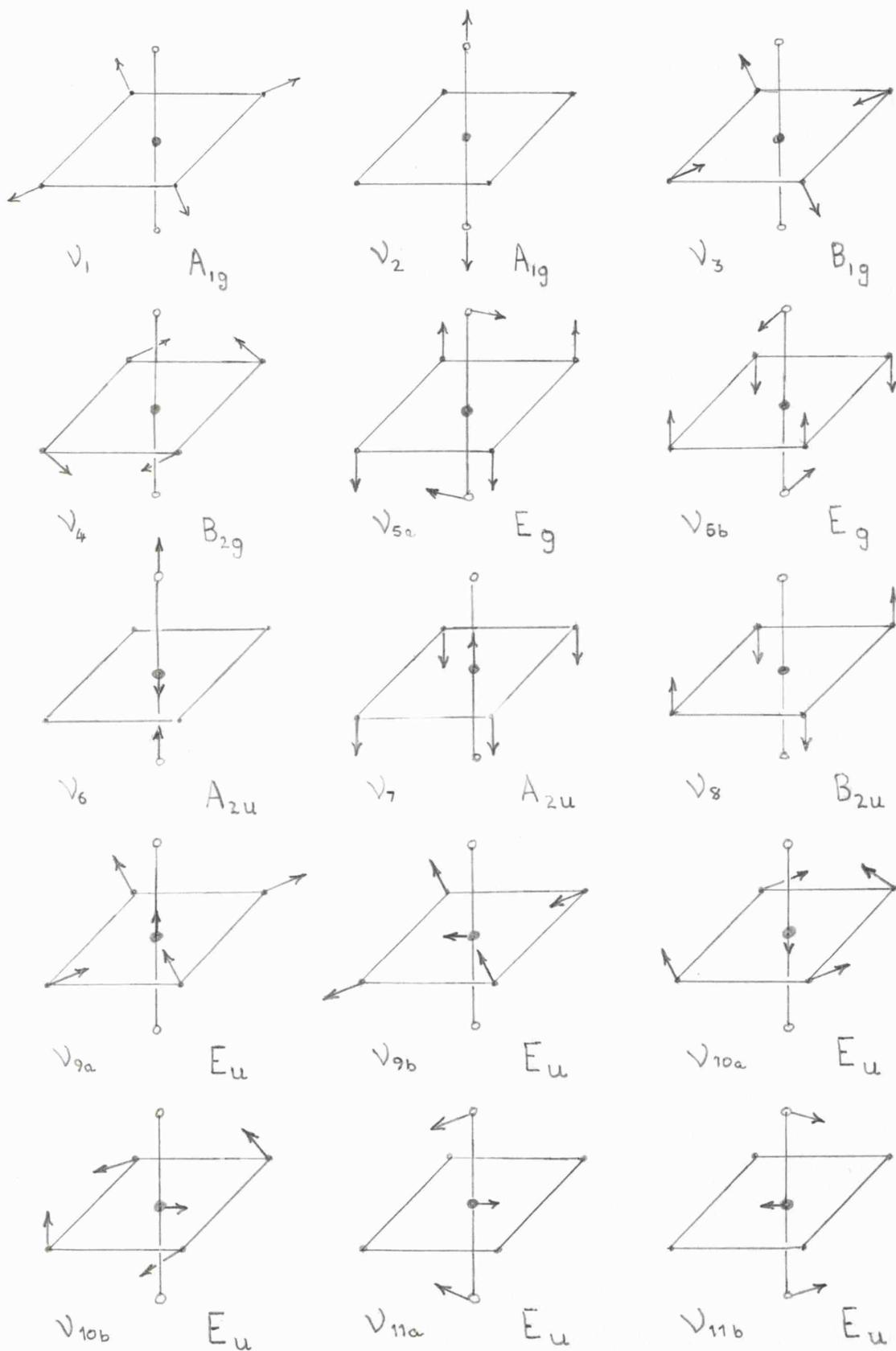


Fig. IV-2. Schematic representations of the normal modes of cis- $[\text{PtX}_4\text{L}_2]$.

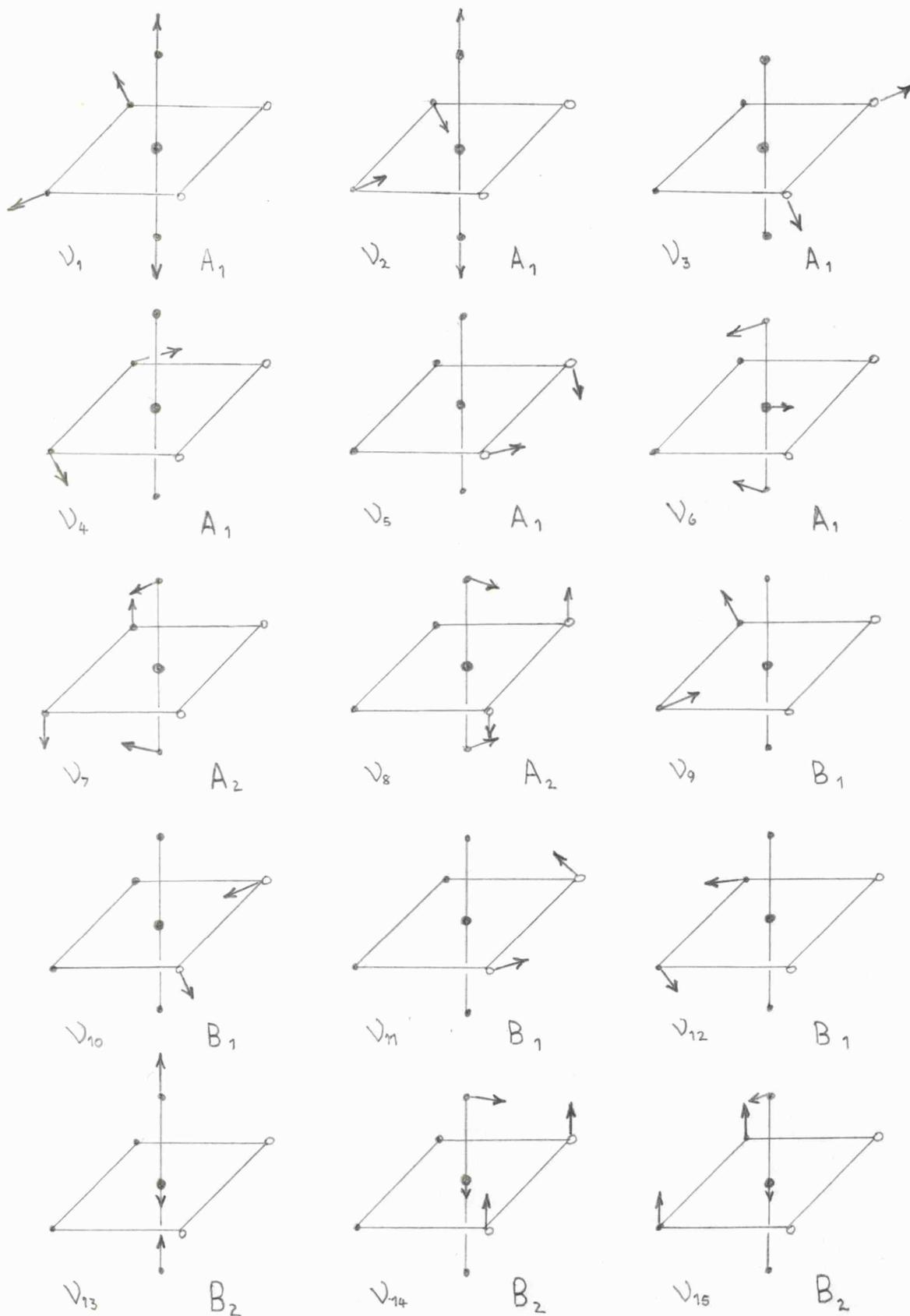


Table IV-1. Infrared-active modes of trans- $[\text{PtX}_4\text{L}_2]$.

Mode	Symmetry species	Approximate description of mode	
ν_6	A_{2u}	Platinum-ligand stretch,	$\nu(\text{PtL}_2)$.
ν_7	A_{2u}	Platinum-halogen out-of-plane bend,	$\kappa(\text{PtX}_4)$.
ν_{9a}	E_u	Degenerate platinum-halogen stretch,	$\nu(\text{PtX}_4)$.
ν_{9b}			
ν_{10a}	E_u	Degenerate platinum-halogen in-plane bend,	$\delta(\text{PtX}_4)$.
ν_{10b}			
ν_{11a}	E_u	Degenerate platinum-ligand bend,	$\delta(\text{PtL}_2)$.
ν_{11b}			

Table IV-2. Infrared-active modes of cis- $[\text{PtX}_4\text{L}_2]$.

Mode	Symmetry species	Approximate description of mode	
ν_1	A ₁	Platinum-halogen stretch,	$\nu(\text{PtX})$.
ν_2	A ₁	Platinum-halogen stretch,	$\nu(\text{PtX})$.
ν_3	A ₁	Platinum-ligand stretch,	$\nu(\text{PtL})$.
ν_4	A ₁	Platinum-halogen bend,	$\delta(\text{PtX})$.
ν_5	A ₁	Platinum-ligand bend,	$\delta(\text{PtL})$.
ν_6	A ₁	Platinum-halogen bend,	$\delta(\text{PtX})$.
ν_9	B ₁	Platinum-halogen stretch,	$\nu(\text{PtX})$.
ν_{10}	B ₁	Platinum-ligand stretch,	$\nu(\text{PtL})$.
ν_{11}	B ₁	Platinum-ligand wag,	$\rho_w(\text{PtL})$.
ν_{12}	B ₁	Platinum-halogen wag,	$\rho_w(\text{PtX})$.
ν_{13}	B ₂	Platinum-halogen stretch,	$\nu(\text{PtX})$.
ν_{14}	B ₂	Platinum-ligand rock,	$\rho_r(\text{PtL})$.
ν_{15}	B ₂	Platinum-halogen rock,	$\rho_r(\text{PtX})$.

atom. Thus, for ammonia, the vibration is $\delta(\text{PtNH})$, the ammonia rock near 800 cm.^{-1} and for a phosphine it is $\delta(\text{PtPC})$.

IV-1.2. Previous infrared studies of MX_4L_2 complexes.

Several infrared investigations⁹⁹⁻¹⁰¹ of cis- complexes, in which the central metal atom M was not platinum, have located more than one $\nu(\text{MCl})$ and other workers¹⁰²⁻¹⁰⁵ have identified the configurations of cis- and trans- $[\text{MX}_4\text{L}_2]$ by the number of $\nu(\text{MX})$ observed, Table IV-3. None of these studies covered the region below 200 cm.^{-1} and for cis- complexes, $\nu(\text{MX})$ have not been completely assigned.

Raman and theoretical data have provided some information on the frequency range of $\nu(\text{MX})$ in cis- $[\text{MX}_4\text{L}_2]$. These modes, $(2A_1 + B_1 + B_2)$, are all Raman-active and were assigned¹⁰⁶ in a Raman study of five coordinate $\text{SnCl}_4 \cdot \text{MeCN}$, (C_{2v}). Shifts at 396 and 388 cm.^{-1} were depolarised and assigned to the B_1 and B_2 modes respectively and those at 353 and 262 cm.^{-1} were polarised and assigned to $2A_1$. Transference of force constant data from $[\text{SnCl}_6]^{2-}$ directly to the SnCl_4 residue in cis- $[\text{SnCl}_4\text{L}_2]$, allowed Beattie¹⁰⁵ to calculate $\nu(\text{SnCl})$ as $A_1 = 310$ and 243 ,

Table IV-3. Relationship between stereochemistry and the number of $\nu(\text{MX})$ bands in MX_4L_2 complexes.

Complex.	$\nu(\text{MCL})$	Stereochemistry	Reference
$\text{GeCl}_4 \cdot 2\text{py}$ (a)	330 (vs,b)	<u>trans</u>	103
$\text{GeCl}_4 \cdot \text{bipy}$ (b)	330 (vs,b) ~300 vs	<u>cis</u>	103
$\text{SiCl}_4 \cdot 2\text{py}$	482 (s), 412 (s), 382 (s)	<u>cis</u>	102
$\text{TiCl}_4 \cdot 2\text{py}$	371 (s), 278 (m)	<u>cis</u>	104
$\text{TiCl}_4 \cdot \text{bipy}$	371 (s,b), 306 (w)	<u>cis</u>	104
$\text{TiCl}_4 \cdot \text{bipy}$	384, 366, (307)*	<u>cis</u>	99
$\text{SnCl}_4 \cdot 2\text{py}$	~324 (vs, b)	<u>trans</u>	103
$\text{SnCl}_4 \cdot \text{bipy}$	~327 (vs,b), ~280 (s,b)	<u>cis</u>	103
$\text{SnCl}_4 \cdot 2\text{SEt}_2$	321 (s)	<u>trans</u>	105
$\text{SnCl}_4 \cdot (\text{NMe}_3)_2$	319 (s)	<u>trans</u>	105
$\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$	341 (s)	<u>trans</u>	105
$\text{SiCl}_4 (\text{CH}_3\text{SCH}_2^-)_2$	327 (vs), 316 (vs), 288 (w)	<u>cis</u>	100
$\text{TiCl}_4 (\text{CH}_3\text{SCH}_2^-)_2$	385 (vs), 370 (vs), 309 (m)	<u>cis</u>	100
$\text{VCl}_4 (\text{C}_2\text{H}_5\text{SCH}_2^-)_2$	350 (vs), 333(vs), 275 (w)	<u>cis</u>	100
$\text{VCl}_4 (\text{bipy})$	366, 356, (301)	<u>cis</u>	99

(a) py = pyridine

(b) bipy = 2, 2'-bipyridyl

* Frequencies enclosed by brackets indicate tentative assignments of weak bands.

$B_1 = 332$ and $B_2 = 297 \text{ cm.}^{-1}$. These results were comparable to the Raman study¹⁰⁶ and as a consequence three fairly closely-spaced absorption bands plus one band at a lower frequency were predicted for $\nu(\text{SnCl})$ in cis- $[\text{SnCl}_4\text{L}_2]$. A normal coordinate analysis¹⁰⁷ of octahedral cis- and trans- $[\text{MX}_4\text{L}_2]$ showed a similar pattern of bands for cis- complexes when $M = \text{silicon}$ and $X = \text{F, Cl and Br}$.

Only two brief investigations have been made of platinum (IV) complexes. In $\text{PtCl}_4(\text{NH}_3)_2$ ¹¹, $\nu(\text{PtCl})$ was assigned at 350, 337 and 330 cm.^{-1} in the cis- complex and at 341 cm.^{-1} in the trans- complex. In cis- $[\text{MCl}_4\text{L}_2]$, ($M = \text{Pt, Zr and Hf}$), (Table IV-4), Ray and Westland⁴³ found three and in one case four $\nu(\text{PtCl})$ but some of the assignments are of doubtful value. They did not have the bromo-complex for comparison in every case and some of the ligand spectra are very complex.

IV-2. Results and Discussion.

The platinum-halogen vibrations are discussed for the trans- and then the cis- complexes; the platinum-ligand vibrations are discussed for both series together but evidence for the assignments is given

Table IV-4.

Assignments of $\nu(\text{PtCl})$ in cis- $[\text{PtCl}_4\text{L}_2]$ ⁴³.

Complex	$\nu(\text{PtCl})$			
PtCl ₄ . 2py	352 (vs)	343 (vs)	329 (vs)	
PtCl ₄ . bipy	346 (vs)	340 (vs)	330 (s)	290 (w)
PtCl ₄ . phen.	361 (s)	348 (vs)	324 (s)	
PtCl ₄ . diph.	345 (vs)	289 (vs)	272 (vs)	
PtCl ₄ . diars.	344 (s)	289 (vs)	270 (vs)	

py = pyridine; bipy = 2, 2'-bipyridyl; phen = 1, 10-phenanthroline; diph = 1, 2-bis (diphenylphosphino) ethane; diar = 1, 2 bis-(diphenylarsino)ethane.

in Chapter V. The infrared spectra are sketched in Figs. IV-3 to 6 and assignments of the recorded frequencies listed in Tables IV-5 to 9.

Pt-X vibrations were identified by their halogen sensitivity in chloro-, bromo- and iodo-analogues, which were assumed to be isostructural. The internal ligand and PtL vibrations remained sensibly constant in the spectra of related complexes.

Fig. IV-3.

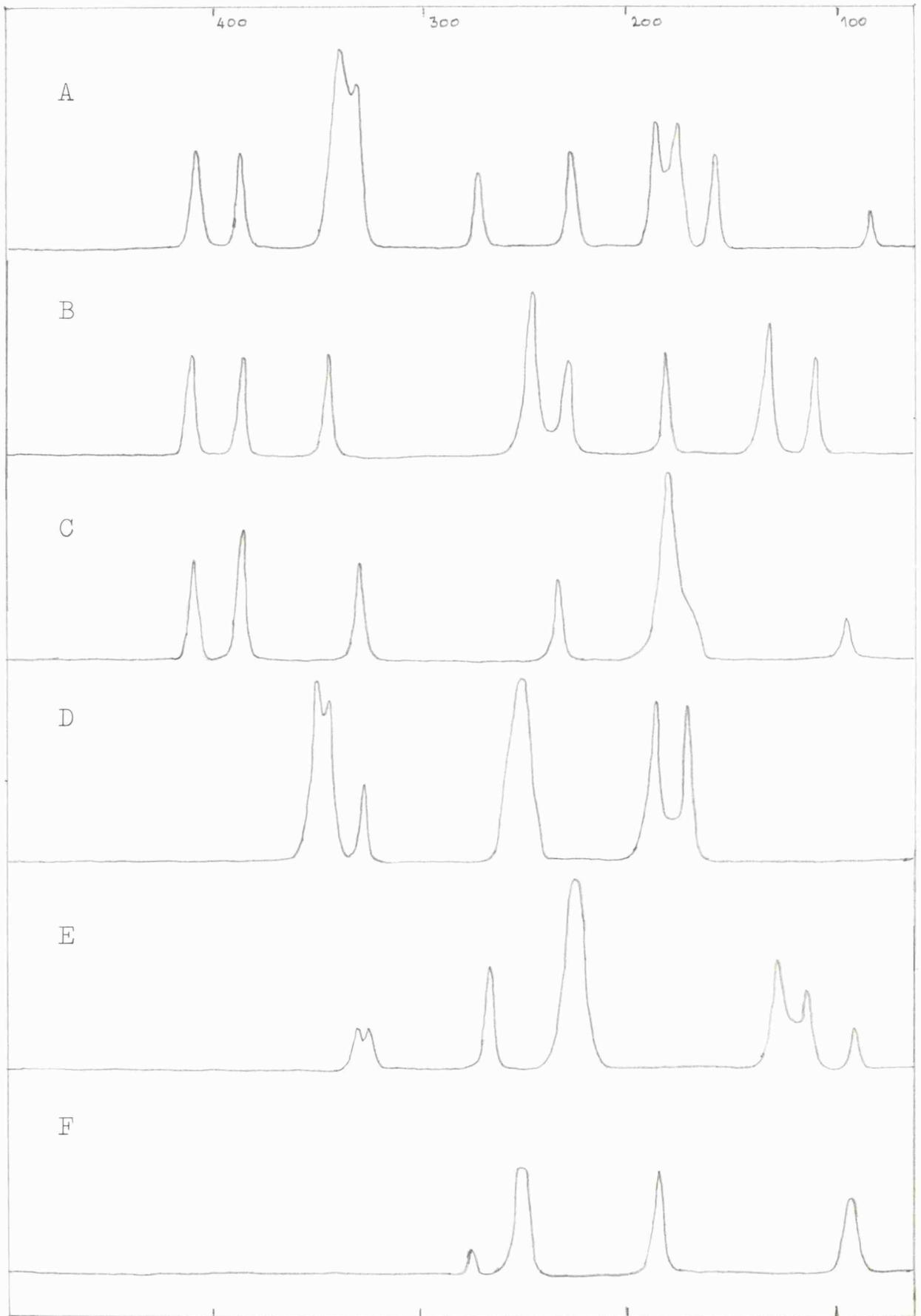


Fig. IV-3 (facing page)

Spectra sketches of trans- [PtX₄L₂].

- A. trans- [PtCl₄(PEt₃)₂] .
- B. trans- [PtBr₄(PEt₃)₂] .
- C. trans- [PtI₄(PEt₃)₂] .
- D. trans- [PtCl₄(NH₃)₂] .
- E. trans- [PtBr₄(NH₃)₂] .
- F. trans- [PtI₄(NH₃)₂] .

Fig. IV-4.

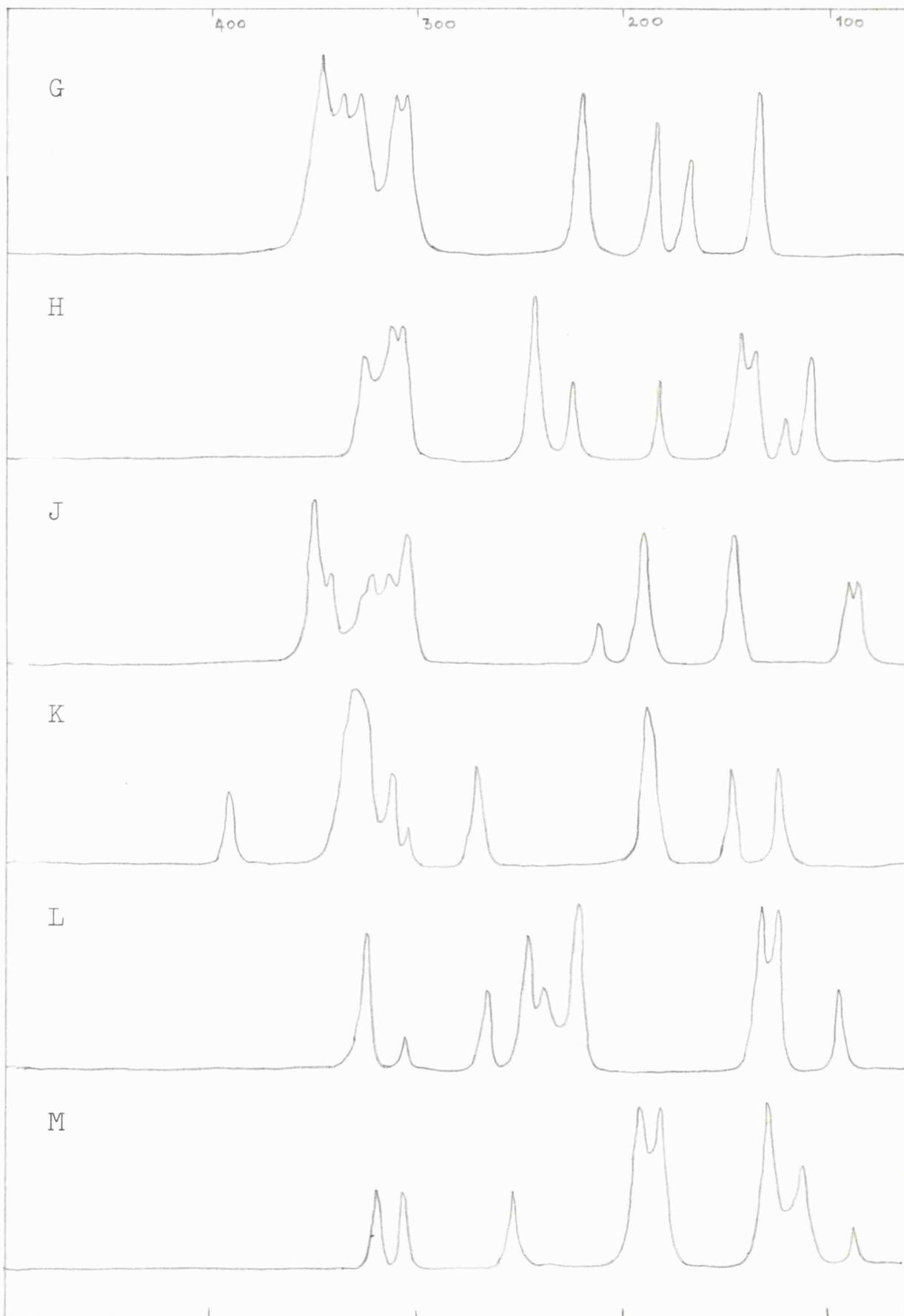


Fig. IV-4 (facing page)

Spectra sketches of $\text{trans-} [\text{PtX}_4\text{L}_2]$.

