145. *Far-infrared Spectra of Some Square-Planar Complexes* $[PtX_2L_2]$ (X = Cl or Br). *The Influence of L upon the Platinum–Halogen Stretching Frequency and its Relation to the* trans-*Effect.*

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The far-infrared spectra (170—460 cm.$^{-1}$) of 43 complexes of the types *cis*- and *trans*-$[PtX_2L_2]$ (X = Cl or Br; L = neutral ligand), and *trans*-$[PtXR(PEt_3)_2]$ (X = Cl or Br; R = H, Me, or Ph) have been recorded, and the metal–halogen stretching frequencies ν(Pt–Cl) and ν(Pt–Br) assigned. ν(Pt–Cl) falls in the range 340—269 cm.$^{-1}$ and ν(Pt–Br) 251—184 cm.$^{-1}$. The wide ranges of ν(Pt–Cl) and ν(Pt–Br) indicate considerable dependence of the platinum–halogen bond strength on L, but this is found only in the *cis*-complexes, *i.e.*, when L is in *trans*-position to the halogen. In the *trans*-complexes ν(Pt–X) is almost insensitive to L. 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 ν(Pt–X), with the notable exception of $[PtX_2\cdot$ cyclo-octadiene] in which ν(Pt–X) 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.

ONE ligand can have a marked effect upon the binding of another to the same metal atom, as shown in substitution reactions of platinum(II) complexes, where ligands exert directing effects very similar to those observed in aromatic substitutions.[1]

From this laboratory we have published several infrared-spectroscopic investigations of the influence of each of a series of similar ligands on one other particular ligand attached to the same metal atom, usually to platinum(II).[2-4] This particular ligand we have called the detector ligand.

For our purpose the most significant stretching frequency (ν) is that of the bond between the metal atom and ligand atom of the detector ligand. In a series of alkyl-platinum complexes *trans*-$[Pt^{II}XMe(PR_3)_2]$ (X = univalent acid radical), we found that ν(Pt–C) of the platinum-methyl bond decreased with increasing *trans*-effect of the anionic ligand X.[4] However, the trend of these ν(Pt–C) values also follows the electronegativities of X, so there is not necessarily any real relation between the *trans*-directing power of X and the platinum–carbon bond strength in this series of compounds.

We have now extended our studies to uncharged ligands of widely different *trans*-effects, electronegativities, and double-bonding abilities. Our detector ligands were chloride and bromide in the series of complexes *cis*- and *trans*-$[PtX_2L_2]$, where L = neutral ligand. Recent construction of a far-infrared spectrometer has enabled us to cover the spectral region in which metal–chlorine and metal–bromine stretching frequencies occur. In this series of complexes we have observed ν(Pt–Cl) in the range 340—269 cm.$^{-1}$ and ν(Pt–Br) from 251 to 184 cm.$^{-1}$.

Difficulties in Relating ν(Pt–X) *to the Platinum–Halogen Bond Strength.*—Strictly speaking, we ought to compare the force constants governing the stretching of the Pt–Cl and

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[1] For early references see Grinberg, *Russ. J. Inorg. Chem.*, 1959, **4**, 683. A summary is given by Basolo and Pearson, " Mechanisms of Inorganic Reactions," John Wiley & Sons Inc., New York, 1958, p. 172.

[2] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131, and references therein.

[3] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.

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

Pt–Br bonds in our complexes if we are to make deductions about bond strength. However, in the absence of a complete vibrational assignment of a molecule, it is not possible to relate a given stretching frequency to the force constant governing the stretching of the associated bond, because other bonds and angles will also take some part in that vibration. Nevertheless, in a series of closely related compounds such as we have used, our conclusions are likely to be substantially correct even if we argue from frequencies only.

The most serious difficulty arises from the possibility that the mutually *trans* ν(Pt–X) and ν(Pt–L) vibrations may couple in the *cis*-series of complexes, especially when ν(Pt–X) and ν(Pt–L) are of the same magnitude; each frequency will than be displaced from its " true " value, but the massive platinum atom should minimise these effects.