- G. trans- $[\text{PtCl}_4(\text{AsEt}_3)_2]$.
- H. trans- $[\text{PtBr}_4(\text{AsEt}_3)_2]$.
- J. trans- $[\text{PtI}_4(\text{AsEt}_3)_2]$.
- K. trans- $[\text{PtCl}_4(\text{SMe}_2)_2]$.
- L. trans- $[\text{PtBr}_4(\text{SMe}_2)_2]$.
- M. trans- $[\text{PtI}_4(\text{SMe}_2)_2]$.

Table IV-5. Frequencies and assignments of trans- [PtCl₄L₂].

Mode	Symmetry species	L =					K ₂ PtCl ₄ ³
		NH ₃	SMe ₂	PEt ₃	AsEt ₃		
ν(PtCl ₄)	E _u	352 (vs)	333 (vs, b)	340 (vs)	343 (vs)	326	
		346 (s)		334 (s)	337 (s)		
δ(PtCl ₄)	E _u	187 (s)	186 (s)	188 (ms)	183 (ms)	194	
π(PtCl ₄)	A _{2u}	174 (s)	146 (m)	159 (m)	168 (m)	175	
ν(PtL ₂)	A _{2u}	554 (w)	311 (m)	410 (m)	328 (s)		
		517 (wm)					
δ(PtL ₂)	E _u	253 (vs, b)	122 (m)	179 (ms)	137 (s)		
δ(PtLA)		N.I.	272 (m)	274 (wm)	220 (ms)		
Other bands		329 (wm)	392 (wm)	388 (m)	314 (s)		
			306 (vw)	229 (m)	308 (s)		
				83 (w)			

N.I. = not investigated.

Table IV-6. Frequencies and assignments of trans- $[\text{PtBr}_4\text{L}_2]$.

Mode	Symmetry species	L =					
		NH_3	SMe_2	PEt_3	AsEt_3	$\text{K}_2\text{PtBr}_4^6$	
$\nu(\text{PtBr}_4)$	E_u	267 (m)	245 (ms) 236 (wm) 220 (s)	247 (s)	242 (s)	233	
$\delta(\text{PtBr}_4)$	E_u	128 (m)	134 (s)	134 (ms)	137 (m)	135	
$\pi(\text{PtBr}_4)$	A_{2u}	115 (wm)	95 (wm)	109 (m)	107 (m)	107	
$\nu(\text{PtL}_2)$	A_{2u}	531 (w) 506 (w)	321 (ms)	411 (m)	325 (m)		
$\delta(\text{PtL}_2)$	E_u	228 (vs, b)	122 (s)	182 (m)	142 (ms)		
$\delta(\text{PtLA})$		N.I.	264 (wm)		223 (wm)		
Other bands		330 (w) 325 (w) 94 (w)	303 (vw)	386 (m) 344 (m) 230 (m)	314 (ms) 309 (ms) 182 (wm) 120 (w)		

N.I. = not investigated

* = see text.

Table IV-7. Frequencies and assignments of trans- $[\text{PtI}_4\text{L}_2]$.

Mode	Symmetry species	L =				
		NH_3	SMe_2	PEt_3	AsEt_3	
$\nu(\text{PtI}_4)$	E_u	183 (m)	187 (s) 179 (s)	181 (vs)	188 (ms)	
$\delta(\text{PtI}_4)$	E_u	94 (wm, b)	107 (m)	95 (w)	90 (wm)	
$\pi(\text{PtI}_4)$	A_{2u}	94 (wm, b)	83 (w)		85 (w-m)	
$\nu(\text{PtI}_2)$	A_{2u}	516 (wm) 507 (w)	319 (wm)	412 (m)	328 (sh) 321 (m)	
$\delta(\text{PtI}_2)$	E_u	249 (m, b)	128 (s)	181 (vs)	144 (ms)	
$\delta(\text{PtIA})$		N.I.	251 (wm)		210 (w)	
Other bands		278 (vw)	303 (wm)	384 (ms) 330 (m) 235 (wm)	348 (s) 341 (m) 314 (m) 309 (ms)	

-140-

N.I. = not investigated.

IV-2.1. Trans- $\left[\text{PtX}_4\text{L}_2 \right]$.

Varying the halogen in this series readily identified three bands in each spectrum which must be associated with Pt-X bonds. These are at frequencies close to the three infrared-active modes^{3,6} of the related $\left[\text{PtX}_4 \right]^{2-}$.

For each halogen, $\nu(\text{PtX}_4)$ lies in a narrow range and is almost insensitive to change of L. Thus, as the halogen is changed from chlorine to bromine to iodine, $\nu(\text{PtX}_4)$ is shifted from 352-340 to 250-240 to 190-180 cm.^{-1} respectively. These shifts are paralleled in K_2PtX_6 ⁶, (344, 240 and 186 cm.^{-1}), and in trans- $\text{K}_2 \left[\text{PtX}_2(\text{CN})_4 \right]$ ¹⁸, (347, 249 and 199 cm.^{-1}). The frequencies are close to the values found for Pt(II) complexes³³ and evidence of the marked insensitivity of $\nu(\text{PtX})$ to change of oxidation state, (cf. Group metals). In the chloro-complexes there is a strong band on the low-frequency side of $\nu(\text{PtCl}_4)$, which is assigned to $\nu(\text{Pt}^{37}\text{Cl}_4)$. In trans- $\left[\text{PtCl}_2(\text{NH}_3)_2 \right]$, Nakamoto et. al.¹⁰⁸ assigned a similar shoulder to the normally Raman-active, symmetric $\nu(\text{PtCl}_2)$. However, the relative intensity of the two bands and the constancy of their separation, (6 cm.^{-1}), are consistent with isotopic splitting. This same

splitting was observed in this work, (Chapter II), for $\text{Pt}_2\text{Cl}_4\text{L}_2$ complexes.

For trans- $[\text{PtBr}_4(\text{NH}_3)_2]$, the value of 267 cm.^{-1} for $\nu(\text{PtBr}_4)$ is anomalously high whilst the band at 228 cm.^{-1} is lower than would be expected for $\delta(\text{PtN}_2)$. By analogy with the chloro- and iodo-complexes $\delta(\text{PtN}_2)$ should be close to 250 cm.^{-1} ,

which would make it almost coincident with a "normal" $\nu(\text{PtBr})$ position, ($250\text{-}240 \text{ cm.}^{-1}$). Since both these vibrations are of the same symmetry, E_u , they interact and split apart as observed. Assignment of the higher frequency to $\nu(\text{PtBr})$ and the lower to $\delta(\text{PtN}_2)$ is arbitrary and each frequency must be a mixture of both types.

The dimethylsulphide complexes show some curious features. In trans- $[\text{PtCl}_4(\text{SMe}_2)_2]$, $\nu(\text{PtCl}_4)$ is at 333 cm.^{-1} and $\pi(\text{PtCl}_4)$ at 146 cm.^{-1} . Both these values fall outside the ranges found for the other Pt(IV) complexes. Trans- $[\text{PtBr}_4(\text{SMe}_2)_2]$ has three halogen-sensitive bands between 245 and 220 cm.^{-1} but only one $\nu(\text{PtS}_2)$ at 321 cm.^{-1} , (as expected for trans- complexes). Two samples of this compound, prepared by different methods, analysed correctly and

had identical spectra. Absorption in this region cannot be assigned to a mode of dimethylsulphide¹⁰⁹, but it is possible that a combination mode might interact with $\nu(\text{PtBr}_4)$ and become abnormally intense. In D_{4h} no first overtones are infrared-active and only combinations between modes of g and u-symmetry are allowed in the infrared. These must be of the type $(A \text{ or } B)_{u,g} \times E_{g,u} = E_u$ if they are to interact with $\nu(\text{PtBr}_4)$. One reasonable possibility is $A_{2u} \times E_g$ where the A_{2u} mode is $\pi(\text{PtBr}_4)$ at 95 cm.^{-1} and E_g is the Raman-active skeletal bend, which would therefore be placed at c.a. 140 cm.^{-1} . In trans- $[\text{PtI}_4(\text{SMe}_2)_2]$, two $\nu(\text{PtI}_4)$ are observed at 187 and 179 cm.^{-1} . Solution spectra would confirm whether this was due to solid state effects or to interaction with modes of the same species.

In the chloro- and bromo- complexes $\delta(\text{PtX}_4)$ is at 185 ± 3 and $133 \pm 5 \text{ cm.}^{-1}$ respectively. The frequencies show little variation as the ligand is changed and correlate well with values found for square-planar anions $[\text{PtX}_4]^{2-}$ ^{3,6}, at 194 and 135 cm.^{-1} . Assignments of $\delta(\text{PtI}_4)$ are tentative as a frequency range has not previously been established for this mode.

The out-of-plane bend, $\pi(\text{PtX}_4)$, vibrates in the PtL_2 plane and, as expected, shows some dependence upon L. $\pi(\text{PtX}_4)$ falls in the sequence NH_3 , AsEt_3 , PEt_3 , SMe_2 except that for the bromides the value is about the same for both phosphine and arsine and $\pi(\text{PtI}_4)$ was not observed in trans- $[\text{PtI}_4(\text{PEt}_3)_2]$.

IV-2.2. cis- $[\text{PtX}_4\text{L}_2]$.

Theory shows that Pt-X and Pt-L vibrations may interact for this class of molecule. However the marked halogen-sensitivity of some bands and the equally marked stability of others observed in the spectra, allow a distinction to be made between the two types of mode, with the few exceptions mentioned below. Thus $\nu(\text{PtX})$, $\delta(\text{PtX})$, $\nu(\text{PtL}_2)$ and $\delta(\text{PtL}_2)$ are assigned in all complexes. The wagging and rocking vibrations, (ν_{11} , ν_{12} , ν_{14} and ν_{15}), which are not assigned are probably coupled and vibrations of the PtX_4L_2 framework. The spectra of the complexes are sketched in Fig. IV-5 to 6 and the assignments made are listed in Tables IV-8 to 9.

Four $\nu(\text{PtX})$ bands were found for all the complexes. The general pattern is three bands fairly

Fig. IV-5.

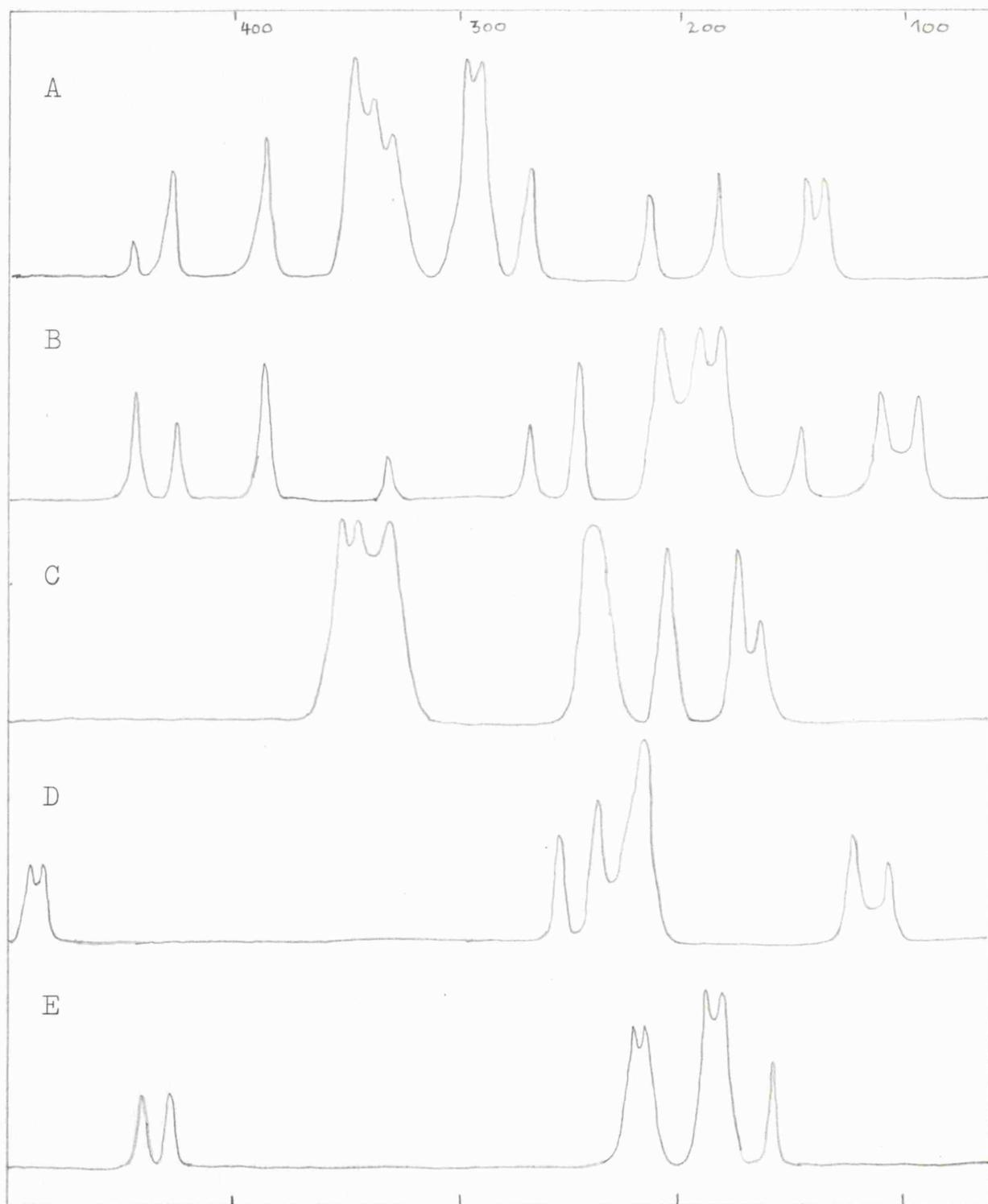


Fig. IV-5. (facing page).

Spectra sketches of $\text{cis-} [\text{PtX}_4\text{L}_2]$.

- A. cis- $[\text{PtCl}_4(\text{PEt}_3)_2]$.
- B. cis- $[\text{PtBr}_4(\text{PEt}_3)_2]$.
- C. cis- $[\text{PtCl}_4(\text{NH}_3)_2]$.
- D. cis- $[\text{PtBr}_4(\text{NH}_3)_2]$.
- E. cis- $[\text{PtI}_4(\text{NH}_3)_2]$.

Fig. IV-6.

Spectra sketches of cis- [PtX₄L₂].

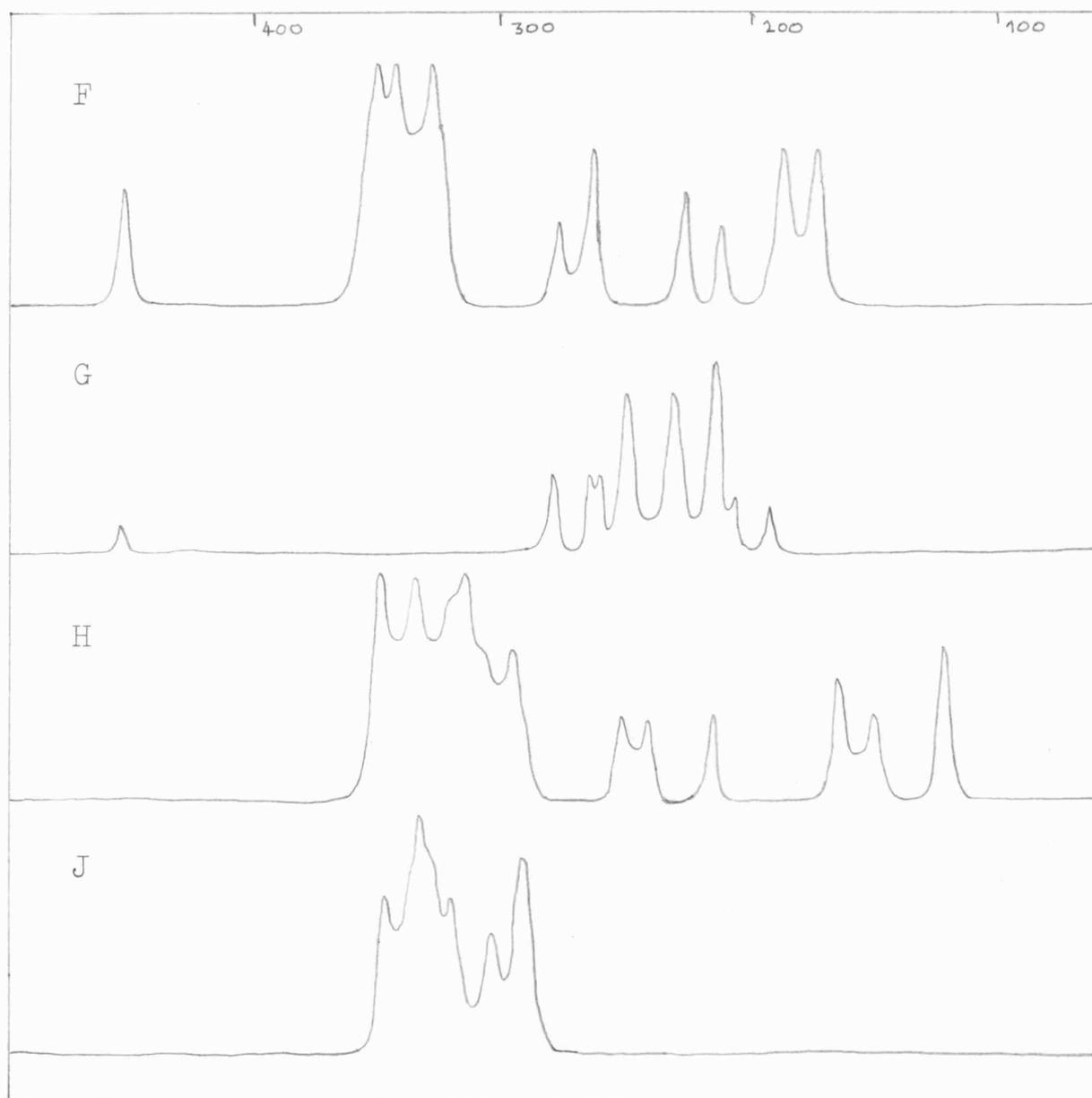


Table IV-8. Frequencies and assignments of *cis*-[PtCl₄L₂].

Mode	Symmetry species	L =				
		NH ₃	Py	SMe ₂	PEt ₃	AsEt ₃
ν(PtCl)	B ₂	353 (vs)	353 (vs)	*	345 (vs), 336 (sh)	**
	A ₁	344 (vs)	345 (vs)	350 _{to}	298 (vs)	346-285 (vs)
	B ₁	330 (vs)	332 (vs)	298 (vs)	291 (vs)	
	A ₁	206 (s)	232 (m)	218 (wm)	215 (wm)	
δ(PtCl)	A ₁	177 (s)	190 (ms)	168 (m)	144 (m)	
	A ₁	161 (m)	177 (ms)	153 (wm)	137 (m)	
	B ₁	558 (w)	280 (wm)	350-	444 (w)	**
	A ₁	518 (m)	267 (ms)	298 (vs)	428 (m)	346-285 (vs)
δ(PtL ₂)	A ₁	240 (vs, b)		124 (ms)	183 (m)	
δ(PtLA)		N.I.		253, 241 (wm)	267 (m)	
Other bands			454 (m)		386 (ms)	
			216 (wm)		330 (ms)	

* Bands at 350 (vs), 337 (vs), 323 (sh), 319 (vs), 313 (sh), 298 (ms); see text.

** Bands at 346 (ms), 337 (vs), 331 (sh), 321 (ms), 304 (m), 294 (s); see text.

N.I. = not investigated.

Table IV-9. Frequencies and assignments of cis- $[\text{PtX}_4\text{L}_2]$.

Mode	Symmetry species	X = Br, L =			X = I
		NH ₃	Py	PEt ₃	
$\nu(\text{PtX})$	B ₂	255 (m)	255 (ms)	246 (ms)	215 (ms)
	A ₁ } B ₁ }	238 (ms)	236 (ms)	209 (s)	189 (s)
	A ₁	219 (vs,b)	218 (s)	192 (s)	180 (s)
	A ₁	183 (s)	198 (w)	144 (wm)	159 (m)
$\delta(\text{PtX})$	A ₁ } A ₁ }	122 (m)		110 (m)	
		107 (wm)		94 (m)	
$\nu(\text{PtL}_2)$	B ₁ } A ₁ }	492 (wm)	282 (wm)	444 (m)	440 (wm)
		485 (wm)	267 (wm), 263 (wm)	425 (wm)	429 (wm)
$\delta(\text{PtL}_2)$	A ₁	219 (vs,b)		182 (s)	220 (ms)
$\delta(\text{PtLA})$		N.I.		266 (wm)	
Other bands			456 (vw)	387 (ms)	
			212 (w)	330 (w)	

close together followed by a further band much lower in frequency. This is comparable with the results of previous studies^{106,107} (Section IV-1.2). The highest $\nu(\text{PtX})$ is not sensitive to L and was found at 349 ± 4 and $250 \pm 5 \text{ cm.}^{-1}$ for X = Cl and Br respectively. This band was assigned to the anti-symmetric stretch of the trans- [X-Pt-X] system. In the comparable complexes trans- $\text{K}_2 [\text{PtCl}_2(\text{CN})_4]$ ¹⁸, the corresponding modes are at 349 and 249 cm.^{-1} ; very similar values were also found for trans- $[\text{PtX}_4\text{L}_2]$, (Tables IV-5 and 6). Two of the $\nu(\text{PtX})$ are markedly sensitive to change of L, reminiscent of the behaviour of $\nu(\text{PtX})$ in cis- $[\text{PtX}_2\text{L}_2]$ complexes in which the position of $\nu(\text{PtX})$ is directly related to the trans- effect of the ligand L³³. These two modes are therefore assigned as the symmetric and antisymmetric stretching frequencies of the Pt-X bonds trans to the donor ligands. They are close to the values reported for the Pt(II) series, Table IV-10.

The independent variation of these two bands is taken as evidence that the modes are not significantly coupled to the others of the same symmetry. Previous Raman¹⁰⁶ and infrared¹⁰⁰ studies of cis- $[\text{MCl}_4\text{L}_2]$

Table IV-10.

$\nu(\text{PtX})$ in $\text{cis-} [\text{PtX}_2\text{L}_2]$ and $\text{cis-} [\text{PtX}_4\text{L}_2]$.

L	$\text{cis-} [\text{PtX}_2\text{L}_2]$.		$\text{cis-} [\text{PtX}_4\text{L}_2]$.	
	X = Cl	X = Br	X = Cl	X = Br
NH_3	326	224, 221	344, 330	238, 219
PEt_3	303, 281	212, 194	298, 291	209, 192

complexes assigned the higher of the two $\nu(\text{MX})$ to the antisymmetric mode, B_1 . In this study, the two $\nu(\text{PtCl})$ are of equal intensity and identification of either of the bands as the A_1 or B_1 species does not cause differing interactions with the other modes and thus precise assignment is not possible. However in $\text{cis-} [\text{PtBr}_4(\text{NH}_3)_2]$, assignment of the higher $\nu(\text{PtBr})$ at 238 cm.^{-1} to the A_1 mode allows the observed coincidence of $\nu(\text{PtBr})$, B_1 , and $\delta(\text{PtN}_2)$, A_1 , at 219 cm.^{-1} . Finally the low $\nu(\text{PtX})$ band is assigned to the symmetric, A_1 , $\nu(\text{PtX}_2)$ of the trans- $[\text{X-Pt-X}]$ system. These $\nu(\text{PtCl})$ at 224 ± 9 and $\nu(\text{PtBr})$ at 200 to 140 cm.^{-1} are the lowest frequencies

recorded for Pt-X vibrations, whether terminal or bridged. The intensity of the bands varies from weak to strong. This is unusual in Pt-X vibrations and may be associated with the symmetric nature of the mode. In cis- $[\text{PtCl}_4(\text{NH}_3)_2]$ a further example of near accidental degeneracy and consequent interaction probably occurs. Two bands of equal intensity are observed at 240 and 206 cm.^{-1} . Comparison with the bromo-complex shows that $\delta(\text{PtN}_2)$ is near 220 cm.^{-1} and the lowest $\nu(\text{PtBr})$ at 183 cm.^{-1} ; the normal chloride/bromide shift would therefore place $\nu(\text{PtCl})$ near 230 cm.^{-1} . Since both these vibrations are of A_1 symmetry they will interact giving the two observed anomalous positions in the chloride complex and bringing the A_1 $\nu(\text{PtCl})$ in line with that of the pyridine complex. The $\nu(\text{PtBr})/\nu(\text{PtCl})$ ratios for this mode when L = pyridine and ammonia are 0.8 compared with ratios of 0.7 for all other $\nu(\text{PtBr})$, $\nu(\text{PtCl})$ pairs in these complexes. No alternative assignments are possible; there is no absorption below 198 cm.^{-1} in cis- $[\text{PtBr}_4(\text{py})_2]$ and alternative assignment of the band at 183 cm.^{-1} in cis- $[\text{PtBr}_4(\text{NH}_3)_2]$ is not tenable.

In cis- $[\text{PtCl}_4\text{L}_2]$, $\text{L} = \text{AsEt}_3, \text{SEt}_2$, both $\nu(\text{PtCl})$ and $\nu(\text{PtL})$ lie in the same narrow frequency range and the possibility of substantial "mixing" must be considered. Six strong bands or shoulders are observed between 350 and 285 cm.^{-1} in each complex and must contain $\nu(\text{PtL})$. It is possible, in view of the way in which many $\nu(\text{PtCl})$ and $\nu(\text{PtL})$ modes in this series appear to behave independently, that two of the bands really do correspond to $\nu(\text{PtL})$ but a normal coordinate analysis is required to confirm this.

In cis- $[\text{PtI}_4(\text{NH}_3)_2]$, four $\nu(\text{PtI})$ were found in the range 215 to 159 cm.^{-1} . These values extend both the upper and lower range of known frequencies for terminal $\nu(\text{PtI})$.

IV-2.3. Platinum-ligand vibrations.

The Pt-L vibrations in this series of complexes are $\nu(\text{PtN})$ for amines and pyridines, $\nu(\text{PtS})$, $\nu(\text{PtP})$, $\nu(\text{PtAs})$ and the related bending vibrations. Apart from $\nu(\text{PtNH}_3)$ which has been identified many times previously, the method of assignment for platinum-ligand modes is discussed in Chapter V and is not repeated here.

The two $\nu(\text{PtN})$ in the pyridine complexes (280-265 cm.^{-1}) are consistent with cis- structure and comparable with Clark and Williams assignment for cis- and trans- $[\text{PtX}_2\text{py}_2]$ ¹¹⁰. In $\text{PtX}_4(\text{NH}_3)_2$, $\nu(\text{PtN})$ and $\delta(\text{PtN})$ are found in the normal frequency range of these vibrations; but $\delta(\text{PtN})$ was observed to have a characteristic appearance. It is strong, broad and roughly gaussian in shape. Nakamoto et. al.¹⁰⁸ found a slight drop in $\nu(\text{PtN})$ with change of X for trans- $[\text{PtX}_2(\text{NH}_3)_2]$, which became more pronounced in the cis- series ($\Delta\nu$ up to 30 cm.^{-1}). This effect is many times greater in the Pt(IV) series; thus the two $\nu(\text{PtN})$ bands in cis- $[\text{PtX}_4(\text{NH}_3)_2]$ drop by 118 and 89 cm.^{-1} respectively on replacing chloride by iodide. Surprisingly, trans- $[\text{PtX}_4(\text{NH}_3)_2]$ are unique in having two $\nu(\text{PtN})$ bands (as was found first by Le Postollec¹¹), but these are lowered only by 38 and 10 cm.^{-1} on replacing chloride by iodide.

In trans- $[\text{PtX}_4(\text{SMe}_2)_2]$, $\nu(\text{PtS})$ is found between 320-310 cm.^{-1} . It is readily assigned in the bromides and iodides where the region is otherwise clear. As discussed previously, the complex spectrum

of cis- $[\text{PtCl}_4(\text{SMe}_2)_2]$ precludes assignment of $\nu(\text{PtS})$. All the dimethylsulphide complexes have further absorption near 250 cm.^{-1} and 120 cm.^{-1} . The ligand has no absorption below 170 cm.^{-1} and the 120 cm.^{-1} bands are assigned to $\delta(\text{PtS})$. The only values in the literature for $\delta(\text{MS}_2)$ are 155, 145 cm.^{-1} for $[\text{MoS}_4]^{2-}$ and $[\text{WS}_4]^{2-}$ respectively¹¹¹. Absorption near 250 cm.^{-1} could be either methyl torsions raised from 180 cm.^{-1} in the vapour-phase spectrum of the ligand¹⁰⁹ or $\delta(\text{PtSC})$. However such a large shift in the torsional mode is unlikely and the latter assignment is consistent with others made for phosphine and arsine complexes.

The $\nu(\text{PtP})$ bands are found in all phosphine complexes and show the predicted correlation with symmetry of complexes. For both cis- and trans- $[\text{PtX}_4(\text{PEt}_3)_2]$, $\nu(\text{PtP})$ is insensitive to halogen; but the two $\nu(\text{PtP})$ in the cis-isomers are higher in frequency than in the trans-isomers. A similar effect was found for Pt(II) complexes and in addition values for the two series are almost identical, (Chapter V). Additional bands are found near 260 and 180 cm.^{-1} in the complexes and are assigned to

$\delta(\text{PtPC})$ and $\delta(\text{PtP})$ respectively. These $\delta(\text{PtP})$ values are close to those of $\delta(\text{PtP})$ and $\pi(\text{PtP})$ found, in this work, in $[\text{Pt}(\text{PEt}_3)_4]^{2+}$; there are no $\delta(\text{MP})$ assignments in the literature, except for $\text{M} = \text{Ni}(\text{O})$.

Arsine and phosphine complexes behave similarly and an analogous assignment for trans- $[\text{PtX}_4(\text{AsEt}_3)_2]$ is given in Tables IV-5 to 7. Unfortunately, for cis- $[\text{PtCl}_4(\text{AsEt}_3)_2]$, $\nu(\text{PtAs})$ is not distinguished from $\nu(\text{PtCl})$ and comparisons with the trans-complexes cannot be made.

IV-3. Conclusions.

For trans- $[\text{PtX}_4\text{L}_2]$ complexes the far-infrared spectra can be interpreted as a superposition of the spectra of square-planar $[\text{PtX}_4]^{2-}$ and linear LPtL ; halogen-sensitive modes are close to those for $[\text{PtX}_4]^{2-}$. The cis-series have $\nu(\text{PtX})$ in the regions $353\text{-}206\text{ cm.}^{-1}$, $255\text{-}144\text{ cm.}^{-1}$ and $215\text{-}159\text{ cm.}^{-1}$ for $\text{X} = \text{Cl}, \text{Br}, \text{I}$ respectively. These ranges therefore include those associated with $\nu(\text{PtX})_b$ in bridged $\text{Pt}(\text{II})$ complexes (Chapter II) and extend the ranges for terminal platinum-halogen stretching frequencies below those previously established. The pronounced ligand dependence of two of the $\nu(\text{PtX})$ modes in cis- complexes

is associated, as in the cis-platinum (II) complexes, with the trans-effect of L; in both series for example, triethylphosphine causes $\nu(\text{PtX})$ to fall to very low values. The many assignments of Pt-X bending modes in both series of complexes have considerably extended knowledge of these modes. In fact these are the first assignments of Pt-Br and Pt-I bending modes for platinum-complexes containing donor ligands, L.

As predicted by theory, two $\nu(\text{PtL})$ are found for all cis-complexes and with the exception of trans- $[\text{PtX}_4(\text{NH}_3)_2]$, a single mode for the trans-complexes. In cis- $[\text{PtX}_4(\text{NH}_3)_2]$, $\nu(\text{PtN})$ show a dramatic dependence upon the halogen, but $\nu(\text{PtP})$ in the cis-phosphine complexes are halogen-insensitive. This is in good agreement with the theory of the trans-effect, since in the ammine complexes, the halogens exert a trans-effect on the ammine groups increasing in the order Cl, Br, I. However, for cis- $[\text{PtX}_4(\text{PEt}_3)_2]$ it is the phosphine which exerts a trans-effect on the halogens. Platinum-ligand bending modes are assigned in both cis- and trans-complexes and values are consistent with the general rule that bending modes

appear at very approximately half the frequency of the related stretching modes, (Chapter V).

There is little evidence of interaction between $\nu(\text{PtX})$ and $\nu(\text{PtL})$ in the cis-complexes except when they are of the same magnitude. It is probable that the great mass of the platinum atom acts to minimise coupling.

CHAPTER V.

Metal-ligand vibrations.

V-1. Introduction.

This chapter is concerned with M-L vibrations where L = S, Se, Te, P, As, pyridine and olefins. The range of ligands discussed is limited to those which have been studied in this thesis. M-NH₃ bond vibrations have been the subject of definitive work^{163,164} and their assignment in cis- and trans- [PtX₄(NH₃)₂] requires no discussion.

Assignments of M-L vibrations made in this work are based upon evidence from several sources. A detailed review is made of relevant data in the literature on both metal-ligand and low frequency ligand vibrations. Infrared spectra are recorded for several Pt(II) complexes and correlated with the data from Chapters II to IV. This mass of evidence has enabled definite assignments for metal-ligand vibrations to be made. The assignments are more complicated than for metal-halogen vibrations because, with few exceptions, L is a complex molecular system in which vibrations other than $\nu(\text{ML})$ or $\delta(\text{ML})$ complicate the spectra. The ligands themselves often have low-frequency deformation or torsional modes, e.g. SMe₂, and the internal vibrations of the ligands

may interact with metal-ligand vibrations giving rise to complex molecular modes. Whereas replacement of chloride by bromide leads to ready assignment of $\nu(\text{MX})$, replacement of (say) PR_3 by AsR_3 alters not only $\nu(\text{MP})$ but also $\delta(\text{CPC})$ and $\delta(\text{MPC})$. The difficulty remains then of distinguishing between the two. In general, however, complex formation does not alter the symmetry of the free ligand and its internal modes may be recognised in the complex spectra. Thus assignment of metal-ligand vibrations is reduced to identifying bands additional to those of L and distinguishing between stretching and bending modes.

V-2. Metal-sulphur vibrations.

The simplest systems are when the sulphur atom only is the ligand. The highest vibrational fundamentals for binary metal sulphides, MS , ($\text{M} = \text{Zn}, \text{Cd}$ and Hg) are at 310, 220¹³⁴ and 349 cm^{-1} ¹³⁵ respectively. They show the expected decrease from Zn to Cd but HgS (cinnabar form) has a higher frequency than ZnS due to the tendency to linear two coordination of $\text{Hg}(\text{II})$. The authors of a recent far-infrared study¹³⁶ of $\text{M}'_2[\text{MoS}_4]$ and $\text{M}'_2[\text{WS}_4]$, ($\text{M}' = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ and Tl), assigned $\nu(\text{MS})$ and for

the first time $\delta(\text{SMS})$. For molybdenum and tungsten, $\nu(\text{MS})$ is at 480 and 466 cm^{-1} and $\delta(\text{SMS})$ at 155 and 145 cm^{-1} respectively.

In thiocyanato complexes, modes associated with the SCN system are easily identified by comparison with the spectra of simple salts such as KSCN. For the metal-sulphur vibrations, $\delta(\text{SMS})$ will probably lie below 150 cm^{-1} , but the relative positions of $\nu(\text{MS})$ and $\delta(\text{MSC})$ are less certain. On the assumption that $\nu(\text{MS})$ is the higher of the two, Sabatini and Bertini¹³⁷ assigned $\nu(\text{MS})$, (M = Pt, Pd, Au and Hg), in the range 305-280 cm^{-1} . Allowing for cation differences, these values are in good agreement with those obtained by Forster and Goodgame¹³⁸ for comparable complexes, except for $\text{K}_2 [\text{Hg}(\text{SCN})_4]$ where there is complete disagreement on the spectrum observed (Table V-1). The complexes $\text{M}^{\text{II}} [\text{Hg}(\text{SCN})_4]$, (M = Mn, Fe, Co and Zn)¹³⁸, which contain bridging thiocyanate groups, all have a band of medium intensity in the range 219-213 cm^{-1} . These bands have been tentatively assigned to $\nu(\text{HgS})$ as the possibility of assignment to $\delta(\text{HgSC})$ does exist.

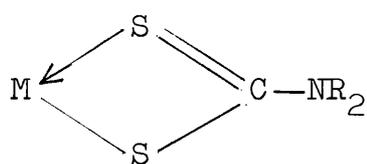
The infrared spectra (400-135 cm^{-1}) of a number of transition metal thiourea complexes have

been studied,¹³⁹ in which thiourea is coordinated through the sulphur atom. These systems are particularly suitable for observation of $\nu(\text{MS})$ since no internal modes of the ligand occur below 400 cm.^{-1} .¹⁴⁰ $\nu(\text{MS})$ was observed in the range $300\text{--}200 \text{ cm.}^{-1}$, although some of the assignments are in doubt. It was found that complexes with tetrahedral geometry have frequencies which are higher than those of octahedral, but lower than those of planar complexes. Walton¹⁴¹ has tentatively assigned $\nu(\text{MS})$ in a similar region, $290\text{--}265 \text{ cm.}^{-1}$, for MCl_2L_2 where $\text{M} = \text{Pt, Pd}$ and $\text{L} = 1, 4\text{-thioxane}$.

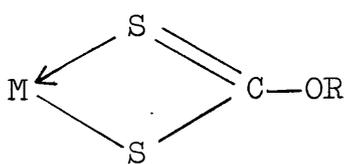
Bidentate ligands introduce difficulties associated with ring vibrations. Thus empirical band assignments based upon the concept of group frequencies are not applicable to chelate ring systems, since coupling between various vibrational modes is anticipated. This point is well illustrated in two important studies, assisted by normal coordinate analysis, made by Nakamoto et. al. of the in-plane vibrations of dithiocarbamate¹⁴² and dithiooxalate¹⁴³ systems. For the former system, the potential energy distribution amongst the internal coordinates shows

that the band at 375 cm.^{-1} may be accurately described as $\nu(\text{PtS})$. In contrast, two further absorptions at 560 and 288 cm.^{-1} are complex normal modes involving both Pt-S bond stretching and ring deformation. The contribution of the ring mode dominates in the 560 cm.^{-1} band, the converse being true for the 288 cm.^{-1} band. $\nu(\text{MS})$ is shifted to higher frequencies as the metal is changed in the order Pt(II), Pd(II), Ni(II), Co(III), Cr(III) and Cd(II). However for the dithiooxalates, it is a good approximation to describe two bands as due to $\nu(\text{PtS})$, viz., 322 cm.^{-1} and a doublet at $436, 422 \text{ cm.}^{-1}$ split by interaction between the rings. Further weak bands at ca. 515 cm.^{-1} are due to a coupling mode between the CO bending, ring deformation and Pt-S bond stretching vibrations. In two recent studies of chelate sulphur systems, the empirical assignments made are based upon the above analyses. Watt and McCormick¹⁴⁴ investigated the spectra, to 200 cm.^{-1} , of methyl and ethyl xanthate complexes which are closely related to the dithiocarbamates, (Fig. V-1). Two bands in the regions $385\text{-}330$ and $350\text{-}310 \text{ cm.}^{-1}$ respectively, were assigned to $\nu(\text{MS})$, Table V-2. The assignment of the higher

Fig. V-1.



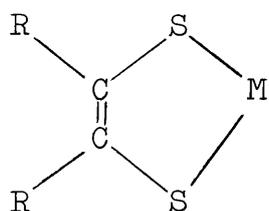
dithiocarbamate



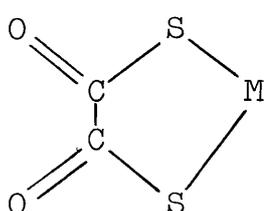
xanthate

frequency band is definite but of the lower only tentative. Schrauzer and Mayweg¹⁴⁵ have assigned bands near 400 and 350 cm.^{-1} in dithietene complexes $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2$, (Table V-2), to $\nu(\text{MS})$ by analogy with results for dithiooxalato complexes¹⁴³. However the bonding, and hence the vibrational interactions, in the dithietenes is very different from that in dithiooxalates, (Fig. V-2). Complexes with ligands of the type $\text{RS}(\text{CH}_2)_n\text{SR}$ have been studied in the

Fig. V-2.



dithietene



dithiooxalate

Table V-1. ν (MS) frequencies for thiocyanato complexes.

	K^+	NEt_4^+	NMe_4^+	K^+
$[Pd(SCN)_4]^{2-}$	300 (w) 286 (m)	294 (m)	294 (sh) 289 (m)	
$[Pt(SCN)_4]^{2-}$	293 (w) 283 (m)		280 (m)	
$[Pt(SCN)_6]^{2-}$	291 (wm) 281 (m)	283 (ms)	282 (m)	
$[Au(SCN)_4]^-$	308 (w) 294 (m)	314 (wm) 292 (m)	301 (m) 277 (w)	
$[Hg(SCN)_4]^{2-}$	285 (m) 255 (w)			210 w
Reference		137	138	

Table V-2. ν (MS) frequencies for xanthate and dithiolate complexes.

	$\text{Cr}(\text{R.Xn})_3$	$\text{Co}(\text{R.Xn})_3$	$\text{Ni}(\text{R.Xn})_2$	$\text{Pd}(\text{R.Xn})_2$	$\text{Pt}(\text{R.Xn})_2$
Xanthates					
R = Me	376 (vs) 338 (vw)	361 (vs) 342 (m)	383 (vs) 360 (vw)	347 (vs) 335 (s)	362 (vs) 330 (m)
R = Et	361 (vs) 340 (w)	358 (vs) 340 (m)	383 (vs) 351 (w)	340 (vs) 323 (m)	338 (vs) 312 (w)
	$\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2$	$\text{Pd}(\text{S}_2\text{C}_2\text{R}_2)_2$	$\text{Pt}(\text{S}_2\text{C}_2\text{R}_2)_2$		
Dithiolates					
R = Me	435 333	- -	- -		405 < 310
R = Ph	408 352	401 352			403 373

far-infrared. For $\text{PdCl}_2(\text{RS.C}_2\text{H}_4.\text{SR})$, $\text{R} = \text{Me}$, a strong band at 338.5 cm.^{-1} was assigned to $\nu(\text{PdS})$ ¹⁴. No corresponding band was observed in the complex for $\text{R} = \text{Et}$, a fact which was later confirmed independently¹⁵. However for $\text{R} = \text{Ph}$, strong bands at 331 and 312 cm.^{-1} were assigned to $\nu(\text{PdS})$ by Pluščec and Westland¹³ who also assigned $\nu(\text{MS})$ for $\text{MX}_2(\text{PhS.C}_3\text{H}_6.\text{SPh})$, ($\text{M} = \text{Pt}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}$), in a similar region, Table V-3. There is no explanation for this inconsistency and these systems clearly need further study.

Studies of complexes containing $-\text{SR}$ and $-\text{SR}_2$ ligands are mainly confined to $\text{R} = \text{alkyl}$. However, $\nu(\text{HgS})$ has been assigned in the range $265-215 \text{ cm.}^{-1}$ in the Raman spectra of $\text{Hg}(\text{S.CF}_3)_2$ and related complexes¹⁴⁶, Table V-4. $\text{Hg}(\text{S.CF}_3)_2$ was studied in the liquid state and in various solvents. A marked shift, ($\Delta\nu = 20 \text{ cm.}^{-1}$), in the frequency of $\nu(\text{HgS})$ was observed only in pyridine solution and is associated with complex formation. Isolated studies of dimethylsulphide complexes have been made. In a tentative assignment of the Raman spectrum of $[\text{MeHgSMe}]^+$ in aqueous solution, Goggin and Woodward¹⁴⁷ assigned

Table V-3.

Assignments of ν (MS) frequencies for $\text{MX}_2(\text{L-L})^{13}$.

Complex	ν (MS)
$\text{PdCl}_2(\text{PhS.C}_2\text{H}_4.\text{SPh})$	331 (s) 312 (s)
$\text{PdCl}_2(\text{PhS.C}_3\text{H}_6.\text{SPh})$	323 (s) 308 (s)
$\text{PdBr}_2(\text{PhS.C}_3\text{H}_6.\text{SPh})$	316 (s)
$\text{PtCl}_2(\text{PhS.C}_3\text{H}_6.\text{SPh})$	350 (s) 329 (s)
$\text{PtBr}_2(\text{PhS.C}_3\text{H}_6.\text{SPh})$	349 (sh) 324 (w)

Table V-4.

Raman-active ν (HgS) frequencies¹⁴⁶.

Complex	ν (HgS)
$\text{Hg}(\text{S.CF}_3)\text{X}$	
X = S.CF ₃	243
Cl	251
Br	264
CN	256
NO ₃	247.5
OC.O.CH ₃	248
OC.O.CF ₃	253.5
$\text{NMe}_4 [\text{Hg}(\text{S.CF}_3)_2\text{X}]$	
X = Cl	223
Br	222
I	219
CN	221

$\nu(\text{HgS})$ at 302 cm.^{-1} . However, $\delta(\text{CSC})$ was observed at 291 cm.^{-1} and the two modes must be substantially mixed. In AuCl.SMe_2^{14} , the strong band at 344 cm.^{-1} was assigned to $\nu(\text{AuS})$ although no similar band was observed in the corresponding bromide. A possible explanation is that vibrational interaction between

$\nu(\text{AuCl})$ at 325 cm.^{-1} and $\nu(\text{AuS})$ greatly increases the intensity of the latter band although it is difficult to understand the complete absence of

$\nu(\text{AuS})$ in AuBr.SMe_2 . $\nu(\text{GaS})$ was found at $308\text{-}297 \text{ cm.}^{-1}$ in $\text{GaX}_3.\text{SMe}_2$, $\text{X} = \text{Cl, Br and I}^{148}$.

In all three complexes a weak ligand band was observed near 280 cm.^{-1} but not assigned. This band, presumably

$\delta(\text{CSC})$, will have the same A_1 symmetry as $\nu(\text{GaS})$ and the possibility of coupling between the two modes exists.

In this thesis the infrared spectra of dimethylsulphide complexes of Pt(II) and Pt(IV) have been recorded, (Fig. V-3), and assignments of $\nu(\text{PtS})$,

$\delta(\text{SPtS})$, $\delta(\text{PtSC})$ and internal ligand modes made, (Table V-5). Assignments are based upon three factors;

(a) the published infrared and Raman data on dimethylsulphide; (b) the halogen insensitivity of modes associated with metal-ligand and ligand

Fig. V-3.

Spectra sketches of dimethylsulphide complexes

- A. $[\text{Pt}(\text{SMe}_2)_4]$ $[\text{PtCl}_4]$ C. trans- $[\text{PtBr}_2(\text{SMe}_2)_2]$
B. cis- $[\text{PtCl}_2(\text{SMe}_2)_2]$ D. trans- $[\text{PtI}_2(\text{SMe}_2)_2]$

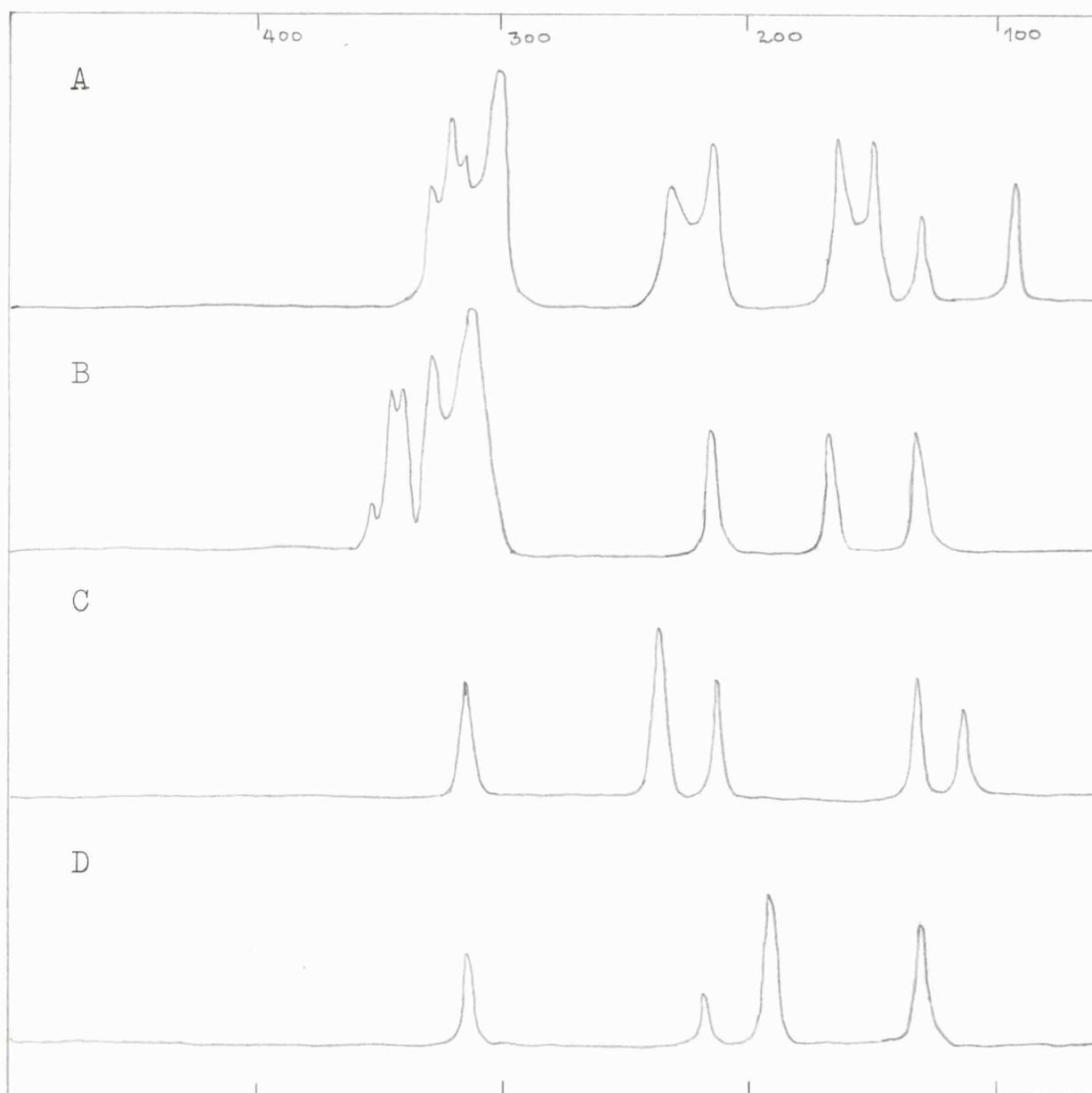


Table V-5. Assignments and frequencies of dimethylsulphide complexes.