Assignment of ν(Pt–Cl) *and* ν(Pt–Br).—Our general method has been to compare the spectra of a pair of isostructural complexes $[PtX_2L_2]$ (X = Cl or Br). Bands due to the ligand L remained fairly constant and were easily recognised in the spectra of related compounds. There is little doubt about the assignment of the ν(Pt–Cl) frequencies: they generally gave rise to the most intense bands in the spectrum and were not present in the spectrum of the corresponding bromo-complex. Sometimes they overlaid bands in the ligand spectrum. In some cases the assignment of ν(Pt–Br) was a little less certain. It seemed to give rather weaker bands than ν(Pt–Cl) and in some of the *cis*-dibromo-complexes we were unable to find the second ν(Pt–Br).

As required by symmetry, one ν(Pt–X) band was found in the spectra of the *trans*- and two in the *cis*-complexes. In the Tables, complexes are arranged in corresponding pairs (chloride and bromide); in each pair the frequencies underneath one another have the same origin and appearance in both spectra, except where bands overlap. No such correspondence of frequencies is implied between anything but these pairs.

We have not attempted to assign the observed internal vibrations of the ligands L, as this would require an extensive study of these and related ligands.

Effect of L upon ν(Pt–Cl) *and* ν(Pt–Br).—In the compounds *trans*-$[PtX_2L_2]$, ν(Pt–X) is almost insensitive to the nature of L, falling in the range $339{\cdot}5 \pm 3{\cdot}1$ cm.$^{-1}$ when X = Cl and in the range $249{\cdot}8 \pm 9{\cdot}2$ cm.$^{-1}$ when X = Br, except in the diammines where intermolecular hydrogen bonding may interfere.[5] This indicates that the ligands L have little effect upon the bonds in the *cis*-positions. It agrees with studies [6] of the rate of replacement of chloride ion in *cis*-$[PtClR(PEt_3)_2]$ (R = Cl, Ph, or Me), which varied only between 1 and 3·6 (k_1 in min.$^{-1}$), although in the corresponding *trans*-series it varied between 10^{-2} and 6×10^{-5}.

In the *cis*-isomers *cis*-$[PtX_2L_2]$, ν(Pt–X) depends greatly on the ligand L and in Figs. 1 and 2 we have plotted the average of the two ν(Pt–X) frequencies. There is broad agreement between the patterns for ν(Pt–Cl) and ν(Pt–Br), although several discrepancies exist. Even if some of the ν(Pt–X) frequencies are displaced by coupling with ν(Pt–L), the fact that they have the same relative position in both Figures is good evidence that we really are studying the effect of L upon the strength of the Pt–X bond *trans* to itself. We can make the following clear-cut observations:

(i) In complex compounds a ligand affects specifically the strength of the bond to the ligand in the *trans*-position to itself and has little effect on those in the *cis*-positions.

(ii) In the compounds *cis*-$[PtX_2L_2]$, ν(Pt–X) covers a surprisingly wide range of values, and it is clear that substantial differences in platinum–chlorine (or bromine) bond strengths exist.

(iii) The lowest values of ν(Pt–X) were found for the complexes *trans*-$[PtXR(PEt_3)_2]$ (X = Cl or Br; R = H, Me, or Ph). The ligands R are groups of very high *trans*-effects and of very high ligand field strengths.[7]

(iv) The highest values of ν(Pt–X) were found for *trans*-$[PtX_2L_2]$ (X = Cl or Br), where

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[5] Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712.
[6] Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.
[7] Chatt and Hayter, *J.*, 1961, 772.

TABLE 1.

Absorption frequencies (cm.$^{-1}$) of complexes *trans*-[Pt(Cl or Br)$_2$L$_2$].