Mode	$[\text{Pt}(\text{SMe}_2)_4]$ $[\text{PtCl}_4]$	$\text{cis-}[\text{PtCl}_2(\text{SMe}_2)_2]$	$\text{trans-}[\text{PtX}_2(\text{SMe}_2)_2]$ X = Br X = I	$\text{trans-}[\text{PtX}_4(\text{SMe}_2)_2]$ X = Cl X = Br X = I
$\nu(\text{PtS})$	328 (m) 322 (s) 317 (ms)	354 (w) 347 (ms) 342 (ms)	318 (m)	311 (m) 321 (ms) 319 (wm)
$\delta(\text{SPtS})$	129 (wm)	134 (m)	134 (m)	122 (m) 122 (s) 128 (s)
$\pi(\text{SPtS})$	93 (m)			
$\delta(\text{PtSC})$	232 (m, b) 215 (ms)	216 (m)	215 (m)	272 (m) 264 (wm) 251 (wm)
$\nu(\text{PtX})$	306 (vs, b)	329 (s) 315 (vs, b)	239 (ms)	
$\delta(\text{PtX})$	166 (ms)	168 (m)	115 (wm)	
$\pi(\text{PtX})$	148 (ms)			

vibrations; (c) the use of $[\text{Pt}(\text{SMe}_2)_4][\text{PtCl}_4]$ as a model for Pt-S vibrations.

With reference to previous studies and their own infrared and Raman spectra, McCullough *et. al.*¹⁴⁹ made a complete assignment of dimethylsulphide. Assuming C_{2v} symmetry, all but two of the fundamental vibrations of SMe_2 were identified above 600 cm.^{-1} . No absorption was observed in the far-infrared but in the Raman spectrum, a polarised line at 282 cm.^{-1} was assigned to $\delta(\text{CSC}) A_1$, and from combination bands the B_1 torsion of the methyl groups was estimated to be near 200 cm.^{-1} . In addition, calculations of the potential barrier to internal rotation gave this latter mode at 180 cm.^{-1} . Subsequently Miller *et. al.*¹⁰⁹ recorded the high resolution gas phase infrared spectrum of dimethylsulphide and assigned a complex absorption, centred at 180 cm.^{-1} , to the B_1 torsion. This simple spectrum of dimethylsulphide allows ready identification of metal-sulphur modes in the spectra of the complexes. In $[\text{Pt}(\text{SMe}_2)_4][\text{PtCl}_4]$, both the anion and cation are of D_{4h} symmetry for which three skeletal fundamentals are allowed in the infrared. Thus for square-planar PtL_4 , ($L = \text{SMe}_2, \text{Cl}$), these are $\nu(\text{PtL}_4) E_u$,

$\delta(\text{PtL}_4)$ Eu, and $\pi(\text{PtL}_4)$ A_{2u} . By comparison with previous data, these modes for the $[\text{PtCl}_4]^{2-}$ anion are at 306, 166 and 148 cm^{-1} respectively. The remaining bands associated with Pt-S bond vibrations are assigned in the same sequence. $\nu(\text{PtS}_4)$ is assigned to a triplet at 328, 322 and 317 cm^{-1} , $\delta(\text{PtS}_4)$ at 129 cm^{-1} and $\pi(\text{PtS}_4)$ to a sharp band at 93 cm^{-1} . A doublet at 232, 215 cm^{-1} not associated with a vibration of the PtS_4 skeleton is assigned to $\delta(\text{PtSC})$. This mode is possible only when L is a complex system. Alternative assignment to the B_1 torsion of SMe_2 , which appears at 180 cm^{-1} in the free ligand is unlikely. The Eu modes and $\delta(\text{PtSC})$ show splitting and broadening associated with lowering of D_{4h} symmetry, possibly to C_4 or S_4 . In trans- $[\text{PtX}_2(\text{SMe}_2)_2]$, X = Br, I) C_{2h} , theory allows a single $\nu(\text{PtS})$ and $\delta(\text{SPtS})$ vibration and these are found near 320 cm^{-1} and 130 cm^{-1} respectively, whilst $\delta(\text{PtSC})$ is at 215 cm^{-1} . The corresponding Pt-X modes are readily identified at frequencies close to those of other Pt(II) complexes³³. In cis- $[\text{PtCl}_2(\text{SMe}_2)_2]$, C_{2v} , theory allows two infrared-active stretching modes ($A_1 + B_2$). $\nu(\text{PtCl})$ is at 329, 315 cm^{-1} and $\nu(\text{PtS})$

at 354, 347 and 342 cm.^{-1} . The remaining spectrum follows the trans- systems closely with $\delta(\text{PtSC})$ at 216 and $\delta(\text{SPtS})$ at 134 cm.^{-1} . Thus Pt-S bond vibrations for dimethylsulphide complexes are well established and assignment of the corresponding modes in trans- $[\text{PtX}_4(\text{SMe}_2)_2]$ follows readily, Table V-5.

The spectrum of diethylsulphide is much more complex than dimethylsulphide. Firstly, the increase in length of the alkyl chain introduces two additional fundamentals, viz., the antisymmetric and

Table V-6. Skeletal bending modes of SEt_2 ¹⁵⁰.

Mode	Symmetry class	Raman frequencies	Infrared frequencies
$\delta(\text{CSC})$	C_{2v}	187	
$\delta(\text{CSC})$	$\text{C}_1 + \text{C}_2$	256	
$\delta(\text{CCS})$	C_{2v}	305	308
$\delta(\text{CCS})$	C_1	334	
$\delta(\text{CCS})$	C_2		345
$\delta(\text{CCS})$	$\text{C}_1 + \text{C}_2 + \text{C}_{2v}$	383	379

symmetric $d(\text{CCS})$. Secondly diethylsulphide exists in four rotational isomeric forms having C_{2v} , C_2 , C_1 and C_s symmetry respectively. However the C_s form is energetically unfavourable because it involves close approach of terminal methyl groups and may be disregarded. Infrared and Raman spectra of diethylsulphide have been assigned¹⁵⁰, (Table V-6), in the liquid phase in which the three isomers are present. The torsional mode was not observed and is expected to be at a very low frequency. In the solid state, SEt_2 adopts the C_{2v} - structure¹⁵¹, but its configuration in complexes is unknown. Evidence from previous spectral studies is inconclusive. Beattie and Rule¹⁰⁵ observed the spectrum of $\text{SnCl}_4 \cdot 2\text{SEt}_2$ but found only a strong, broad band at 321 cm.^{-1} associated with $\nu(\text{SnCl})$. In trans- $[\text{PdCl}_2(\text{SEt}_2)_2]$ ¹⁴, only one halogen insensitive band at 300 cm.^{-1} was observed and assignment to either $d(\text{CCS}) C_{2v}$ or $\nu(\text{PdS})$ is possible. In the infrared spectra ($550-20 \text{ cm.}^{-1}$) of $\text{GaX}_3 \cdot \text{SEt}_2$, ($\text{X} = \text{Cl, Br, I}$)¹⁴⁸, $\nu(\text{GaS})$ was assigned at $328-323 \text{ cm.}^{-1}$, but only one internal mode of the ligand was observed at 380 cm.^{-1} . This latter frequency is indicative of either of the three isomers of diethylsulphide. In this work, the spectra of cis- and trans- $[\text{PtX}_2(\text{SEt}_2)_2]$,

(X = Cl, Br)³³, $\text{Pt}_2\text{X}_4(\text{SEt}_2)_2$, (X = Cl, Br), and $\text{Pd}_2\text{Cl}_4(\text{SEt}_2)_2$, (Chapter II) are examined. Comparison of the spectra shows that for each chloro- and bromo-pair, the ligand spectra are consistent but overall the modes of the complexed ligand do not correlate with those of the free ligand. However by comparison with $\nu(\text{PtS})$ for dimethylsulphide complexes and assuming SEt_2 adopts the C_{2v} configuration in complexes, $\nu(\text{PtS})$ is tentatively assigned at $340\text{-}330\text{ cm.}^{-1}$. The spectra of all the complexes studied show a band in this region and it is the strongest band in the spectra apart from the metal-halogen vibrations.

The infrared spectra of higher dialkylsulphides are not known, but the spectra of $\text{Pt}_2\text{X}_4(\text{SR}_2)_2$, (R = Pr^n , Bu^n ; X = Cl, Br), have a large number of bands between $450\text{-}300\text{ cm.}^{-1}$ which must contain $\nu(\text{PtS})$.

V-2.1. Summary of M-S bond vibrations.

Metal-sulphur stretching vibrations lie in the frequency range $480\text{-}210\text{ cm.}^{-1}$. Chelate ligands such as dithiooxalate and dithietene give rise to modes, due mainly to $\nu(\text{MS})$, absorbing in the range $440\text{-}300\text{ cm.}^{-1}$. Discussion of the variation of $\nu(\text{MS})$ as between various chelate systems is meaningless,

although conclusions may be drawn from the variation with M for a given chelate, as for example in the dithiooxalate series. $\nu(\text{MS})$ for thiourea complexes is found between $300\text{-}200\text{ cm.}^{-1}$ although some assignments are in doubt. In the thiocyanates, $\nu(\text{MS})$ is at $314\text{-}280\text{ cm.}^{-1}$ with the possible exception of mercury which is still in dispute. In this work,

$\nu(\text{PtS})$ for dimethyl- and diethylsulphide complexes is identified at $360\text{-}300\text{ cm.}^{-1}$ and new assignments for the bending modes are made. $\delta(\text{SPtS})$ and $\pi(\text{SPtS})$ lie in the ranges $150\text{-}90\text{ cm.}^{-1}$ and $\delta(\text{PtSC})$ at $280\text{-}210\text{ cm.}^{-1}$. The only previous determination of $\delta(\text{SMS})$ was at $155\text{-}145\text{ cm.}^{-1}$ for $[\text{MS}_4]^{2-}$, where M = W and Mo.¹¹¹

V-3. Metal-selenium and -tellurium vibrations

Very few studies of these vibrations have been made, Table V-7. The highest vibrational fundamental of binary metal selenides and tellurides shows the expected decrease from selenium to tellurium and from zinc to cadmium¹³⁴.

In a few selenocyanato complexes, $\nu(\text{PtSe})$ was found at $222\text{-}203\text{ cm.}^{-1}$ ¹³⁷ and $\nu(\text{PdSe})$ at 240 cm.^{-1} ¹³⁸.

Complexes of the type $(\text{PhSe.C}_3\text{H}_6.\text{SePh})\text{MX}_2$,

(M = Pt, Pd; X = Cl, Br) have been studied¹³ along with the corresponding sulphides. $\nu(\text{MSe})$ was at $315\text{--}280\text{ cm.}^{-1}$ and the authors account for the order of $\nu(\text{MSe})$ and $\nu(\text{MS})$ by postulating that, whilst platinum forms a weaker π -bond with selenium than with sulphur, the reverse is true for palladium.

In this work complexes of the alkylselenides and tellurides are studied, viz., $\text{Pd}_2\text{Cl}_4(\text{SeR}_2)_2$ and $\text{Pt}_2\text{Cl}_4(\text{TeR}_2)_2$ (R = Et and Pr^n). The infrared spectrum of SeEt_2 has not been examined, but related SeMe_2 has no bands between $500\text{--}250\text{ cm.}^{-1}$ ⁷¹. Diethylselenide is expected to have one additional band in this region,

$\delta(\text{CCSe})$. The spectrum of $\text{Pd}_2\text{Cl}_4(\text{SeEt}_2)_2$ has five bands in this region which can be $\nu(\text{PdCl})$, $\nu(\text{PdSe})$ and $\delta(\text{CCSe})$. $\nu(\text{PdCl})$ are readily assigned and $\nu(\text{PdSe})$ and $\delta(\text{CCSe})$ are at 282 and 322 cm.^{-1} respectively. The modes in the corresponding diethylsulphide complex are near 330 and 400 cm.^{-1} respectively. $\text{Pd}_2\text{Cl}_4(\text{SePr}_2^n)_2$ has a similar spectrum in which $\nu(\text{PdSe})$ is found at 290 cm.^{-1} .

From the infrared spectrum of TeEt_2 to 250 cm.^{-1} $\nu(\text{TeC})$ lies at 503 cm.^{-1} and the bending modes were unobserved⁷¹. In $\text{Pt}_2\text{Cl}_4(\text{TeEt}_2)_2$, four bands occur below 250 cm.^{-1} which may be Pt-Cl bending, TeEt_2 bending

Table V-7.

Assignments of $\nu(\text{MSe})$ and $\nu(\text{MTe})$ frequencies.

	Reference
A. Binary metal chalcogenides (Zinc Blende structure)	134
ZnSe 215	
ZnTe 190	
CdSe 185	
CdTe 150	
B. $\text{MX}_2(\text{PhSe} \cdot \text{C}_3\text{H}_6 \cdot \text{SePh})$	13
M = Pd; X = Cl 314(s), 296 (s)	
Br 314.5 (w), 297 (s)	
M = Pt; X = Cl 294(s), 285 (s)	
Br 296(s), 283 (w)	
C. Selenocyanates.	
$\text{M}_2 [\text{Pt}(\text{SeCN})_6]$;	
M = K 222 (w) 207 (w)	137
Cs 219 (wm) 203 (wm)	
NMe ₄ 218 (w) 210 (w)	
NEt ₄ 219 (sh) 212 (m)	
$[\text{NMe}_4]_2 [\text{Pd}(\text{SeCN})_4]$	
240 (m)	138

or $\nu(\text{PtTe})$ modes. This complexity prevents definite assignment but comparison with ZnTe suggests that

$\nu(\text{Pt-Te})$ is either at 197 or 177 cm.^{-1} . The former is most likely as the latter may well be $\delta(\text{PtCl})$. The spectrum of $\text{Pt}_2\text{Cl}_4(\text{TePr}_2^{\text{n}})_2$ resembles the ethyl analogue but no comparable data exists for TePr_2^{n} .

V-3.1. Summary of Metal-selenium and -tellurium vibrations.

$\nu(\text{MSe})$ are found in the range 334 to 185 cm.^{-1} . Almost all values are for $\text{M} = \text{Pt}, \text{Pd}$ and in comparable complexes $\nu(\text{PdSe})$ is the higher, a reflection of the anomalously weak Pt-Se π -bonding. The only firm assignments of $\nu(\text{MTe})$ are for simple MTe systems in the range 200-150 cm.^{-1} . This range includes the tentative assignments of alkyltelluride complexes in this work and shows the expected decrease from $\nu(\text{MSe})$.

V-4. Metal-phosphorus vibrations.

Little has been established about the vibrations of metal-phosphorus bonds. Simple phosphides and chelate systems have not been examined and the few assignments of $\nu(\text{MP})$ are confined to phosphine complexes.

In some cases previous far-infrared work has observed, but not recognised $\nu(\text{MP})$.

The first assignment of M-P vibrations was that due to the Raman work of Woodward and Hall on $\text{Ni}(\text{PF}_3)_4$ ^{152, 153}. $\nu(\text{NiP})$ sym., $\nu(\text{NiP})$ asym. and $\delta(\text{NiP})$ were placed at 195, 219 and 54 cm^{-1} respectively. Infrared work¹⁵⁴ on $\text{Ni}(\text{PF}_3)_4$ and related compounds was only extended to 280 cm^{-1} and did not find the Ni-P vibrations. Further Raman studies have assigned $\nu(\text{NiP})$ at 178 cm^{-1} in $\text{Ni} [\text{P}(\text{OMe})_3]_4$ ¹⁵⁵ and between 262 to 209 cm^{-1} for $\text{Ni}(\text{CO})_{4-n}(\text{PF}_3)_n$ ($n = 1-3$)¹⁵⁶. In the more complex spectrum of $\text{Ni}(\text{CO})_3\text{PPh}_3$, Edgell and Dunkle¹⁵⁷ tentatively assigned $\nu(\text{NiP})$ at 192 cm^{-1} . This is very close to an absorption expected from complexed PPh_3 but assignment was made on intensity grounds. The drop in $\nu(\text{NiP})$, ($\Delta\nu = 70 \text{ cm}^{-1}$), as L changes from PF_3 to PPh_3 in $\text{Ni}(\text{CO})_3\text{L}$ is associated with a corresponding drop in $\nu(\text{CO})$, i.e. the high electronegativity of PF_3 makes back donation from nickel to the CO groups less effective. This Raman work on zero-valent nickel compounds is summarised in Table V-8. In this work the only infrared study of a zerovalent compound is that of $\text{Pt}(\text{PPh}_3)_4$, (Fig. V-4). As in Edgell and Dunkle's

work on $\text{Ni}(\text{CO})_3\text{PPh}_3$, one intense band was found in addition to those of PPh_3 , viz. 424 cm.^{-1} , and is tentatively assigned to $\nu(\text{PtP})$. This is extremely high compared with the nickel compounds and is close to the position of $\nu(\text{PtP})$ in $\text{Pt}(\text{II})$ and $\text{Pt}(\text{IV})$ phosphine complexes.

V-4.2. Complexes of metals in "normal" oxidation states.

In contrast to the Raman work on zero-valent compounds, these assignments are made from infrared studies of complicated systems and are therefore more tentative. However correlation of previous work with the spectra in this thesis enables a consistent picture of M-P vibrations to emerge.

Rosenbaum et. al.¹⁵⁸ have assigned the four skeletal modes of PMe_3 (C_{3v}), only the symmetric and antisymmetric $\nu(\text{PC}_3)$ occur below 500 cm.^{-1} , at 263 and 305 cm.^{-1} respectively and should show small variation on coordination to metal. The simplicity of the ligand spectra has enabled ready assignment of M-P modes in trimethylphosphine complexes. Coates and Parkin¹⁴ found $\nu(\text{MP})$ at $390-340 \text{ cm.}^{-1}$ for a series of complexes where $\text{M} = \text{Au}, \text{Ni}, \text{Pd}$ and Pt ,

Table V-8.

Summary of Raman assignments of
Ni-P bond vibrations

Complex	$\nu(\text{NiP})$	$\delta(\text{NiP})$	Reference
$\text{Ni}(\text{PF}_3)_4$	219, 195	54	152, 153
$\text{NiCO}(\text{PF}_3)_3$	253, 216		156
$\text{Ni}(\text{CO})_2(\text{PF}_3)_2$	254, 209		156
$\text{Ni}(\text{CO})_3\text{PF}_3$	262		156
$\text{Ni}(\text{CO})_3, \text{PPh}_3$	192		157
$\text{Ni} [\text{P}(\text{OMe})_3]_4$	178		155

Table V-9. The frequencies these authors list as other bands are certainly due to $\delta(\text{PC}_3)$ and $\delta(\text{PtPC})$. Greenwood^{159, 160} similarly assigned $\nu(\text{GaP})$ at 326 and 360 cm^{-1} in $\text{GaH}_3 \cdot \text{PMe}_3$ and $\text{GaH}_3 \cdot \text{PHMe}_2$ respectively. In this work the spectrum of cis- $[\text{PtCl}_2(\text{PMe}_3)_2]$ was examined, Fig. V-4. As predicted by theory for C_{2v} symmetry, two $\nu(\text{PtCl})$ and $\nu(\text{PtP})$, ($A_1 + B_2$), are found. The former appear as strong, broad bands at 306, 280 cm^{-1} and the latter at 409 (w) and 382 (s) cm^{-1}

Table V-9.

Assignment of ν (MP) frequencies in
trimethylphosphine complexes¹⁴.

			ν (MP)
A.	AuX(PMe ₃);	X = Cl	381 (m)
		Br	376 (s)
		I	371 (s)
		Me	357 (m)
		C \equiv C.Bu ^t	368 (m)
		C \equiv C.Ph	347 (s)
		AuMe ₃ (PMe ₃)	391 (w)
B.	NiX ₂ (PMe ₃) ₂ ;	X = Cl	361 (w)
		Br	360 (w)
		I	366 (s)
C.	<u>cis</u> - [PdX ₂ (PMe ₃) ₂] ;	X = Cl	365 (w)
		Me	365 (w), 347 (w)
	PdX ₂ (PMe ₃) ₂ ;	X = Br	344 (w)
		I	341 (m)
D.	<u>cis</u> - [PtCl ₂ (PMe ₃) ₂]		377 (m), 362 (m)
	<u>trans</u> - [PtCl ₂ (PMe ₃) ₂]		364 (w)

$\delta(\text{PC}_3)$ is masked by the lower $\nu(\text{PtCl})$ band and $\delta(\text{PtPC})$ is at 249 cm.^{-1} . Two bands at 172 and 161 cm.^{-1} are possibly the Pt-P and Pt-Cl bending modes although it is probably more accurate to consider them as deformations of the PtCl_2P_2 skeleton.

The Raman spectrum of triethylphosphine¹⁶¹ has seven lines below 650 cm.^{-1} at $619, 410, 368, 333, 306, 278$ and 249 cm.^{-1} but no assignments were made. Infrared work¹⁶² was extended only to 650 cm.^{-1} . To provide more complete information, the far-infrared of liquid PEt_3 was determined, (Fig. V-4). Four bands at $417, 371, 334$ and 307 cm.^{-1} are observed, agreeing closely with the Raman lines. Triethylphosphine, C_{3v} , has a greater number of carbon atoms and hence a more complicated spectrum than PMe_3 . In addition to C-P-C bending modes there are C-C-P bending modes and torsional modes associated with ethyl and methyl groups. A large shift in the position of $\delta(\text{CPC})$ is not expected on changing from PMe_3 to PEt_3 and the broad band at 334 cm.^{-1} is assigned to this vibration ($A_1 + E$). The two higher bands at 417 and 371 cm.^{-1} are assigned to the E and A_1 $\delta(\text{CCP})$ respectively, cf. SEt_2 where the antisymmetric vibrations are at higher frequencies

than symmetric vibrations. The remaining band at 307 cm.^{-1} is assigned to the methyl torsion, the ethyl torsion is expected to be even lower and was not observed.

The frequencies of the vibrations of PEt_3 are now established and the complexes $[\text{Pt}(\text{PEt}_3)_4]$ $[\text{PtBr}_4]$ and trans- $[\text{PtPh}_2(\text{PEt}_3)_2]$ serve as models for identification of Pt-P vibrations, (Table V-10 and Fig. V-4.). In addition to the ligand modes, three Pt-Br and three Pt-P vibrations are predicted by theory for $[\text{Pt}(\text{PEt}_3)_4]$ $[\text{PtBr}_4]$, cf. $[\text{Pt}(\text{SMe}_2)_4]$ $[\text{PtCl}_4]$. $\nu(\text{PtBr})$ and $\delta(\text{PtBr}_2)$ lie at 228 and 117 cm.^{-1} respectively and compare well with frequencies found for K_2PtBr_4 . All but four of the remaining bands correlate with known absorption of PEt_3 .

$\nu(\text{PtP})$, $\delta(\text{PtP})$ and $\pi(\text{PtP})$ are assigned to bands at 453, 200 and 185 cm.^{-1} respectively. The remaining band at 255 cm.^{-1} is possibly the ethyl torsion of PEt_3 or $\delta(\text{PtPC})$. The latter assignment is preferred as the methyl torsion is not observed in spectra of the complexed ligand and the ethyl torsion is expected to behave similarly. In trans- $[\text{Pt Ph}_2(\text{PEt}_3)_2]$,

$\nu(\text{PtP})$ is assigned at 415 cm.^{-1} . Although only this one band is found in the spectrum above 400 cm.^{-1} ,

Fig. V-4.

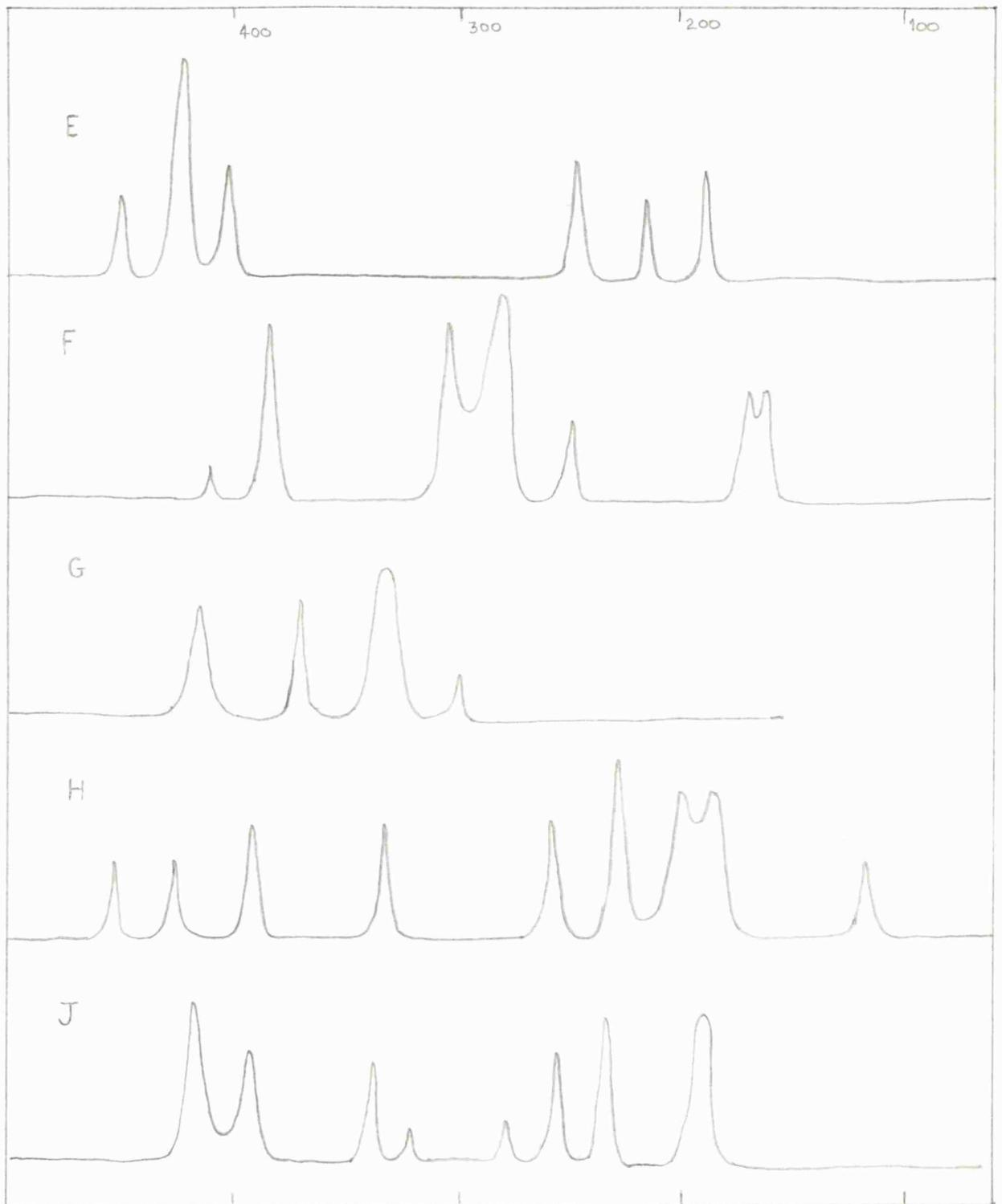


Fig. V-4. (facing page)

Infrared spectra sketches of Pt-P bonded complexes

- E. $\text{Pt}(\text{PPh}_3)_4$
- F. cis- $[\text{PtCl}_2(\text{PMe}_3)_2]$.
- G. PEt_3 .
- H. $[\text{Pt}(\text{PEt}_3)_4]$ $[\text{PtBr}_4]$.
- J. trans- $[\text{PtPh}_2(\text{PEt}_3)_2]$.

Table V-10.

Assignment of PEt_3 and Pt-P bond vibrational frequencies.

Mode	PEt_3	$[\text{Pt}(\text{PEt}_3)_4]$ $[\text{PtBr}_4]$	<u>trans-</u> $[\text{PtPh}_2(\text{PEt}_3)_2]$
$\delta(\text{CCP})$	417 (m)	425 (wm)	415 (ms)
$\delta(\text{CCP})$	371 (m)	386 (m)	389 (m)
$\delta(\text{CPC})$	334 (ms, b)	332 (m)	334 (m)
Methyl torsion	307 (w)		317 (w)
$\nu(\text{PtP})$		453 (wm)	415 (ms)
$\delta(\text{PtP})$		200 (ms)	187 (s, b)
$\pi(\text{PtP})$		185 (ms)	
$\delta(\text{PtPC})$		255 (m)	231 (m)

its intensity is much greater than expected for a ligand mode and $\nu(\text{PtP})$ and $\delta(\text{CCP})$ are considered to be coincident. The remaining bands correlate with PEt_3 apart from a broad band at 187 cm.^{-1} assigned to $\delta(\text{PtP})$ and a band near 250 cm.^{-1} assigned to the t- mode of the substituted phenyl group, cf.

256 cm.^{-1} for SnPh_4 ¹⁶⁵.

Comparison between the spectra of the bridged complexes $\text{M}_2\text{X}_4(\text{PEt}_3)_2$, ($\text{M} = \text{Pt}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), (Chapter II), cis- and trans- $[\text{PtX}_4(\text{PEt}_3)_2]$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), (Chapter IV), and the above assignments allows identification of M-P vibrations in these complexes. The bridge complexes have a trans- structure C_{2h} and the single $\nu(\text{MP})$ predicted by theory was observed at 450-430 cm.^{-1} and 440-420 cm.^{-1} for $\text{M} = \text{Pt}$ and Pd respectively. The values are halogen insensitive and $\nu(\text{PdP})$ is slightly lower than $\nu(\text{PtP})$. The reverse is found for $\nu(\text{MX})$ in these complexes. Bands occur in the region associated with $\delta(\text{MP})$ but are probably more accurately described as 'mixed' bending modes, $\delta(\text{X-M-P})$.

Apart from the Pt-X modes, the spectra of cis- and trans- $[\text{PtX}_4(\text{PEt}_3)_2]$ closely resemble the bridged complexes and Pt-P modes are readily identified, (Table V-11). For trans- complexes, a single $\nu(\text{PtP})$ at 412-410 cm.^{-1} and for cis- complexes two $\nu(\text{PtP})$ at 444 and 428-425 cm.^{-1} are observed. This is in accord with theoretical predictions and is a valid method of distinguishing between these cis- and trans- isomers, cf. Pt-X modes. The narrow frequency ranges

reflect the complete halogen insensitivity of

$\nu(\text{PtP})$ in these complexes. The higher $\nu(\text{PtP})$ found in the cis- complexes are due to stronger Pt-P bonding, when trans- to a Pt-Cl bond rather than a second Pt-P bond. $\delta(\text{PtP})$ was found consistently for both series of Pt(IV) complexes at 183-179 cm^{-1} , comparing well with the range established for $[\text{Pt}(\text{PEt}_3)_4]$ $[\text{PtBr}_4]$.

Other triethylphosphine complexes have been studied in the far-infrared by both Adams et. al.³³ and Coates and Parkin.¹⁴ The former assigned only

$\nu(\text{PtX})$ whilst the latter assigned $\nu(\text{MX})$ and some $\nu(\text{MP})$. The $\nu(\text{MP})$ frequencies are assigned from the published spectra by comparison with the work in this thesis, (Table V-12). Considering the work of Adams et. al., for cis- $[\text{PtX}_2(\text{PEt}_3)_2]$, $\nu(\text{PtP})$ is at 450-420 cm^{-1} and for trans- $[\text{PtX}_2(\text{PEt}_3)_2]$ at 420-400 cm^{-1} . As required by theory two $\nu(\text{PtP})$ bands were found for cis- complexes whilst only one for the trans- series. A similar observation was made by Adams et. al. for $\nu(\text{PtX})$ ³³. The $\nu(\text{PtP})$ modes are halogen insensitive and show a close similarity in frequency to those found for corresponding Pt(IV) complexes. Whilst a shift to higher frequencies is

Table V-11.

Assignment of ν (MP) and δ (PMP) frequencies.

		ν (MP)	δ (PMP)
$\text{Pt}_2\text{X}_4(\text{PEt}_3)_2$;	X = Cl	445 (m)	
	Br	449 (m)	
	I	433 (m)	
$\text{Pd}_2\text{X}_4(\text{PEt}_3)_2$;	X = Cl	435 (m)	
	Br	431 (m)	
	I	438 (m), 423 (m)	
<u>cis-</u> $[\text{PtX}_4(\text{PEt}_3)_2]$;	X = Cl	444 (w) 428 (m)	183 (m)
	Br	444 (m) 425 (wm)	182 (s)
<u>trans-</u> $[\text{PtX}_4(\text{PEt}_3)_2]$;	X = Cl	410 (m)	179 (ms)
	Br	411 (m)	182 (m)
	I	412 (m)	181 (vs)

expected for ν (PtP) when $\text{Pt(II)} \rightarrow \text{Pt(IV)}$, the accompanying increase in coordination number $4 \rightarrow 6$ will cause a decrease in ν (PtP) and the two effects cancel out.

Table V-12.

Assignment of ν (MP) frequencies from published spectra^{33,14}

	ν (MP)	Reference
<u>cis</u> - $[\text{PtX}_2(\text{PEt}_3)_2]$; X = Cl	443 (m), 427 (m)	33
Br	440 (m) 424 (m)	
<u>trans</u> - $[\text{PtX}_2(\text{PEt}_3)_2]$; X = Cl	418 (s)	
Br	416 (s)	
$[\text{PtXY}(\text{PEt}_3)_2]$; X=Ph, Y = Br	413 (m)	
X=Me, Y = Cl	417 (m)	
X=CD ₃ , Y = Br	413 (m)	
AuX ₃ .PEt ₃ .; X = Cl	421 (w)	14
Br	421 (m)	
AuCl ₂ Br.PEt ₃	423 (m)	
AuClBr ₂ .PEt ₃	422 (m)	
<u>trans</u> - $[\text{PdX}_2(\text{PEt}_3)_2]$; X = Cl	409 (w)	
Br	408 (m)	
I	408 (m)	
<u>trans</u> - $[\text{PtCl}_2(\text{PEt}_3)_2]$	413 (w)	

In Coates and Parkin's work on triethylphosphine-gold complexes, the unassigned bands at 423-421 cm.^{-1} are $\nu(\text{AuP})$ modes. The authors assignments of $\nu(\text{MP})$ for $\text{MX}_2(\text{PEt}_3)_2$, ($\text{M} = \text{Pt}, \text{Pd}$), at 380-360 cm.^{-1} are considered to be in error and are reassigned to bands near 410 cm.^{-1} (Table V-12), although for cis- $[\text{PtX}_2(\text{PEt}_3)_2]$ they do not appear to have found bands in this latter region.

These results have been confirmed in work published subsequently by Goggin and Goodfellow¹⁶⁶, which assigned $\nu(\text{PtP})$ at 442, 427 and 419 cm.^{-1} for cis- and trans- $[\text{PtCl}_2(\text{PEt}_3)_2]$ respectively. Following this assignment, Rosevear and Stone² found $\nu(\text{PtP})$ at similar frequencies for cis- and trans- $[\text{PtX}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]$, Table V-13. For lighter elements, Greenwood has assigned $\nu(\text{GaP})$ at 370 cm.^{-1} in $\text{GaH}_3 \cdot \text{PEt}_3$ ¹⁶⁷.

Thus for PEt_3 complexes, $\nu(\text{MP})$ lies in the range 460-370 cm.^{-1} , ($\text{M} = \text{Ga}, \text{Au}, \text{Pd}, \text{Pt}$), $\delta(\text{PPtP})$ is at 200-180 cm.^{-1} and $\delta(\text{PtPC})$ at 280-220 cm.^{-1} . The ligand modes are readily identified in complex spectra, the shift in frequency being less than 20 cm.^{-1} .

No spectral data for tri-n-propylphosphine exist and assignments of $\nu(\text{MP})$ made for $\text{M}_2\text{X}_4(\text{PPr}_3^n)_2$,

(M = Pt, Pd) in Chapter II are tentative. The spectra of these complexes resemble the corresponding PEt_3 complexes apart from an additional band in the 470-350 cm.^{-1} frequency range and are assigned accordingly. Bands at 378-372 and 437-423 cm.^{-1} are assigned to $\delta(\text{CCP})$ and the bands at 466-444 cm.^{-1} to $\nu(\text{PtP})$. For trans- $[\text{PdCl}_2(\text{PPr}_3^n)_2]$, Coates and Parkin¹⁴ found $\nu(\text{PdP})$ at 420 cm.^{-1} .

In addition to the bridged $\text{M}_2\text{X}_4(\text{PPh}_3)_2$ complexes in Chapter II, several other triphenylphosphine complexes are examined. To aid interpretation the vibrational spectrum of triphenylphosphine itself is first studied. Several infrared and Raman investigations of PPh_3 have been made and are summarised in Table V-14, along with the infrared spectrum recorded in this work. The spectra of the complexes (Fig. V-5) show good correlation with the PPh_3 spectrum apart from the region between 500-400 cm.^{-1} , in which additional bands are present, (Table V-15). Deacon and Green¹⁶⁸ have shown that the bands at 433, 422 cm.^{-1} in PPh_3 , (the X-sensitive t-mode according to Whiffen's notation for PhX), shift to higher frequencies in complexes, viz. $\Delta\nu = 10-30 \text{ cm.}^{-1}$. Thus on this basis the bands between 471-442 cm.^{-1} in the complexes in

Table V-13.

Assignment of $\nu(\text{PtP})$ frequencies for
cis- and *trans-* $[\text{PtX}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]$ ²

	$\nu(\text{PtP})$	
	<u>cis</u> -isomer	<u>trans</u> -isomer
$[\text{PtX}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]$;		
X = Cl	439, 423	417
Br	437, 418	412
I	433, 417	410
C_6F_5	429, 416	414

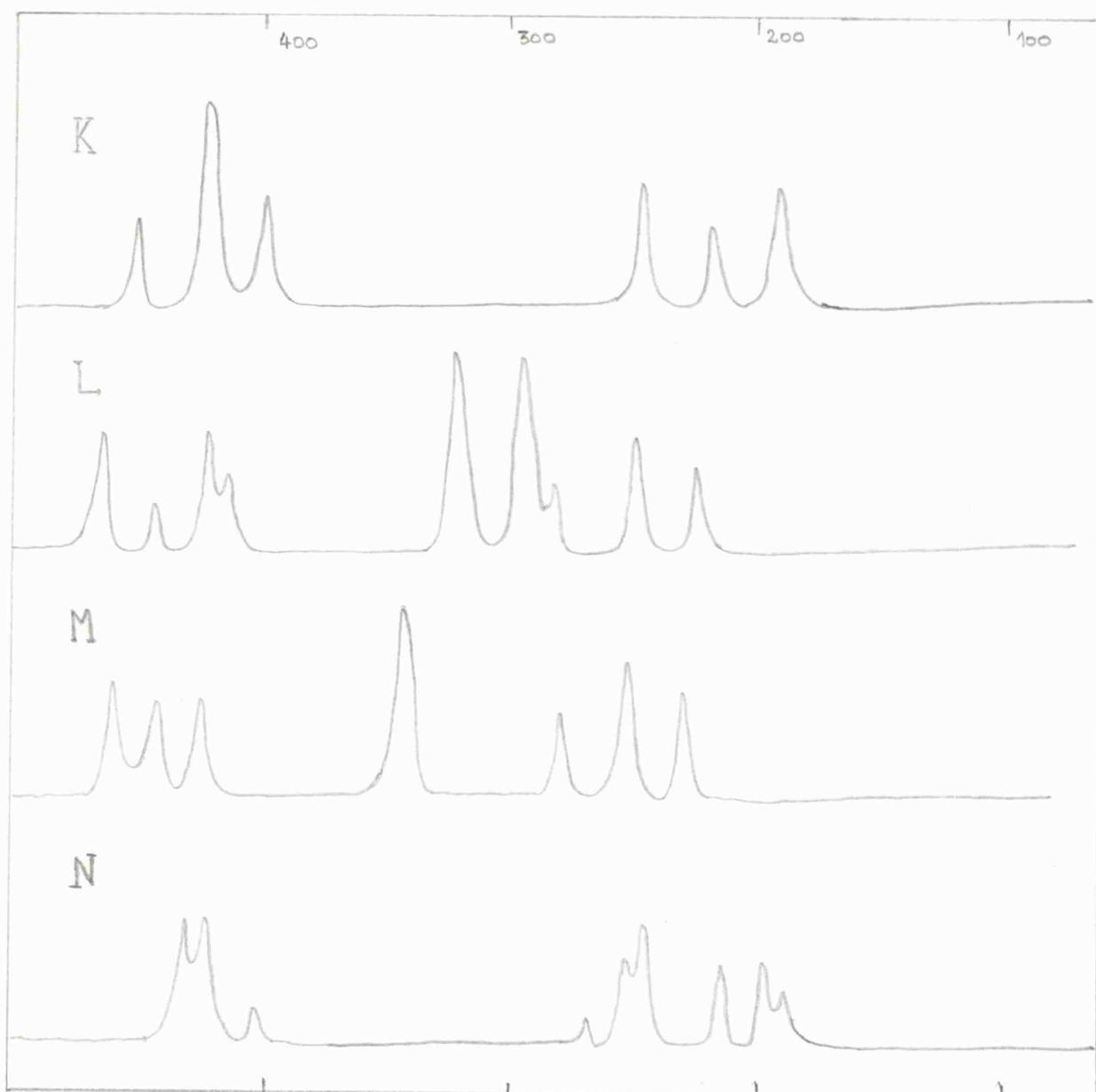
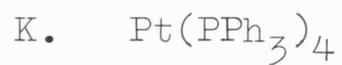
this work correspond to bands at 433, 422 cm^{-1} in PPh_3 and $\nu(\text{MP})$ is assigned at 438-424 cm^{-1} . trans- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $\text{M}_2\text{X}_4(\text{PPh}_3)_2$ have a single $\nu(\text{PtP})$ frequency and cis- $[\text{PtCl}_2(\text{PPh}_3)_2]$ has two $\nu(\text{PtP})$ frequencies in accord with theory. In previous work¹⁶⁰, $\nu(\text{GaP})$ for $\text{GaH}_3 \cdot \text{PPh}_3$ was found at 365 cm^{-1} and for triphenylphosphine and related complexes of titanium, Westland and Westland¹⁶⁹ assigned

Raman and infrared frequencies of triphenylphosphine below 550 cm^{-1}

Raman		Infrared			
519 (2)	507 (m)	499 (vs)	508 (ms)	512 (s)	514 (vs)
		493 (vs)	494 (s)	502 (s)	499 (vs) N.I.
				487 (m)	493 (vs)
		430 (w)	434 (wm)		432 (s) 433 (m)
417 (2)	400 (vw)	420 (w)	422 (wm)	425 (w)	422 (s) 422 (m)
				395 (w)	401 (vw)
289 (1)					271 (vvw)
254 (2)	246 (m)				254 (wm)
		N.I.	N.I.	N.I.	246 (m)
201 (1)	205 (m)				213 (wm)
					196 (wm)
	188 (w)				188 (w)
Reference	172	171	170	157	173
	157				This work

Fig. V-5.

Spectra sketches of triphenylphosphine complexes.



$\nu(\text{TiP})$ at 463-414 cm^{-1} .

$\nu(\text{MP})$ in complexes containing PCl_3 and $\text{P}(\text{OEt})_3$ ligands complete this survey of M-P vibrations. A detailed explanation of the assignment of $\text{Pt}_2\text{Cl}_4(\text{PCl}_3)_2$ has been given in Section II-2.11. Whilst assignment of $\nu(\text{PtP})$ at 346 cm^{-1} is not certain, the spectrum of $\text{Pt}_2\text{Cl}_4(\text{PCl}_3)_2$ does contain six bands in the region 375-320 cm^{-1} , one of which must be due to $\nu(\text{PtP})$.

Triethylphosphite has been studied by Baudler who found five Raman lines below 500 cm^{-1} , viz. 447, 409, 315, 248 and 213 cm^{-1} .⁶⁸ For $\text{Pd}_2\text{Br}_4[\text{P}(\text{OEt})_3]_2$, no bands are observed above 400 cm^{-1} and excluding Pt-Br vibrations, all but one of the remaining absorptions correspond to those of $\text{P}(\text{OEt})_3$. This band at 354 cm^{-1} is assigned to $\nu(\text{PtP})$. By analogy, $\nu(\text{MP})$ for $\text{M}_2\text{Cl}_4[\text{P}(\text{OEt})_3]_2$, (M = Pt, Pd) should lie near 350 cm^{-1} . Unfortunately this region is masked by intense $\nu(\text{MCl})$ bands and $\nu(\text{MP})$ is not observed.

V-4.1. Summary of metal-phosphorus vibrations.

$\nu(\text{M-P})$ lies in the range 460-180 cm^{-1} .

The zero-valent nickel compounds absorb below 265 cm^{-1} ,

Table V-15.

Frequencies of halogen insensitive bands in PPh_3 complexes.

Complexes	$\nu(\text{MP})$	PPh_3 modes								
PPh_3		433	422	401	271	254	246	213	196	188
$\text{Pt}(\text{Ph}_3)_4$	424	451	404	251	226	205				
<u>cis</u> - $[\text{PtCl}_2(\text{PPh}_3)_2]$	426, 418	468	445	281	250	227				
<u>trans</u> - $[\text{PtCl}_2(\text{PPh}_3)_2]$	428	461	442	280	251	230				
$\text{Pt}_2\text{I}_4(\text{PPh}_3)_2$	438	457	278	255	233	208	190			
$\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2$	438	461	457	278	254	228	218	200		
$\text{Pd}_2\text{Br}_4(\text{PPh}_3)_2$	433	467	450	280	257	248	234	207	193	

whereas for Ni^{II} planar complexes $\nu(\text{NiP})$ rises 100 cm.⁻¹ to 360 cm.⁻¹. This is not a large shift compared with the change in $\nu(\text{CoN})$ in $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Co}^{\text{II}}(\text{NH}_3)_6]^{2+}$, i.e. $\Delta\nu = 140 \text{ cm.}^{-1}$. For complexes of metals in normal oxidation states, the range 460-320 cm.⁻¹ is applicable, but in contrast to nickel, the change in oxidation state from Pt(II) to Pt(IV) has no apparent effect on $\nu(\text{PtP})$. This is because there is a parallel change in coordination number from 4 to 6 which causes a frequency shift in the opposite direction and the two effects cancel out.

For zero-valent nickel complexes, $\delta(\text{NiP})$ lies in the range 80-50 cm.⁻¹. New assignments, in this work, for Pt(II) and Pt(IV) complexes place $\delta(\text{PtP})$ between 200-175 cm.⁻¹.

V-5. Metal-arsenic vibrations.