[PtCl$_2$(SEt$_2$)$_2$]	368·4w	*341·9vs*	310·9m	303·7sh		243·0m				
[PtBr$_2$(SEt$_2$)$_2$]	369·0w	337·5s	324·2m-s		*253·5s*	236·7m	208·0w-m	184·0m		
[PtCl$_2$(SeEt$_2$)$_2$]		*337·2vs*								
[PtBr$_2$(SeEt$_2$)$_2$]					*240·7vs*					
[PtCl$_2$(Py)$_2$]	*342·6vs*	326·7sh	283·1vs	256·4m	241·5m	231·9s				
[PtBr$_2$(Py)$_2$]			297·7s	*251·2vs*	239·6m	215·5s				
[PtCl$_2$(NH$_3$)$_2$]	*331·5vs, asym*		261·0s	255sh	225m, br					
[PtBr$_2$(NH$_3$)$_2$]	336·5w	325·8m	319·8w	261·9m		*227vs, br*				
[PtCl$_2$(AsEt$_3$)$_2$]			*338·8vs*	330·7sh	306·7m-s					
[PtBr$_2$(AsEt$_3$)$_2$]		344sh		330·4s	305·0m-s	*250·9s*				
[PtCl$_2$(AsPr$^n_3$)$_2$]	413·0vw	401·9vw	*336·5vs*	322·5sh	287·0w					
[PtBr$_2$(AsPr$^n_3$)$_2$]	413·0vw		336·3sh	322·1s	286·4w	*244·8m*				
[PtCl$_2$(PPr$^n_3$)$_2$	441·0w	425·7m	372·7m	*338·8vs*						
[PtBr$_2$(PPr$^n_3$)$_2$]		423·0s	371·5m		278·0sh	*259·0vs*				
[PtCl$_2$(PEt$_3$)$_2$]	443·0sh	417·6s	382·6m	*340·3vs*			272·3m		230·2w-m	181·0m
[PtBr$_2$(PEt$_3$)$_2$]	444·9sh	416·1sh	383·5m		331·0s	317·2w		*254·4s*	224·5w-m	182·0m
[PdCl$_2$(PEt$_3$)$_2$]	431·3m	374·6w	357·5m	330·2w	304sh	*281·5vs*	266·8s, sh			

TABLE 2.

Absorption frequencies (cm.$^{-1}$) of complexes *cis*-[Pt(Cl or Br)$_2$L$_2$].

[PtCl$_2$(SEt$_2$)$_2$]	362·6sh	337·2s	*330·0vs*	*318·2s*			177m			
[PtBr$_2$(SEt$_2$)$_2$]	362·2w	336·2s			*254·0s*	*226·2s*				
[PtCl$_2$(SeEt$_2$)$_2$]	457·0vw	381·5w	344·3vs	*333·0vs*	*316·6vs*					
[PtCl$_2$(TeEt$_2$)$_2$]	*302·2s*	*282·2vs*						184·3m		
[PtBr$_2$(TeEt$_2$)$_2$]		282·1m		257·0vw	250·0vw	*217·0vs*	*208·2vs*	174w		
[PtCl$_2$(TePr$^n_2$)$_2$]	401·5w-m	384·7w	*306·0vs*	*290·6vs*	246·0w	177m				
[PtCl$_2$(Py)$_2$]	455·5w	*343·4s*	*327·9vs*	290·0vw	259·6m		232·6m	228·2sh		
[PtBr$_2$(Py)$_2$]	452·1m				254·3s		233·9m	225·7vw	*219·4s*	*210·6s*
[PtCl$_2$(NH$_3$)$_2$]	*326·0vs*	258·8m				192m	160w			
[PtBr$_2$(NH$_3$)$_2$]		256·8m	250·7sh	*224·3m*	*220·5m*	189m				
[PtCl$_2$(AsEt$_3$)$_2$]	339·5w	*314·2s*	303·0s	*287·5vs*						
[PtCl$_2$(AsPr$^n_3$)$_2$]	413·5vw	341·5m	323sh	*309·6vs*	*285·5vs*					
[PtBr$_2$(AsPr$^n_3$)$_2$]		338·6m	329·0m		294·2vw	*220·0m*				
[PtCl$_2$(PEt$_3$)$_2$]	443·0m	427·3m	383·2m	336·2sh	*303·2vs*	*280·8vs*	247·8w	208vw		174m
[PtBr$_2$(PEt$_3$)$_2$]	440·2m	424·1m	382·3m	332·3w	298·0m	289·1m		*211·6m*	*193·7m*	
[PtCl$_2$(PPr$^n_3$)$_2$]	451·6w-m	428·0vw	413·0w	378·0w	*307·3vs*	*277·0vs*				
[PtCl$_2$(SbPr$^n_3$)$_2$]	400·0w	383·5w	*311·0s*	295·0s	*280·6s*		211·5w			
[PtBr$_2$(SbPr$^n_3$)$_2$]	400·0w	383·5w	327sh	294·2s		*217·4w*	211·5w			
[PtCl$_2$cod]*	477·7w	457·9w	380·6w	348·5sh		*338·0vs*	*316·2vs*	303sh	233·1w	
[PtBr$_2$cod]*	471·5w	452·4w	376·5w	339·4w-m	327sh			304w-m	*229·5w-m*	*215·3vs*