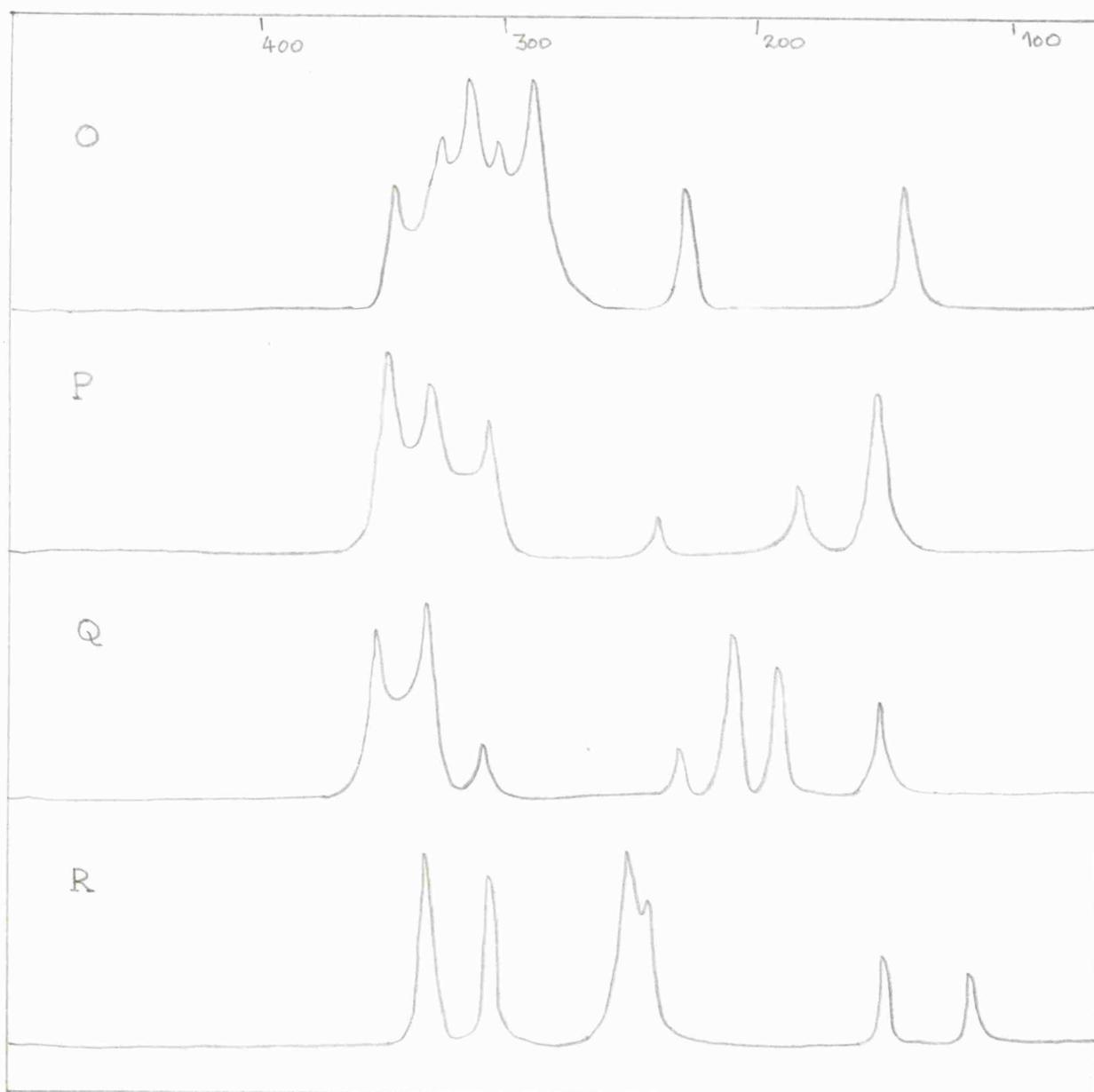
Very little is known about M-As vibrations. Bigorgne¹⁷⁴ has assigned $\nu(\text{NiAs})$ to a polarised line at 207 cm.⁻¹ in the Raman spectrum of zero-valent Ni(CO)₃.AsEt₃ and for complexes of AsMe₃, Coates and Parkin¹⁴ found $\nu(\text{MAs})$, (M = Au, Pt and Pd), at

280-240 cm.^{-1} . In AsMe_3 , $\delta(\text{CAsC})$ was found at 240-220 cm.^{-1} ¹⁷⁵ and the absence of further ligand absorption makes the assignments of $\nu(\text{MAs})$ fairly certain.

Assignments of M-As vibrations made in this work are based upon comparison between the spectra of cis- and trans- $[\text{PtX}_2(\text{AsEt}_3)_2]$, (X = Cl, Br), Fig. V-6. The spectrum of triethylarsine has not been recorded. However it is a reasonable assumption to expect absorptions of similar origin to those for PEt_3 but shifted to a lower frequency. For $\text{PtBr}_2(\text{AsEt}_3)_2$, a band at 330 cm.^{-1} in the trans-complex appears as a doublet at 354, 332 cm.^{-1} in the cis, and is assigned to $\nu(\text{PtAs})$. A similar but, due to Pt-Cl bond absorptions, less clear cut situation is observed for cis- and trans- $[\text{PtCl}_2(\text{AsEt}_3)_2]$. Bands near 300 and 235 cm.^{-1} appear in all the complexes and are possibly the ligand modes $\delta(\text{CCAs})$ and $\delta(\text{CAsC})$ respectively. Further halogen insensitive bands near 140 cm.^{-1} are considered too low to be a fundamental of AsEt_3 and are assigned to $\delta(\text{AsPtAs})$, (Table V-16). These data allow M-As vibrations to be identified in $\text{M}_2\text{X}_4(\text{AsEt}_3)_2$, (M = Pt, Pd; X = Cl, Br, I) and trans- $[\text{PtX}_4(\text{AsEt}_3)_2]$, (X = Cl, Br, I), (Table V-17).

Fig. V-6.

Spectra sketches of cis- and trans- [PtX₂(AsEt₃)₂].



The absorptions of $M_2X_4(AsPr_3^n)_2$,
(M = Pt, Pd; X = Cl, Br, I) are similar to those
of the corresponding $AsEt_3$ complexes in the region
associated with $\nu(MAs)$ vibrations and the spectra
are assigned accordingly. $\nu(PtAs)$ and $\nu(PdAs)$
lie between 335-325 and 332-328 $cm.^{-1}$ respectively.
Low-frequency bands which could be described as
 $\delta(AsMAs)$ are not observed.

V-5.1. Summary of metal-arsenic vibrations.

$\nu(MAs)$ vibrations lie between 355-205 $cm.^{-1}$
and are consistent with those of $\nu(MP)$. In this
work the first assignments of $\delta(AsMAs)$ are made
between 150-120 $cm.^{-1}$. However further work is
necessary before M-As vibrations are well understood.
In particular Raman and infrared investigations of
simple metal-arsenic compounds would give the required
standard of proof for assignment of $\nu(MAs)$ and
 $\delta(AsMAs)$.

V-6. Metal-pyridine vibrations.

The assignment of the spectrum of pyridine
is well established¹⁷⁶⁻⁸. The lowest infrared and
Raman-active fundamentals are at 405 and 375 $cm.^{-1}$
respectively, (ν_{16b} and ν_{16a} in the notation of Kline

Table V-16.

Assignment of $\nu(\text{PtAs})$ and $\delta(\text{AsPtAs})$ frequencies in
cis- and trans- [PtX₂(AsEt₃)₂]

	$\nu(\text{PtAs})$	$\delta(\text{AsPtAs})$	$\delta(\text{CCAs})$	$\delta(\text{CAsC})$
<u>cis-</u> [PtCl ₂ (AsEt ₃) ₂]	345 (m)	329 (ms)	140 (m)	303 (ms)
<u>trans-</u> [PtCl ₂ (AsEt ₃) ₂]	330 (ms)	149 (ms)	303 (m)	231 (m)
<u>cis-</u> [PtBr ₂ (AsEt ₃) ₂]	354 (ms)	332 (s)	145 (m)	240 (vw)
<u>trans-</u> [PtBr ₂ (AsEt ₃) ₂]	332 (s)	144 (wm)	310 (w)	228 (w)
			304 (ms)	242 (sh)

Table V-17.

Assignment of $\nu(\text{MAs})$ and $\delta(\text{AsMAs})$ frequencies.

		$\nu(\text{MAs})$	$\delta(\text{AsMAs})$
$\text{Pt}_2\text{X}_4(\text{AsEt}_3)_2$;	X = Cl	318	139
	Br	320	134
	I	319	134
$\text{Pd}_2\text{X}_4(\text{AsEt}_3)_2$;	X = Cl	342	134
	Br	335	132
	I	346, 316	124
$\text{PtX}_4(\text{AsEt}_3)_2$;	X = Cl	328	137
	Br	325	142
	I	328, 321	144

and Turkevitch¹⁷⁶). A subsequent infrared study of liquid pyridine found additional very weak bands at 472, 361, 345 and 208 cm^{-1} , but no assignments were made¹⁷⁹. A sample layer thickness of at least 1 mm. was required to detect these bands which are possibly weak difference modes.

The effect of coordination on the vibrations of pyridine has been the subject of much study, the most systematic was that of Gill et. al.¹⁸⁰ who also summarised previous work. They found that although the spectrum of complexed pyridine was little changed from that of the free base, the low-frequency band at 405 cm^{-1} did suffer a significant shift to higher frequencies. The shift being greater (50-80 cm^{-1}) in second and third row transition metal complexes than in those of the first row. Recently several authors have studied the far-infrared spectra of pyridine complexes and assigned skeletal vibrations^{148, 181-5}. Bicelli originally suggested that M-py bond stretching frequencies would be in the range 200-150 cm^{-1} ¹⁸⁶, whilst Clark and Williams^{181, 182} found $\nu(\text{M-py})$ at 300-200 cm^{-1} for a wide range of complexes. These bands were below the lowest ones due to the pyridine ring (405 cm^{-1}) and were insensitive

to change of halogen. Further work has confirmed this assignment. For a similar range of complexes, $\nu(\text{M-py})$ was observed between 280-210¹⁸³ and 270-210 cm.⁻¹ 185 and in infrared studies to 20 cm.⁻¹, Greenwood *et. al.* found $\nu(\text{Ga-py})$ at 270-255 cm.⁻¹ for $\text{GaX}_3 \cdot \text{py}$, (X = Cl, Br, I)¹⁴⁸ and Goldstein *et. al.* assigned $\nu(\text{Cu-py})$ and $\delta(\text{Cu-py}_2)$ near 270 and 200 cm.⁻¹ respectively for $\text{CuX}_2(\text{py})_2$, (X = Cl, Br)¹⁸⁴. The last authors observed that the bands assigned to $\nu(\text{Cu-py})$ are at a somewhat higher frequency than predicted¹⁸⁶ supporting the suggestion that in these compounds there is appreciable back-bonding from the copper atoms to the pyridine rings. Allen and Theophanides²⁷ have assigned bands between 480-450 cm.⁻¹ in platinum complexes of pyridine to $\nu(\text{Pt-py})$. This is in error as they are clearly due to the 16b vibrational mode of pyridine. The spectra of $[\text{Pt}(\text{py})_4] \text{X}$, (X = 2Cl, PtBr₄), are examined in this work, (Fig. V-7), and the frequencies observed allow assignment of cis- $[\text{PtX}_4(\text{py})_2]$, (X = Cl, Br), (Table V-18). In $[\text{Pt}(\text{py})_4] \text{Cl}_2$, the lowest pyridine fundamental (405 cm.⁻¹) is shifted to higher frequencies and splits to a doublet at 473, 426 cm.⁻¹, indicating interaction between the pyridine rings. Several bands below 400 cm.⁻¹

are observed which cover a frequency range such that they cannot all be $\nu(\text{Pt-py})$ modes. However, bands at 393 and 213 cm.^{-1} correspond to weak absorptions found for pyridine¹⁷⁹ and the broad band at 188 cm.^{-1} , which is absent from $[\text{Pt}(\text{py})_4][\text{PtBr}_4]$ may be the lattice mode of the chloride anion.

$\nu(\text{Pt-py})$ is assigned to bands at 307 and 272 cm.^{-1} whilst the band at 109 cm.^{-1} is possibly $\delta(\text{Ptpy}_2)$, although no comparable absorptions are found in cis- $[\text{PtX}_4(\text{py})_2]$. Only one $\nu(\text{Pt-py})$, Eu, is allowed by theory for $[\text{Pt}(\text{py})_4]^{2+}\text{D}_{2h}$, and the two bands observed indicate a lower symmetry. This may well arise from steric interaction between the four pyridine molecules attached to one platinum atom causing them to lie out of the PtN_4 plane. This interaction similarly affects $\nu(\text{PtBr})$ in $[\text{Pt}(\text{py})_4][\text{PtBr}_4]$ and the 16b fundamental of pyridine in both complexes. For cis- $[\text{PtX}_4(\text{py})_2]$, two bands between 280-260 cm.^{-1} are assigned to $\nu(\text{Pt-py})$ by comparison with the above results. Only one pyridine fundamental near 450 cm.^{-1} is observed, indicating that in this case the number of $\nu(\text{M-py})$ bands observed relates to the predicted cis-symmetry of these complexes and not to interaction between the pyridine rings.

Fig. V-7.

Spectra sketches for pyridine complexes.

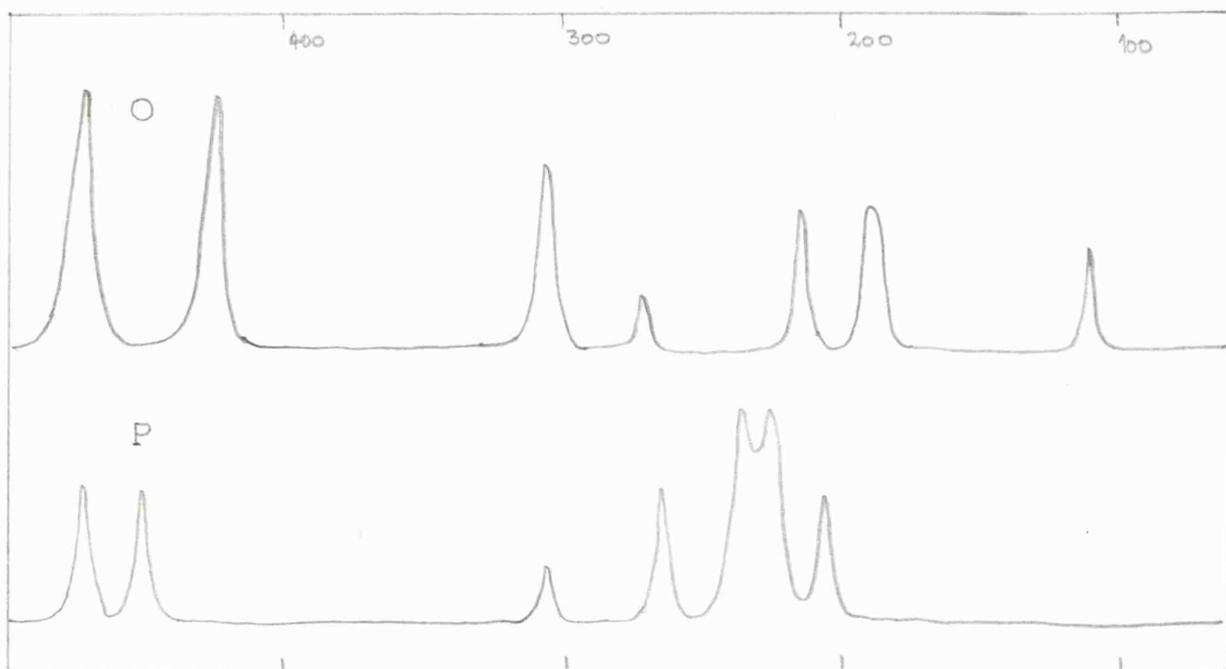
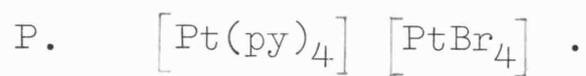


Table V-18.

Assignment of pyridine and ν (M-py) frequencies.

Assignment	pyridine 179	$[\text{Pt}(\text{py})_4] \cdot \text{Cl}_2$	$\begin{matrix} [\text{Pt}(\text{py})_4] \\ [\text{PtBr}_4] \end{matrix}$	$\begin{matrix} \text{cis-} \\ [\text{PtCl}_4(\text{py})_2] \end{matrix}$	$\begin{matrix} \text{cis-} \\ [\text{PtBr}_4(\text{py})_2] \end{matrix}$
ν_{16b}	405 (s)	473 (vs)	473 (m)	454 (m)	456 (vw)
	361 (vw)	426 (vs)	453 (m)		
ν (Pt-py)	208 (w)	213 (m)	210 (m)	216 (wm)	212 (w)
		307 (ms)	306 (w)	280 (wm)	282 (wm)
		272 (w)	262 (m)	267 (ms)	267 (wm)
$\nu_{\text{L}}(\text{Cl}^-)$		188 (m, b)			263 (wm)
ν (PtBr)		109 (wm)			
			235 (s)		
			225 (s)		

V-7. Metal-olefin vibrations.

Ethylene has no absorption below 800 cm.^{-1} ⁹⁸ and low-frequency halogen-insensitive bands in complex spectra may be assigned to MC_2 vibrations. An approach to metal-olefin vibrations is to consider the translations and rotations of ethylene which in the free ligand are spectroscopically inactive. On coordination these become vibrations of the MC_2 skeleton and become infrared-active (Fig. V-8). These modes and their approximate frequency positions are listed below.

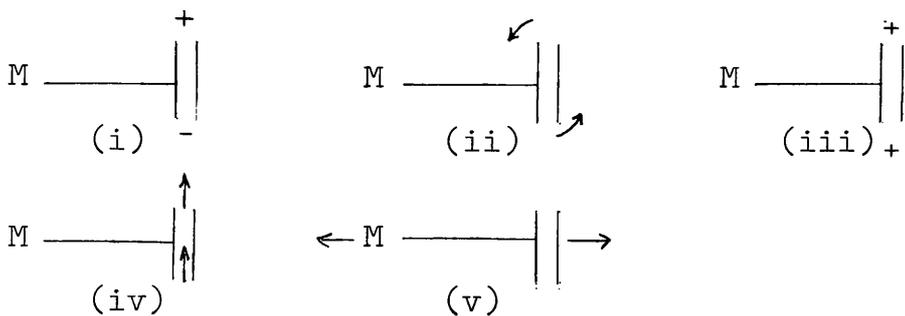
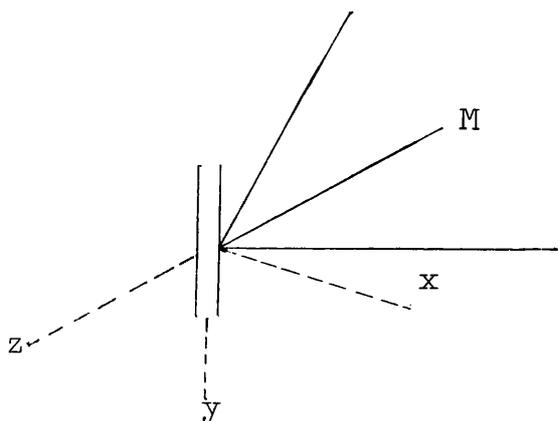
$\nu(\text{MC}_2)$	$500-400 \text{ cm.}^{-1}$
$\delta(\text{MC}_2)$	$\sim 200 \text{ cm.}^{-1}$
MC_2 torsion	$< 200 \text{ cm.}^{-1}$
$\pi(\text{MC}_2)$	$\ll 200 \text{ cm.}^{-1}$

Propylene will behave similarly except that in addition it has two low frequency skeletal modes at 428 and 177 cm.^{-1} due to $\delta(\text{CCC})$ and the C-CH_3 torsion^{69, 70}. The general pattern observed for the complexes resembles the predicted frequencies. Bands between $420-400 \text{ cm.}^{-1}$ are assigned to $\nu(\text{MC}_2)$ comparing well with previous work on Zeise's salt^{39, 32}, which

Fig. V-8.

Relation between translations and rotations of ethylene and MC_2 vibrations.

For a square-planar M-olefin bond;



- (i) Rotation about x axis - MC_2 torsion
- (ii) Rotation about z axis - $\surd(MC_2)as.$
- (iii) Translation about x axis - $\delta(MC_2)$
- (iv) Translation about y axis - $\pi(MC_2)$
- (v) Translation about z axis - $\surd(MC_2)s.$

assigned $\nu(\text{PtC}_2)_s$ and $\nu(\text{PtC}_2)_{as}$ at 493 and 411 cm^{-1} respectively. Bands at 450 and 425 cm^{-1} have been similarly assigned for $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$ ¹⁹ but as they are insensitive to deuteration the assignment may be in error. The remaining bands in the spectra may be divided into frequency regions. Those near 250 cm^{-1} are probably the in-plane bending modes $\delta(\text{MC}_2)$, whilst those at 180-100 cm^{-1} are associated with torsional modes and out-of-plane bending modes. In $\text{Pt}_2\text{X}_4(\text{C}_2\text{H}_4)_2$, these modes occur in the same region as Pt-X bending modes and the bands observed may be complex vibrations of the ClPtC_2 framework. This problem does not occur in $\text{Rh}_2\text{X}_2(\text{C}_2\text{H}_4)_4$ but the low frequency spectra are still difficult to interpret. The number of bands is consistent with a non-planar structure but further work is required before definite assignments can be made.

CHAPTER VI

Metal-metal bond vibrations.

VI-1. Introduction.

A complete survey of metal-ligand vibrations requires a study of metal-metal bond vibrations.

Little is known about M-M stretching frequencies,

$\nu(M-M)$; Raman spectroscopy has been used to identify $\nu(M-M)$ in a number of cases, (Table VI-1), but infrared studies have been confined to Herzberg's¹¹² listed values for diatomic, heteronuclear metal molecules in the gas phase and recent work by Cook et. al. These authors assigned $\nu(Hg-Fe)$ at 196 and $\nu(Cd-Fe)$ at 226 and 216 $cm.^{-1}$ in polymeric $Fe(CO)_4Hg$ and $Fe(CO)_4Cd$ respectively¹¹³. The molecules

Table VI-1.

Summary of published Raman data on $\nu(M-M)$.

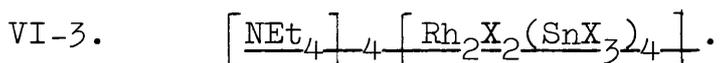
Species	State	$\nu(M-M)$	Reference
Hg_2^{2+}	Aqueous solution	169	114
Hg_2Cl_2	Single crystal	167	115
Cd_2^{2+}	Melt	183	116
$Sn_2(CH_3)_6$	Liquid	190	117
$Ge_2(CH_3)_6$	Liquid	273	117
$Hg [Co(CO)_4]_2$	Solution	132	118
$Cd [Co(CO)_4]_2$	Solution	161	118
$Re_2(CO)_{10}$	Solid	120	119

in Table VI-1 are all centro-symmetric and the frequencies listed are for the symmetric metal-metal bond stretching vibrations. These are Raman-active only and were identified by their polarisation property. No similar criterion exists in the infrared but the above data indicate the region in which the antisymmetric vibrations should be found. Thus Stammreich¹¹⁸, for $M^{II} [Co(CO)_4]_2$, (M = Hg, Cd), has estimated the maximum possible values for the antisymmetric $\nu(M-Co_2)$ as 265 and 305 $cm.^{-1}$ respectively. These values follow the general rule that for the same species, infrared-active antisymmetric stretching vibrations occur at a higher frequency than Raman-active symmetric stretching vibrations.

VI-2. Transition metal-tin bonds.

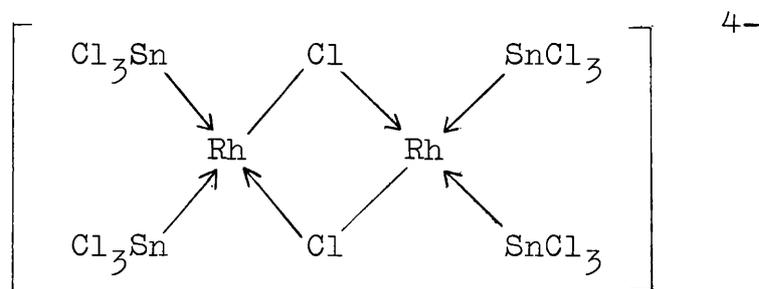
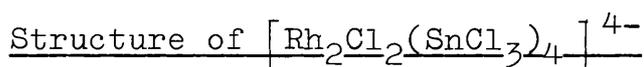
It has long been known that addition of stannous chloride to acid solutions of rhodium or platinum salts results in the formation of highly coloured, anionic species¹²⁰. Recently, complexes containing these species, and the corresponding iridium, ruthenium, osmium and palladium compounds, have been isolated¹²¹⁻¹³⁰. Several authors have

suggested that the complex anions contain tin-transition metal bonds. The far-infrared spectra to 70 cm.^{-1} of some of these compounds have been recorded (Figs. VI-1 and 2) and the results obtained (Table VI-2) are consistent with the structures proposed.



Davies, Wilkinson and Young¹²² suggested a planar-bridged structure with Rh-Sn bonds (Fig. VI-3) for the tetramethylammonium complex of the chloro-anion. This structure is the same as for

Fig. VI-3.



$\text{Rh}_2\text{Cl}_2(\text{COD})_2$, (Chapter III), and from theory should have two terminal $\nu(\text{RhSn})$ (B_{2u} and B_{3u}), and two bridge $\nu(\text{RhCl})$ (B_{2u} and B_{3u}). Only $\nu(\text{RhCl})$, $\nu(\text{SnCl})$ and $\nu(\text{RhSn})$ are expected to lie between $470\text{-}170 \text{ cm.}^{-1}$

$\nu(\text{RhSn})$ alone is halogen insensitive and therefore the bromo-analogue was prepared in the expectation that $\nu(\text{RhSn})$ would remain sensibly constant whilst the X-sensitive modes would shift to a lower frequency as X changed from Cl to Br.

In the chloro-anion bands at 289, 268 cm.^{-1} which shift to lower frequencies by c.a. 90 cm.^{-1} in the bromo-analogue are assigned to $\nu(\text{RhX})_b$. These compare well with values obtained for $\text{Rh}_2\text{X}_2\text{D}_2$ complexes in Chapter III and are taken as good evidence for the presence of a Rh X_2 Rh system in the anions. Absorptions near 360 and 325 cm.^{-1} in the chloro- and at 270 and 260 cm.^{-1} in the bromo-anion are assigned to $\nu(\text{SnX}_3)$. The spectra of $\text{M}[\text{SnX}_3]$, (M = K, NH_4 ; X = Cl, Br) were examined and show bands at similar frequencies which must be $\nu(\text{SnX}_3)$. There is one further band, near 210 cm.^{-1} in the spectra of the anions $[\text{Rh}_2\text{X}_2(\text{SnX}_3)_4]^{4-}$. It remains sensibly constant when Br replaces Cl and is assigned to $\nu(\text{Rh-Sn})$. Other possible vibrations such as the SnX_3 bending modes and $\pi(\text{Rh}_2\text{X}_2)$ are all expected below 150 cm.^{-1} . One $\nu(\text{Rh-Sn})$ was found whereas theory requires two, however both $\nu(\text{Rh-Sn})$ bands are broad and may be unresolved doublets. This is consistent with the results found for $[\text{M}_2\text{X}_6]^{2-}$, (Chapter I), where the

Fig. VI-1.

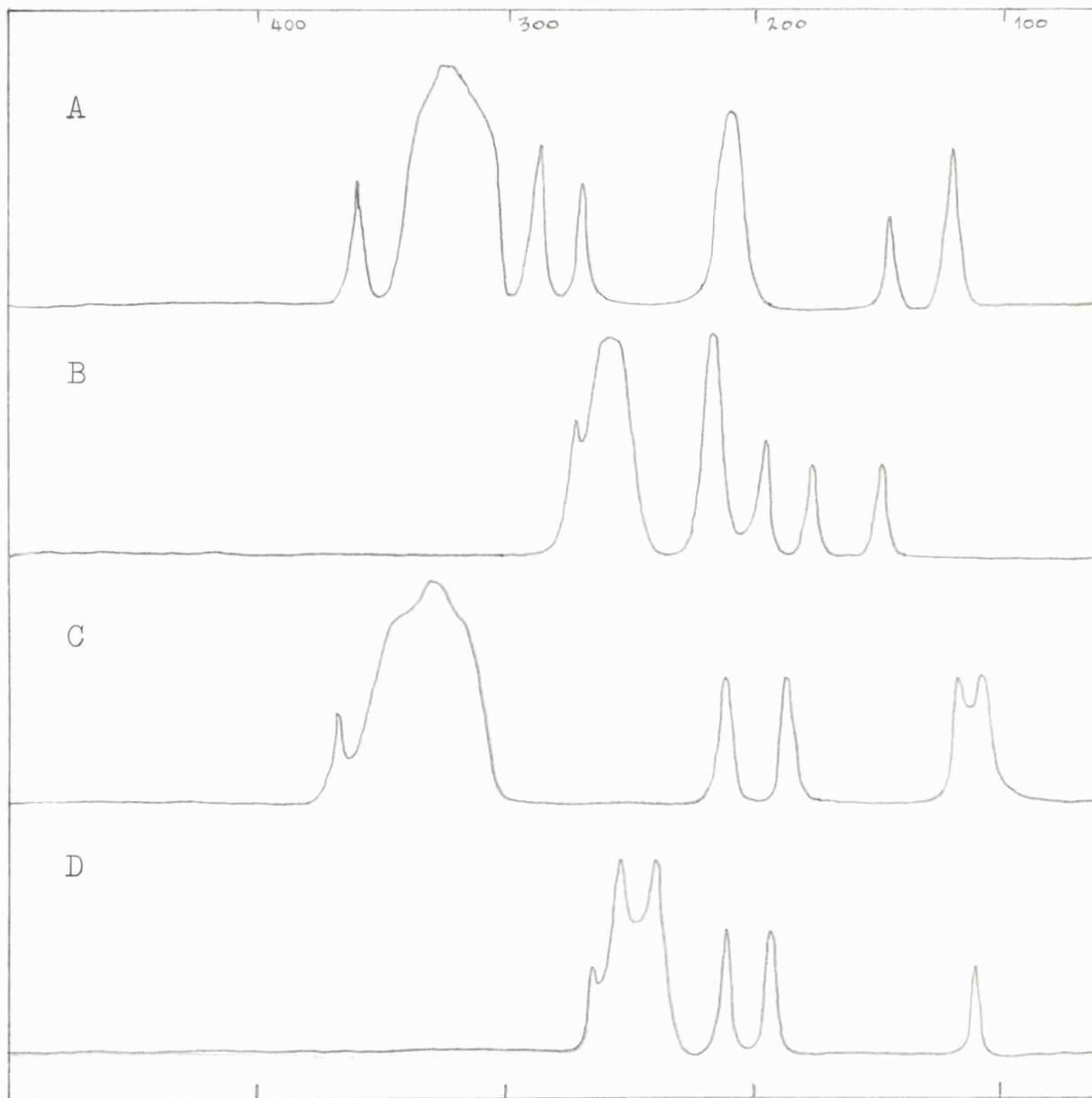


Fig. VI-1. (facing page).

Spectra sketches of transition
metal-tin complexes.

- A. $[\text{NEt}_4]_4 [\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4] \cdot$
B. $[\text{NEt}_4]_4 [\text{Rh}_2\text{Br}_2(\text{SnBr}_3)_4] \cdot$
C. $[\text{NEt}_4]_3 [\text{Pt}(\text{SnCl}_3)_5] \cdot$
D. $[\text{NEt}_4]_3 [\text{Pt}(\text{SnBr}_3)_5] \cdot$

Fig. VI-2.

Spectra sketches of transition
metal-tin complexes.

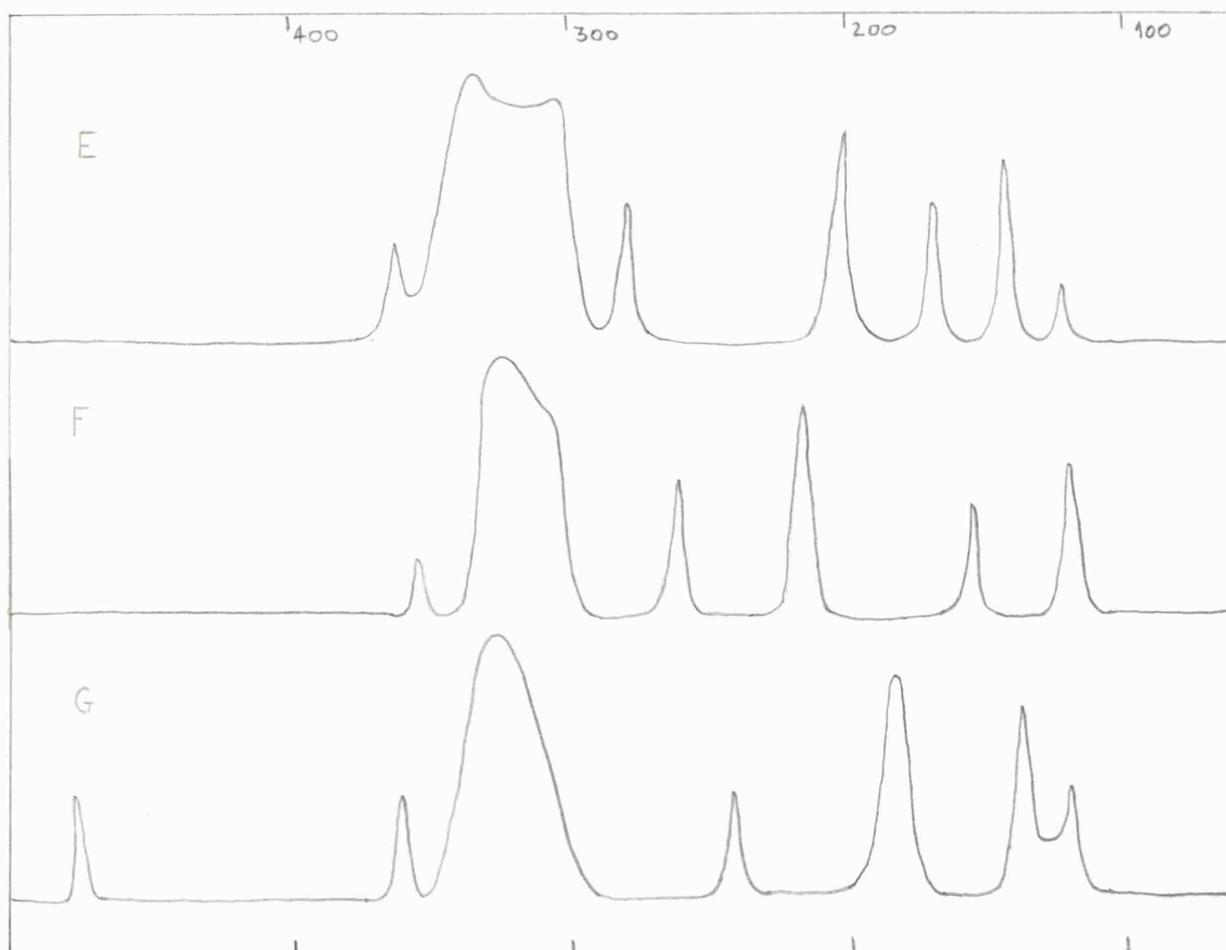


Table VI-2. Frequencies and assignments of transition metal-tin complexes.

Complex	$\nu(\text{SnX}_3)$	$\delta(\text{SnX}_3)$	$\nu(\text{MX})_t$	$\nu(\text{MX})_b$	$\delta(\text{MX}_2)$	$\nu(\text{M-Sn})$	$\delta(\text{M-Sn})$	Other bands
$[\text{NEt}_4]_4$								
$[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]$	361 (wm) 325 (vs, b)	120 (ms)		289 (ms) 268 (m)		209 (s, b)	145 (wm)	
$[\text{NEt}_4]_4$								
$[\text{Rh}_2\text{Br}_2(\text{SnBr}_3)_4]$	272 (m) 260 (vs, b)			197 (m) 176 (wm)		217 (vs)	148 (wm)	
$[\text{NEt}_4]_3$								
$[\text{Pt}(\text{SnCl}_3)_5]$	365 (wm) 325 (vs, vb)	118 (m)				212 (m) 185 (m)	111 (m)	
$[\text{NEt}_4]_3$								
$[\text{Pt}(\text{SnBr}_3)_5]$	264 (wm) 254 (s) 236 (s)					211 (m) 193 (m)	110 (wm)	
$[\text{NMe}_4]_4$								
$[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4]$	363 (wm) 335 (vs, b)	124 (w)	(335)*	305 (s) 281 (m)	(173)	203 (s) 173 (m)	144 (ms)	
$[\text{NMe}_4]_2$								
$[\text{RuCl}_2(\text{SnCl}_3)_2]$	355 (w) 325 (vs, b)	120 (m)		(325) 261 (m)		216 (s)	156 (wm)	
$[\text{AsPh}_4]_2$								
$[\text{PdCl}_2(\text{SnCl}_3)_2]$	361 (wm) 328 (vs, vb)	120 (wm)	(328)		(185)	185 (s, b)	476 (wm) 242 (wm) 139 (ms)	

* Coincident bands, approximate frequencies enclosed by brackets.

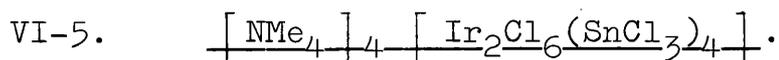
maximum separation between the two terminal $\nu(\text{MX})$ was 5 cm.^{-1} . The apparent rise in $\nu(\text{Rh-Sn})$ from 209 to 217 cm.^{-1} , when X is changed from Cl to Br, is almost certainly caused by vibrational coupling between the bridge and Rh-Sn stretching modes.

$\nu(\text{RhSn})$ in the bromide would be expected to appear at a lower frequency than in the chloro- complex. Then the higher of the two bridge frequencies in the bromo- complex would be very close to the position of $\nu(\text{RhSn})$. The two modes are of the same symmetry species and their interaction would cause, as was observed, an increase in $\nu(\text{Rh-Sn})$ and a decrease in $\nu(\text{RhBr})_b$. Bands near 145 cm.^{-1} occur in both the chloro- and bromo- anions and must be associated with Rh-Sn vibrations. The values are too high to be due to lattice modes of the tetraethylammonium cation and a tentative assignment as in-plane $\delta(\text{RhSn})$ is made. The band at 120 cm.^{-1} in the chloro- anion is assigned to $\delta(\text{SnCl}_3)$; cf. Raman study by Woodward found $\delta(\text{SnCl}_3)$ (E) at 103 cm.^{-1} ¹³¹.

VI-4. $\left[\frac{[\text{NEt}_4]_3}{\text{Cramer et. al.}^{121}} \frac{[\text{Pt}(\text{SnX}_3)_5]}{\text{reported the preparation of}} \right]$
 $\left[\text{Ph}_3\text{PCH}_3 \right]_3 \left[\text{Pt}(\text{SnCl}_3)_5 \right]$ but no structure was

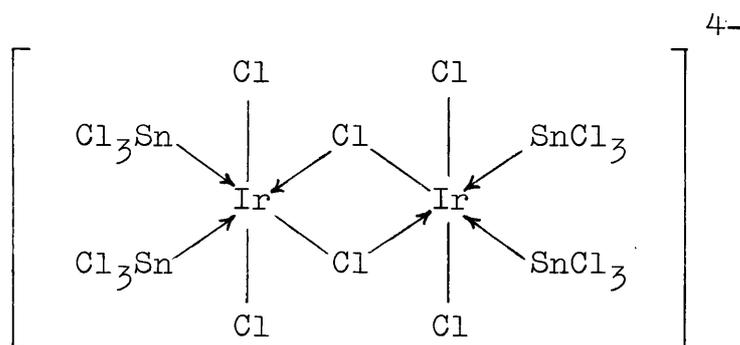
postulated. Subsequent X-ray diffraction of this complex¹²⁵ showed that $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ has a trigonal bi-pyramidal structure D_{3h} , consisting of a central platinum atom surrounded by five $[\text{SnCl}_3]^-$ ligands attached through platinum-tin bonds. Theory allows five infrared-active skeletal modes for this PtSn_5 structure; two $\nu(\text{PtSn})$ (A_2'' and E') and three Pt-Sn bending modes, ($A_2'' + 2E$). The infrared spectra of $[\text{NEt}_4]_3 [\text{Pt}(\text{SnX}_3)_5]$ may be explained in terms of this structure.

Complex absorptions centred at 325 and 250 cm^{-1} in the chloro- and bromo- anions respectively are assigned to $\nu(\text{SnX}_3)$. These values agree with those found for Rh-Sn complexes and in trans- $[\text{PtHSnCl}_3(\text{PEt}_3)_2]^{124}$. $\nu(\text{PtSn})$ is assigned near 200 cm^{-1} in both complexes. The bands at 212, 185 and 211, 193 cm^{-1} for X = Cl and Br respectively, are halogen-insensitive and consistent with a trigonal bi-pyramidal structure. The halogen-sensitive band at 118 cm^{-1} in $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ is assigned to $\delta(\text{SnCl}_3)$ and the bands near 110 cm^{-1} in both complexes are tentatively assigned to the bending mode of the equatorial Pt-Sn bonds.



The suggested structure for this anion¹²³ contains bridging chlorine atoms with Ir(III) in octahedral coordination, Fig. VI-4.

Fig. VI-4. Structure of $\left[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4 \right]^{4-}$.



In addition to $\nu(\text{SnCl}_3)$, theory shows that for this structure, five stretching vibrations are infrared-active, viz. $\nu(\text{IrCl})_t$ (B_{1u}), $\nu(\text{IrCl})_b$ ($B_{2u} + B_{3u}$) and $\nu(\text{IrSn})$ ($B_{2u} + B_{3u}$). The M-Cl modes are expected to lie in a different region of the spectrum to $\nu(\text{IrSn})$. The spectrum of $\left[\text{Ir}_2\text{Cl}_6(\text{SnCl}_3)_4 \right]^{4-}$ is consistent with this structure. A very strong, broad absorption centred at 325 cm^{-1} with maxima at 363 , 335 and 305 cm^{-1} is assigned to $\nu(\text{SnCl}_3)$ and $\nu(\text{IrCl})$. The range of $\nu(\text{SnCl}_3)$ has previously been established and for Ir(III), $\nu(\text{IrCl})_t$ has been

found between 340-300 cm.^{-1} in trans- $[\text{IrCl}_3\text{L}_3]^{132}$
and $[\text{IrD}_2\text{Cl}_2] \text{X}$ (D = diarsine, X = Cl, ClO_4)¹³³.

This absorption may embrace $\nu(\text{IrCl})_b$ and the maximum
at 305 cm.^{-1} is possibly the higher bridge mode

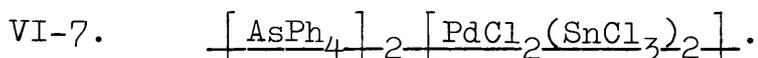
$\nu(\text{IrCl})_b$, consistent with values found for $\nu(\text{PdCl})_b$.
The assignment of $\nu(\text{IrCl})_b$ at 281 cm.^{-1} is more
certain as this position rules out alternative assignment
to terminal stretching modes and it compares well with
previous assignments of $\nu(\text{MX})_b$, (M = Pt, Pd, Rh).
By comparison with the values found for the rhodium
and platinum complexes, $\nu(\text{IrSn})$ is at 203 and 173 cm.^{-1} .
Assignment of the lower band is less certain as the bending
vibration of the terminal trans- [Cl-Ir-Cl] bonds
is expected near 180 cm.^{-1} . In line with previous
assignments, $\delta(\text{SnCl}_3)$ is at 124 cm.^{-1} and $\delta(\text{IrSn})$
at 145 cm.^{-1} .

VI-6. $[\text{NMe}_4]_2[\text{RuCl}_2(\text{SnCl}_3)_2]$.

The species $[\text{RuCl}_2(\text{SnCl}_3)_2]^{2-}$ exists in
solution but the solid was thought to be polymeric,
linked through chloro-bridges¹²³. The spectrum supports
this conclusion. The band at 261 cm.^{-1} is not
associated with $\nu(\text{RuCl})_t$, $\nu(\text{SnCl}_3)$ or $\nu(\text{RuSn})$ and
is assigned to $\nu(\text{RuCl})_b$. The characteristic broad

absorption centred at 328 cm.^{-1} is assigned to

$\nu(\text{SnCl}_3)$. The presence of $\nu(\text{RuCl})_t$ would certainly be masked by this band as $\nu(\text{RuCl})$ in $\text{Ru}(\text{diarsine})_2\text{Cl}_2$ ¹³³ was found at 316 cm.^{-1} . $\nu(\text{RuSn})$ at 216 cm.^{-1} is in line with previous assignments and the remaining bands at 120 and 156 cm.^{-1} are assigned to $\delta(\text{SnCl}_3)$ and $\delta(\text{RuSn})$. The latter must be regarded as very tentative in view of its close proximity to $\nu(\text{RuSn})$.



This complex was first prepared by Khattak and McGee¹²⁸ who proposed a structure identical with the Rh-Sn complex, Fig. VI-3, i.e. $\left[\text{AsPh}_4 \right]_4 \left[\text{Pd}_2\text{Cl}_2(\text{SnCl}_3)_4 \right]$. No evidence was given to support this structure which would require Pd(I). Interpretation of the spectrum allows an alternative structure to be proposed. Bands at 476 , 242 and 139 cm.^{-1} correlate with known absorptions of $\left[\text{AsPh}_4 \right]^+$. The characteristic strong and broad absorption at 328 cm.^{-1} will include $\nu(\text{SnCl}_3)$, modes of $\left[\text{AsPh}_4 \right]^+$ and $\nu(\text{PdCl})_t$ but distinction is not possible. However, no band was observed between 300 - 250 cm.^{-1} which suggests that bridge Pd-Cl bonds are absent, cf. Chapter II. The strong broad band at 185 cm.^{-1}

can only be $\nu(\text{PdSn})$ or $\delta(\text{PdCl})_t$ or a coincidence of both modes. The remaining band at 120 cm.^{-1} is assigned to $\delta(\text{SnCl}_3)$. From this evidence a structure involving the Pd_2Cl_2 bridge system is not tenable. Elemental analysis of the complex will allow the alternative formulation $[\text{AsPh}_4]_2 [\text{PdCl}_2(\text{SnCl}_3)_2]$ which is consistent with the observed spectrum. However, coincidence of bands prevents designation to cis- or trans- form. This square-planar Pd(II) anion resembles familiar cis- and trans- $[\text{PdX}_2\text{L}_2]$ complexes and corresponding Pt(II) complexes, $[\text{NMe}_4]_2 [\text{PtCl}_2(\text{SnCl}_3)_2]$ have been prepared¹²³.

VI-8. Conclusions.

$\nu(\text{MSn})$, (M = Rh, Pt, Ir, Ru and Pd) are found in the narrow frequency range $217\text{-}173 \text{ cm.}^{-1}$. This compares with concurrent determinations¹¹³ of $\nu(\text{HgFe})$ and $\nu(\text{CdFe})$ between $230\text{-}190 \text{ cm.}^{-1}$ and with Stammreich's¹¹⁸ estimated maximum value for $\nu(\text{HgCo})$ of 265 cm.^{-1} . Assignment of $\nu(\text{MSn})$ has confirmed the presence of definite M-Sn bonds in these complexes. In contrast, infrared study³ of $[\text{Pt}(\text{NH}_3)_4] [\text{PtCl}_4]$, (Magnus' Green Salt), has shown that metal-metal interaction, unlike metal-metal bond formation, has

no significant effect upon the infrared spectra of complex ions. $\delta(\text{MSn})$ lies in the range 155-110 cm.^{-1} . Assignment is tentative because it places the bending mode at frequencies close to $\nu(\text{MSn})$. Alternative assignments are ruled out as the bands are halogen insensitive and $[\text{NR}_4]^+$ lattice vibrations are found below 100 cm.^{-1} .

Structural conclusions drawn from the spectra agree with published data with the exception of the Pd-Sn complex, for which an alternative structure is proposed. Of particular importance in interpretation of the data was the recognition of bridged MX_2M systems by comparison with values found for $\nu(\text{MX})_b$ in Chapters I and II.

All the spectra show the characteristic absorption of $\nu(\text{SnX}_3)$ and $\delta(\text{SnX}_3)$, confirming the presence of this species in each of the complexes.