* cod = cyclo-octo-1,5-diene.

chloride and bromide are *trans*-ligands. These are both groups of moderate *trans*-effect and very low ligand field strengths. *cis*-[$PtCl_2Py_2$] also has a high ν(Pt–Cl) which is difficult to reconcile with the relatively low ν(Pt–Br) of *cis*-[$PtBr_2Py_2$].

(v) Cyclo-octa-1,5-diene (cod) causes ν(Pt–X) in [PtX_2cod] to appear at a high frequency relative to other complexes in which the ligand atoms have high *trans*-effects (P, As, Sb, Te, H, Me, and Ph), although olefins are ligands of very high *trans*-effect.

(vi) The order of ν(Pt–Cl) (Fig. 1) for *cis*-complexes containing Group V ligand atoms falls in the order As > Sb > P. The same order is found in the bromides, although for the arsenic and antimony compounds we could not find the lowest ν(Pt–Br).

(vii) In the *cis*-complexes both ν(Pt–Cl) and ν(Pt–Br) are higher when sulphur is the donor atom than when it is tellurium. The only *cis*-selenide complex has ν(Pt–Cl) very slightly lower than that of the sulphide, leading to the ν(Pt–Cl), order S $\sim$ Se $\gg$ Te.

(viii) The palladium compound *trans*-[$PdCl_2(PEt_3)_2$] has ν(Pd–Cl) at 281·5 cm.$^{-1}$, much lower than its platinum analogue (340·3 cm.$^{-1}$), in agreement with the looser bonding generally found in palladium complexes.[6]

(ix) ν(Pt–Cl) in *cis*-[$PtCl_2L_2$] is lower when L = NH_3 than when L = Py, although pyridine has the higher *trans*-effect. This anomaly may be caused by hydrogen bonding from ammonia to chloride.[5]

In previous studies of this nature [2-4,8] we attempted to correlate the detector ligand frequencies with the *trans*-effects and electronegativities of the ligands *trans* to the detector ligand. Again in this series of complexes we find some degree of correlation with the *trans*-effects of the ligands L. The greater the *trans*-effect the lower ν(Pt–Cl) and ν(Pt–Br), with the notable exception of the cyclo-octadiene complex (Figs. 1 and 2). Olefins have so high a *trans*-effect that ν(Pt–Cl) might have been expected to be lower than those of the phosphine complexes. There is also a general correlation with the electronegativities of the ligand atom in L, the greater the electronegativity the greater the frequency, the main exceptions now being phosphorus, selenium, and tellurium. These observations are in general accord with previous studies but the irregularities are greater.

TABLE 3.

Absorption frequencies (cm.$^{-1}$) of complexes *trans*-[Pt(Cl or Br)X($PEt_3)_2$].

[$PtHCl(PEt_3)_2$] ...	442·3w	406·4s	402·4s	383·4w	346·2vs	*269·3vs*		
[$PtHBr(PEt_3)_2$] ...	440·1w-m	406·4s	402·2s	376·7w	345·1vs		*184·4vs*	
[$PtPhCl(PEt_3)_2$] ...	413·6m	384·2m	334·0m	316·2w	*270vs, br*	232·5m	222·7sh	184·0w
[$PtPhBr(PEt_3)_2$]...	413·0m	384·4m	334·3m	316·6w		232·0m	222·4sh	*184·0vs*
[$PtMeCl(PEt_3)_2$] ...	417·0m	383·4m	332·2s	316·0w	*274·4vs*			
[$PtCD_3Br(PEt_3)_2$]	413·3m	382·6m	331·4s	316·0w		245·1w		

We explained the smaller anomalies in previous studies by invoking π-bonding and mesomeric effects from the ligands L.[8] These could act only by reducing or increasing the electron density on the metal atom but not by direct interaction with the detector ligand atoms (N and C) because they had no *d*-orbitals or filled *p*-orbitals on a suitable energy level for such interaction. In this study the detector ligands have both vacant *d*-orbitals and filled *p*-orbitals in their valency shells. Although they do not have a strong tendency to form π-bonds to platinum(II), we believe the interaction is sufficient to account for the poorer correlation between the electronegativities of L and the frequencies found in the complexes now under study. Nevertheless the main factor affecting the Pt–Cl and Pt–Br frequencies appears to be the electronegativity of L, with the *trans*-effect, except when it is inductive and high, playing a minor role.