EXPERIMENTAL

1. Instruments.

Spectra were recorded for Nujol mulls using the following instruments:

(i) Perkin-Elmer 225 ($600-190\text{ cm.}^{-1}$): This instrument develops a high temperature at the sample holder (80°C) and poorly resolved spectra with broad bands were obtained. This was overcome by placing the polythene plates in a holder made of hollow copper tubing inside an evacuated chamber and cooling with liquid nitrogen.

(ii) Evacuated grating instrument ($475-170\text{ cm.}^{-1}$): This instrument has been previously described and was used without modification¹⁸⁸.

(iii) Research and Industrial Instruments Co. FS-520 interferometer ($350-70\text{ cm.}^{-1}$). Fourier transforms were computed to an effective resolution of 5 cm.^{-1} .

Calibration of the instruments was checked periodically using water vapour¹⁸⁹.

All bands listed above 170 cm.^{-1} have been observed in spectra recorded on at least two of the instruments to avoid possible error. Instruments

(ii) and (iii) give spectra with background absorption from use of polythene cells. Where possible bands in the region of this absorption were verified on the Perkin-Elmer 225. The correlation between the spectra recorded on different instruments for the same compound was good, maximum deviation being 5 cm.^{-1} . The resolution of the interferometer is 5 cm.^{-1} so that above 170 cm.^{-1} , frequencies listed were taken from spectra recorded on the other instruments ($\pm 1 \text{ cm.}^{-1}$). Below 170 cm.^{-1} the frequencies are accurate to $\pm 3 \text{ cm.}^{-1}$. Band shapes were consistent but intensities did show some variation. Intensity data were taken from spectra run on the Perkin-Elmer 225 on these occasions.

2. Preparations.

For reference purposes, preparations of the complexes are listed in Chapter sequence.

2.1. Chapter I.

With the exception of the new compounds described below, the complexes were prepared as described previously⁴⁹.

(a) Tetraphenylarsonium Tetrachloro- $\mu\mu'$ -dichlorodipalladium (II). - An aqueous solution of

potassium tetrachloropalladate (0.64 g.) was added to a solution of 1.67 g. of tetraphenylarsonium chloride in 10 ml. of water. The pink precipitate was washed with water and ethanol, and dried. Recrystallisation from aqueous acetone gave brown-orange crystals (0.8 g.) m.p. 225-235° (decomp) (Found: C, 48.2; H, 3.3; Cl, 17.9. $C_{48}H_{40}As_2Cl_6Pd_2$ requires C, 48.3; H, 3.3; Cl, 17.8%). Analogous preparations yielded the tetrabutyl ammonium (b) and n-cetyltrimethylammonium salts (c) for which recrystallisation solvent, m.p. and analytical data are given below.

(b) Aqueous acetone; > 300° (d); (Found C, 41.9; H, 7.9. $C_{32}H_{72}Cl_6N_2Pd_2$ requires C, 42.2; H, 8.0%).

(c) Methylene dichloride; > 300° (d); (Found: C, 44.1; H, 8.4. $C_{38}H_{84}Cl_6N_2Pd_2$ requires C, 45.5; H, 8.5%).

(d) Tetraphenylarsonium Tetrachloro- $\mu\mu'$ -dichlorodiplatinum (II). - An aqueous solution of potassium tetrachloroplatinite (0.42 g.) was added to a solution of tetraphenylarsonium chloride (0.44 g.)

in 10 ml. of water. The pink precipitate was washed with water and ethanol, and dried. It was then extracted three times with boiling methylene dichloride and the extracts taken to dryness.

Recrystallisation from a small volume of methylene dichloride gave pink-brown microcrystals (0.25 g.), m.p. 230° (decomp.) (Found: C, 42.1; H, 3.0; Cl, 15.4. $C_{48}H_{40}As_2Cl_6Pt_2$ requires C, 42.1; H, 3.0; Cl, 15.5%). This anion was first prepared by Chatt as the $[Pr_3POH]^+$ salt⁵⁰.

2.2. Chapter II.

With the exception of the new compounds described below, the complexes were prepared as described previously⁶⁰, 190-202. Authenticity was checked by comparison with known melting point and colour.

(a) The majority of the new complexes were prepared by the following method. An acetone solution of the chloro- complex $M_2Cl_4L_2$ was refluxed for 1-1½ hours with a two-fold excess of lithium bromide (anhydrous) or sodium iodide to give the corresponding bromo- or iodo- complex. The solution was taken to dryness, and the resulting solid washed with hot

water and recrystallised. Substitution of the chloride is immediate as witnessed by the sharp colour change on addition of the alkali halide. Compounds prepared by this method are listed and recrystallisation solvent, colour, m.p. and analysis are given.

$\text{Pt}_2\text{Br}_4(\text{PEt}_3)_2$: ethanol; red; 202° . (Found: C, 15.1; H, 3.0. $\text{C}_{12}\text{H}_{30}\text{Br}_4\text{P}_2\text{Pt}_2$ requires C, 15.2; H, 3.2%). Iodo-analogue: acetone, bright red, 209.5° . (Found: C, 12.6; H, 2.8. $\text{C}_{12}\text{H}_{30}\text{I}_4\text{P}_2\text{Pt}_2$ requires C, 12.7; H, 2.7%).

$\text{Pt}_2\text{Br}_4(\text{AsEt}_3)_2$: ethanol, orange-red, $182-3^\circ$ (Found: C, 14.2; H, 3.0. $\text{C}_{12}\text{H}_{30}\text{As}_2\text{Br}_4\text{Pt}_2$ requires C, 13.9; H, 2.9%). Iodo-analogue: acetone, claret, 193° (d). (Found: C, 12.0; H, 2.6. $\text{C}_{12}\text{H}_{30}\text{As}_2\text{I}_4\text{Pt}_2$ requires C, 11.8; H, 2.5%).

$\text{Pt}_2\text{Br}_4(\text{AsPr}^n)_2$: acetone, red, $144-5^\circ$. (Found: C, 19.5; H, 4.0. $\text{C}_{18}\text{H}_{42}\text{As}_2\text{Br}_4\text{Pt}_2$ requires C, 19.3; H, 3.8%). Iodo-analogue: acetone, deep red, $170-1^\circ$ (d). (Found: C, 16.7; H, 3.4. $\text{C}_{18}\text{H}_{42}\text{As}_2\text{I}_4\text{Pt}_2$ requires C, 16.6; H, 3.2%).

$\text{Pt}_2\text{Br}_4(\text{SEt}_2)_2$: insoluble, mustard yellow, 200° (d).

(Found: C, 11.0; H, 2.4. $C_8H_{20}Br_4Pt_2S_2$ requires C, 10.8; H, 2.3%).

$Pt_2Br_4(SPr^N)_2$: acetone, yellow, 174 (d). (Found: C, 15.1; H, 2.9. $C_{12}H_{28}Br_4Pt_2S_2$ requires C, 15.2; H, 3.0%).

$Pt_2Br_4(SBu^N)_2$: acetone, deep yellow, 175-80°. (Found: C, 19.5; H, 3.7. $C_{16}H_{36}Br_4Pt_2S_2$ requires C, 19.2; H, 3.6%).

$Pd_2Br_4(PEt_3)_2$: ethanol, red, 212-3°. (Found: C, 18.9; H, 3.9. $C_{12}H_{30}Br_4P_2Pd_2$ requires C, 18.7; H, 3.9%).

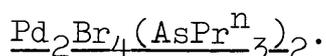
Iodo-analogue: acetone, red-brown, 191-2°. (Found: C, 15.0; H, 3.2. $C_{12}H_{30}I_4P_2Pd_2$ requires C, 15.1; H, 3.2%).

$Pd_2Br_4(AsEt_3)_2$: ethanol, red-brown, 180-2°. (Found: C, 17.0; H, 3.6. $C_{12}H_{30}As_2Br_4Pd_2$ requires C, 16.8; H, 3.5%). Iodo-analogue: acetone, purple-black, 158-9°. (Found: C, 14.0; H, 2.9. $C_{12}H_{30}As_2I_4Pd_2$ requires C, 13.8; H, 2.9%).

(b) The following complexes were prepared by adaption of published methods.

$Pt_2Br_4(C_2H_4)_2$:

Apparatus used was as described for the corresponding chloro-complex²⁰¹. To an aqueous solution of potassium tetrabromoplatinate (1.4g.) was added concentrated hydrobromic acid (1 ml.) and a catalytic quantity of stannous bromide¹²¹. The red-brown solution was shaken in contact with ethylene under pressure until golden-yellow (2½ hrs.). Water was removed *in vacuo* over concentrated sulphuric acid and potassium hydroxide pellets. Residual solid was powdered and extracted with absolute ethanol: concentrated hydrobromic acid (20:1). The orange-red solution was filtered and taken to dryness *in vacuo* (15 mm.) at 20° and then at 50° just prior to complete removal of the solvent. Resulting brown solid was dried, and recrystallisation from toluene gave orange-brown crystals (0.25 g.), m.p. 160-70° (d). Animal charcoal was added during recrystallisation to remove traces of colloidal platinum. (Found: C, 6.4; H, 1.1 . C₄H₈Br₄Pt₂ requires C, 6.3; H, 1.1%).



Bis-(tri-n-propylarsine)dibromopalladium(II)
(1.0 g.) in ethanol (25 ml.) was added to potassium

tetrabromopalladate (0.8 g.) in 1:1 ethanol: water (30 ml.). The solution was refluxed for $1\frac{1}{4}$ hours, filtered hot and filtrate left to stand overnight. Precipitate formed was filtered off, dried and recrystallisation from acetone gave red-brown crystals. (1.1 g.), m.p. 153° . (Found: C, 23.1; H, 4.5. $C_{18}H_{42}As_2Br_4Pd_2$ requires C, 23.0; H, 4.5%).

$Pd_2Br_4(PPh_3)_2$.

Potassium tetrabromopalladate (0.66 g.) dissolved in the smallest volume of ethanol: water (10:1) was added to triphenylphosphine (0.32 g.) in chloroform (50 ml.) and refluxed for 2 hours. An orange complex, bis-(triphenylphosphine) dibromopalladium (II), initially formed, redissolved to give the dark-brown bridge complex. This was filtered off, washed with water, ethanol and cold chloroform and purified from chloroform solution by precipitation with petroleum ether ($40-60^{\circ}$) to give red-brown crystals (0.4 g.), m.p. $260-280^{\circ}$ (d). (Found: C, 40.8; H, 2.7. $C_{36}H_{30}Br_4P_2Pd_2$ requires C, 40.9; H, 2.9%).

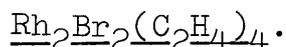
$Pd_2Cl_4[P(OEt)_3]_2$.

An aqueous solution of potassium tetrachloropalladate (0.5 g.) was added to triethylphosphite

(0.2 g.) in acetone (10 ml.) and left to stand for 24 hours. A beige solid, bis-(triethylphosphite) dichloroplatinum (II), was removed by filtration and the filtrate evaporated to dryness at 15 m.m. A viscous yellow-brown oil; insoluble in petroleum ether (40-60°) but soluble in benzene was obtained. Recrystallisation from a 4:1 mixture of these solvents reproduced the oil. Scratching with a glass rod and freezing a petroleum ether suspension also failed to produce a solid. The oil was finally dried in vacuo and stored over concentrated sulphuric acid to give a yellow/brown oily solid. The bromo-analogue prepared by the same method, was obtained as a deep red, viscous oil.

2.3. Chapter III.

With the exception of the new compounds described below, the complexes were prepared as described previously^{86-88, 203}.



An aqueous solution of anhydrous lithium bromide (0.6 g.) was added to hydrated rhodium trichloride (0.5 g.) in aqueous methanol (5 ml.). The solution was stirred but not heated for 2 hours

and then ethylene was bubbled into the stirred solution for a further 6 hours. The solid formed was filtered off, washed with methanol and ether and dried to give an orange-brown powder, (0.2 g.), m.p. 85-100°(d). Further purification resulted in decomposition (Found: C, 19.6; H, 3.8. $C_8H_{16}Br_2Rh_2$ requires C, 20.1; H, 3.4%).

$Rh_2Br_2(NBD)_2$.

Aqueous solutions of hydrated rhodium trichloride (0.4 g.) and lithium bromide (0.5 g.) were mixed and shaken for 30 minutes. Norbornadiene (1.5 ml.) was added and the solution shaken for 2 days. The solid formed was filtered off, dried and recrystallisation from chloroform gave a bright yellow powder (0.2 g.), m.p. 190-200° (d). (Found: C, 30.8; H, 3.2. $C_{14}H_{16}Br_2Rh_2$ requires C, 30.6; H, 3.2%).

$Rh_2Br_2(dCPD)_2$.

This complex was prepared by the action of LiBr on the chloro- complex in acetone solution. Recrystallisation of the solid obtained on evaporation of the solvent from glacial acetic acid gave red-brown crystals. m.p. 190-5° (d). (Found: C, 44.9;

H, 4.7; $C_{20}H_{24}Br_2Rh_2$ requires C, 44.6; H, 4.5%).

2.4. Chapter IV.

With the exception of the new compounds described below, the complexes were prepared by established methods^{195, 197, 204}. Their identities were confirmed by colour, solubility, m.p. and the distinction between cis and trans forms checked by Nyholm's acetone-silver nitrate test²⁰⁴.

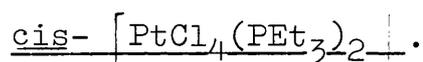
trans- $[PtCl_4(PEt_3)_2]$.

Chlorine was bubbled through a solution of trans-bis(triethylphosphine) dichloroplatinum (II) (0.2 g.) in 20 ml. of chloroform until no further reaction occurred. The solution was evaporated to dryness under reduced pressure and the solid residue recrystallised from alcohol giving deep yellow crystals (0.17 g.), m.p. 152-153^o (Found: C, 25.1; H, 5.3. $C_{12}H_{30}Cl_4P_2Pt$ requires C, 25.1; H, 5.3%).

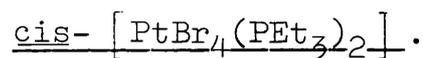
trans- $[PtI_4(PEt_3)_2]$.

Resublimed iodine (0.2 g. in 20 ml. of chloroform) was added to 0.42 g. of trans-bis(triethylphosphine)di-iodoplatinum (II) in 25 ml. of

chloroform. After $1\frac{1}{2}$ hr. the solution was evaporated to dryness under reduced pressure and the solid residue recrystallised from alcohol, giving shiny black crystals (0.3 g.) m.p. $110-111^{\circ}$ (Found: C, 15.5; H, 3.3. $C_{12}H_{30}I_4P_2Pt$ requires C, 15.4; H, 3.2%).



Chlorine was bubbled through a solution of cis-bis(triethylphosphine)dichloroplatinum(II) (0.25 g.) in cold chloroform (40 ml.) until no further reaction occurred. The solution was evaporated to dryness under reduced pressure and the residue recrystallised from alcohol giving lemon-yellow crystals (0.15 g.), m.p. $133-134^{\circ}$ (Found: C, 25.2; H, 5.4. $C_{12}H_{30}Cl_4P_2Pt$ requires C, 25.2; H, 5.3%).



0.14 g. of bromine in 10 ml. of carbon tetrachloride was added to a solution of 0.5 g. of cis-bis(triethylphosphine)dibromoplatinum (II) in 40 ml. of 1:1 chloroform-benzene. A precipitate immediately formed and was recrystallised from a large volume of alcohol giving a voluminous yellow

solid (0.46 g.), m.p. 120° (at which it isomerises to the trans form). (Found: C, 19.1; H, 4.1. $C_{12}H_{30}Br_4Pt$ requires C, 19.1; H, 4.0%).

trans- [PtBr₄(SMe₂)₂].

0.16 g. of bromine in 10 ml. of chloroform was added to a solution of 0.45 g. of trans-bis(dimethylsulphide)dibromoplatinum (II) in 25 ml. of chloroform. After 2 hr. the solution was evaporated to dryness and the solid residue recrystallised from chloroform giving vermilion-red microcrystals (0.3 g.), darkening at 160° , m.p. $230-240^{\circ}$ (decomp.) (Found: C, 7.6; H, 2.0; S, 10.0. $C_4H_{12}Br_4PtS_2$ requires C, 7.5; H, 1.9; S, 10.0%).

trans- [PtI₄(SMe₂)₂].

0.1 g. of resublimed iodine in 15 ml. of chloroform was added to 0.2 g. of trans-bis(dimethyl sulphide)di-iodoplatinum (II) in 20 ml. of chloroform. A dark solid separated after 1 hr. and was washed with chloroform, alcohol, and then ether giving lustrous green-black crystals, 0.1 g., m.p. $210-220^{\circ}$ (decomp.) (Found: C, 5.9; H, 1.6. $C_4H_{12}I_4PtS_2$ requires C, 5.8; H, 1.5%).

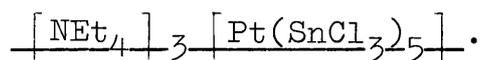
2.5. Chapter V.

All complexes studied in this chapter were prepared as described previously²³, 195-8, 205-8.

2.6. Chapter VI.

$\left[\text{NEt}_4 \right]_4 \left[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4 \right]$.: This complex was prepared by the established method¹²³ for the tetramethylammonium salt. Recrystallisation from ethanolic hydrochloric acid gave yellow orange powder, m.p. $> 300^\circ$ (d). (Found: C, 22.2; H, 4.6; N, 3.1; Cl, 29.5. $\text{C}_{32}\text{H}_{80}\text{N}_4\text{Cl}_{14}\text{Rh}_2\text{Sn}_2$ requires C, 22.6; H, 4.7; N, 3.3; Cl, 29.2%).

Bromo- analogue: prepared as above. Recrystallisation from ethanolic hydrobromic acid gave claret red powder, m.p. 260° (d). (Found C, 16.2; H, 3.3; N, 2.2; Br, 50.1. $\text{C}_{32}\text{H}_{80}\text{N}_4\text{Br}_{14}\text{Rh}_2\text{Sn}_4$ requires C, 16.6; H, 3.5; N, 2.4; Br, 48.2%).



3 M. hydrochloric acid solutions of stannous chloride and potassium chloroplatinate were mixed (Sn: Pt = 10:1). Addition of a slight excess of tetraethylammonium chloride to the deep red solution gave an orange precipitate. This was filtered, washed

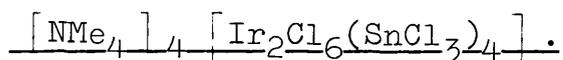
with 3 M. hydrochloric acid and dried in vacuo.

Darkens at 180°, decomposition 260°. (Found: C, 16.9; H, 3.6; N, 2.3; Cl, 30.0. $C_{24}H_{60}Cl_{15}N_3PtSn_5$ requires C, 16.7; H, 3.5; N, 2.5; Cl, 31.1%).

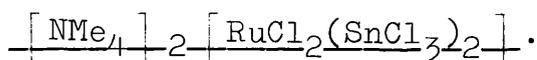
Bromo- analogue

Prepared by same method. Claret red powder, 230° (d). (Found: C, 12.2; H, 2.6; N, 1.6; Br, 50.6. $C_{24}H_{60}Br_5N_3PtSn_5$ requires C, 12.1; H, 2.5; N, 1.8; Br, 50.4%).

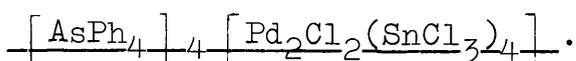
These complexes were prepared as described previously^{123, 128}.



(Found: C, 10.1; H, 2.7; N, 3.0; Cl, 35.6. $C_{16}H_{48}Cl_{18}Ir_2N_4Sn_4$ requires C, 10.2; H, 2.7; N, 3.1; Cl, 35.8%).



(Found: C, 12.3; H, 3.2; N, 3.7; Cl, 36.8. $C_8H_{24}Cl_8N_2RuSn_2$ requires C, 12.5; H, 3.1; N, 3.6; Cl, 36.8%).



(Found: C, 42.3; H, 3.0; Cl, 18.6. $C_{48}H_{40}As_2PdCl_7Sn_2$ requires C, 42.4; H, 3.0; Cl, 18.3%).

Spectroscopic evidence did not agree with bridged-halogen structure proposed for this complex¹²⁸.

For $[\text{AsPh}_4]_2 [\text{PdCl}_2(\text{SnCl}_3)_2]$ the required analysis is C, 41.4; H, 2.9; Cl, 20.5%. (See text - Chapter VI).

APPENDIX.

Isotopic splitting of metal-chlorine
stretching vibrations.

1. Discussion.

Chlorine is a mixture of two isotopes ^{35}Cl (75%) and ^{37}Cl (25%) and from the mass effect an M-Cl bond should have two stretching vibrations at different frequencies with an intensity ratio of 3:1, the weaker band being on the low frequency side of the main band. In this work the splitting, ($\Delta = 6-9 \text{ cm.}^{-1}$), is observed for terminal $\nu(\text{PtCl})_t$ in thirteen complexes but not for the bridge modes or either mode in palladium or rhodium complexes. In the wealth of published data on metal-chlorine stretching vibrations there are only two assignments of $\nu(\text{M } ^{37}\text{Cl})$, viz. for gold complexes ($\Delta = 6 \text{ cm.}^{-1}$)¹⁴ and for $\text{K} [\text{PtCl}_3(\text{C}_2\text{H}_4)]$ ³⁹, ($\Delta = 10 \text{ cm.}^{-1}$). Both these metals have atomic weights > 190 and simple calculations are made to assess the effect of the mass of the metal atom and the magnitude of the splitting. To reduce the complexity of the problem only a single M-Cl bond is considered and assumptions about the bond force constant and the nature of the vibration are made, (Section 2). The results show that expected splittings for $\text{M} = \text{Pt}$, Au and Rh are 8, 7 and 7 cm.^{-1} respectively. Further, if the mass of M

is made very large (>300) or very small. (40), probable splittings will be 10 and 5 cm.^{-1} respectively. From this calculation it is concluded that isotopic splitting should be observed generally. An explanation of why the phenomenon is confined to gold and platinum is found from the discussion on vibrational interactions. Very heavy metal atoms move with small amplitudes so that the M-Cl stretching vibration is effectively the oscillation of the chlorine atom against the metal atom. Little interaction occurs with other modes and a "pure" M-Cl vibration results. For lighter metals, significant movements of the metal atom will cause interactions with other vibrations and the designation $\nu(\text{MCl})$ becomes a good approximation for a more complex vibration of the whole molecule. Thus additional factors which affect the band position are introduced and the mass effect of the Cl isotopes is masked. This hypothesis is tentative and a further and fuller study is required. This could be directed towards examining complexes of the elements directly preceding and following gold and platinum in the Periodic Table viz., osmium, iridium and mercury, lead.

2. Calculation.

(a) Isotopic abundances of naturally occurring elements²⁰⁸.

¹⁹⁷ Au	100	¹⁹⁰ Pt	0.012
		¹⁹² Pt	0.78
³⁵ Cl	75.4	¹⁹⁴ Pt	32.8
³⁷ Cl	24.6	¹⁹⁵ Pt	33.7
		¹⁹⁶ Pt	25.4
¹⁰³ Rh	100	¹⁹⁸ Pt	7.23

(b) Isotopic splitting for $\nu(\text{PtCl})$

For a Pt-Cl bond, eight isotopic combinations are possible and their statistical contribution in a hundred Pt-Cl bonds is computed.

Assuming the Pt-Cl bond force constant (K) remains unaltered and that the stretching vibration is a simple harmonic motion, the formula

$$= \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad ; \quad \frac{1}{\mu} = \frac{1}{M_{\text{Cl}}} + \frac{1}{M_{\text{Pt}}}$$

gives the stretching frequency (ν) of the isotopic combinations and the deviation from a mean value (ν_M). The most abundant isotopic combination

$^{195}\text{Pt}-^{35}\text{Cl}$ is given $\nu_{\text{M}} = 350 \text{ cm.}^{-1}$. The results show that two bands should occur near 350 and 342 cm.^{-1} with a 3:1 intensity relationship. For gold and rhodium the splitting is 7.1 and 6.8 cm.^{-1} respectively.

M	M isotope	Cl isotope	% M-Cl bonds	$\nu(\text{MCl})$
Pt	194	35	24.8	350.1
	195	35	26.3	350 (ν_{M})
	196	35	18.8	349.8
	198	35	5.3	349.6
	194	37	8.3	342.1
	195	37	8.8	342.0
	196	37	6.3	341.8
	198	37	1.8	341.6
Au	197	35	75.4	310(ν_{M})
	197	37	24.6	302.9
Rh	103	35	75.4	330(ν_{M})
	103	37	24.6	323.2

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