There is one significant point from the anomalies concerning the *trans*-effect. Generally the ligands of highest *trans*-effect, *viz.*: PR_3, CH_3^-, $C_6H_5^-$, and H^- produce the lowest frequencies, but cyclo-octadiene, which by analogy with ethylene must have a higher *trans*-effect than the phosphines, produces one of the highest Pt–Cl frequencies. This

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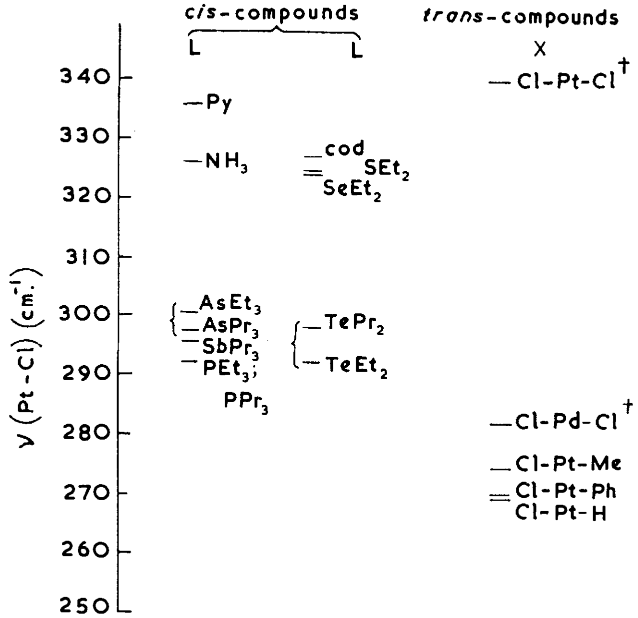
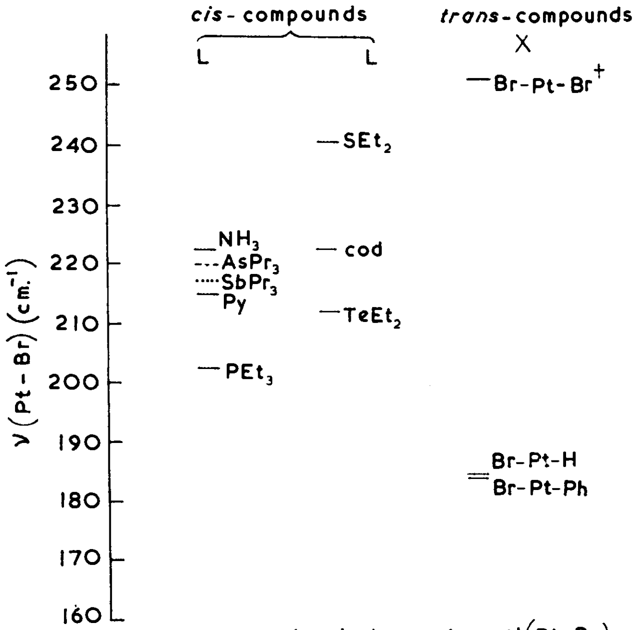
[8] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.



† average value-see text

FIG. 1. Metal–chlorine stretching frequencies in *trans*-[$PtCl_2L_2$] and *cis*-[$MClX(PEt_3)_2$] (M = Pt or Pd).



----only one band observed for ν(Pt-Br)
† average value-see text

FIG. 2. Platinum–bromine stretching frequencies in *trans*-[$PtBr_2L_2$] and *cis*-[$PtBrX(PEt_3)_2$].

result is consistent with the previous suggestion that the *trans*-effect has no single cause, and that a ligand of high *trans*-effect can exert its influence either by electron release in the σ- or electron withdrawal in the π-co-ordinate bonds, the former enhancing S_N1 and the latter S_N2 substitution of the *trans*-ligand.[6] The inductive electron-release mechanism is probably the main cause of the high *trans*-effects of hydride and alkyl and aryl carbanions as ligands and the mesomeric electron-withdrawal mechanism of the high *trans*-effect of olefins. In the bonding of most ligand atoms both effects will operate but our previous spectroscopic studies [2] and this work indicate that for most uncharged ligands the inductive mechanism is dominant.

We believe hydride ion to be typical of the ligands owing their high *trans*-effects to an inductive mechanism. The hydride ion affects the ligand, A, in *trans*-position to itself by repelling the electrons in the σ-bond binding A to the metal M. This increases the M–A bond length and passes greater negative charge to A, so causing ready dissociation of the M–A bond.[9] This work shows moreover that it also causes considerable lowering in ν(M–A) as typified by ν(Pt–Cl) and ν(Pt–Br) in *trans*-[$PtHX(PEt_3)_2$] (X = Cl or Br). Thus "*trans*-bond weakening," with its attendant effects of *trans*-bond lengthening and the enhancement of negative (or decrease of positive) charge on the *trans*-ligand, is characteristic of the inductive mechanism of the *trans*-effect. It is the operation of this inductive electron release which accounts for the exceptionally low value of the platinum–halogen stretching frequencies observed in the *trans*-hydride, -methyl, and -phenyl complexes.

The mesomeric mechanism of the *trans*-effect need not cause *trans*-bond weakening; it might even cause a strengthening.[8] It would cause weakening if the *trans*-ligand was one which formed significantly strong π-bonds with the metal, *e.g.*, another olefin,[10] or perhaps even an iodide ion. In this work the *trans*-ligand in [$PtCl_2$cod] is chloride, which on all evidence is capable only of forming weak π-bonds. Thus no marked weakening of the Pt–Cl bond is to be expected from the presence of cyclo-octadiene in spite of the fact that olefins as ligands attached to platinum(II) have a very high *trans*-effect.

EXPERIMENTAL

Complexes.—With the exception of the new compounds described below, the complexes were prepared as described previously.[11–13]

cis-*Bis(tri-n-propylstibine)dibromoplatinum*. To a solution of *cis*-bis(tri-n-propylstibine)dichloroplatinum (1·0 g.) in acetone (15 ml.) was added lithium bromide (1·5 g.) in acetone (50 ml.). After 15 hr. the mixture was evaporated to dryness under reduced pressure. The solid residue was extracted with chloroform and the extract evaporated to dryness. The *product* was twice recrystallised from methanol giving yellow crystals (0·55 g.), m. p. 93—95·5° (Found: C, 24·9; H, 5·0. $C_{18}H_{42}Br_2PtSb_2$ requires C, 25·2; H, 4·9%).

cis-*Bis(diethyl telluride)dibromoplatinum*. Diethyl telluride (1·43 g.) was added to potassium bromoplatinite (2·28 g.), dissolved in water (50 ml.), and the mixture was shaken for 15 hr. The orange-red *solid* was separated and washed with water. Recrystallisation twice from ethanol yielded orange crystals (1·9 g.), m. p. 125—127° (Found: C, 13·4; H, 2·8. $C_8H_{20}Br_2PtTe_2$ requires C, 13·2; H, 2·8%).

Spectroscopy.—Spectra in the 170—460 cm.$^{-1}$ region were recorded by using an evacuated grating instrument which has been described previously.[14] Samples were examined as Nujol mulls supported on low-density polythene plates ("Alkathene" grade 7) 1 mm. thick and were maintained at $-10°$.

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[9] See Chatt, *Proc. Chem. Soc.*, 1962, 318.

[10] Cf. Chatt and Wilkins, *J.*, 1952, 2622.

[11] Gmelin's "Handbuch de Anorganischen Chemie," Platin, Teil D, System Nummer 68, Verlag Chemie, 1957.

[12] Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496.

[13] Chatt and Shaw, *J.*, 1959, 705, 4020; 1962, 5075.

[14] Adams, *Spectrochim. Acta*, 1962, **18**, 1039.