Directing Effects in Inorganic Substitution Reactions. Part II. An Infrared Spectroscopic Investigation of the Inductive Effects of a Variety of Uncharged Ligands in Complex Compounds of Platinum*(II).

By J. Chatt, L. A. Duncanson, and L. M. Venanzi.

[Reprint Order No. 6501.]

The infrared spectra of a series of complex compounds of the type *trans*-[L,amPtCl$_2$] were examined in carbon tetrachloride solution. In these compounds "am" is a primary or secondary amine, especially *p*-toluidine and piperidine, and L a series of ligands, piperidine, 4-*n*-alkylpyridine, PR$_3$, AsR$_3$, SbR$_3$, R$_2$S, R$_2$Se, R$_2$Te, P(OR)$_3$, and C$_2$H$_4$ (R = *n*-alkyl). The complex compounds containing primary amines associate by hydrogen bonding. The N–H stretching frequencies of the monomeric complexes were measured, and also the band intensities of the piperidine complexes and bimolecular association constants of the *p*-toluidine complexes (Table 1). The differences in these properties from one complex to another are interpreted in terms of changes in electron distribution in the L–Pt–N–H bonds. Strong inductive effects are transmitted across the platinum atom from the ligands L to the N–H bond, and the donor capacities of the various donor atoms are correlated with their electronegativities. Nitrogen is certainly the poorest and phosphorus about the best donor to platinum(II). Certain irregularities are attributed to the transmission of slight but significant mesomeric effects. By using these peculiarities the ligands have been arranged in a series: 4-*n*-alkylpyridine, piperidine, R$_2$S, R$_2$Se, R$_2$Te, AsR$_3$, PR$_3$, SbR$_3$, P(OR)$_3$, and C$_2$H$_4$, such that all the measured properties run in similar sequence. This order is determined by electronegativity from piperidine to R$_2$Te, but from AsR$_3$ to C$_2$H$_4$ the order is probably that of increasing tendency to co-ordinate by double bonds.

The investigation shows that the *trans*-directing effect of a ligand is not directly related to its inductive effect or electronegativity; also the *trans*-effect does not operate by *trans*-bond weakening (*i.e.*, by increasing the tendency to heterolytic fission of the bond in *trans*-position to the ligand, L). This is evidence against a dissociative (S_N1) mechanism of *trans*-directed substitution, but it is consistent with the "double bonding hypothesis" which is discussed in Part I.*

In Part 1* we discussed the phenomena of directing effects in the substitution reactions of inorganic complex ions and presented a new hypothesis as to their origin. In one very important particular that hypothesis conflicted with the currently accepted theory, which supposes that ligands which direct incoming groups into the *trans*-position to themselves in complex-ion substitution reactions do so by weakening the bond in *trans*-position to themselves (for references see Part I). "Bond weakening" in this context and throughout this communication means a greater tendency of the ligand-to-metal bond to undergo heterolytic fission, the ligand carrying away the bonding electrons. For example in the system L–M–B, where L and B are ligands in *trans*-positions about the metal M, current theory requires that the greater the *trans*-directing effect of L the greater the electron drift in the bond M–B towards the group B, and the greater the tendency for B to separate with its bonding electrons. Such an explanation of the operation of the *trans*-effect also implies that *trans*-substitution occurs by an S_N1 mechanism.

The experiments described in this communication were designed to investigate the distribution of electrons in the M–B bond under the influence of various groups L. For this purpose it was essential that the M–B bond should be a single bond or nearly so: hence amines were chosen as B. Platinum(II) was chosen as the metal because it is only in relation to platinum(II) that there is any great volume of existing knowledge about directing effects in inorganic complexes. The nature of the ligands, L, was determined mainly by the ease with which a series of suitable compounds could be synthesised. This

---

* Part I, preceding paper.

was achieved by making L a series of uncharged ligands having as great a variety of donor atoms as possible; ethylene, amines, and the *n*-alkyl derivatives $P(OR)_3$, PR_3, AsR_3, SbR_3, R_2S, R_2Se, and R_2Te were used. Little is known with certainty of the *trans*-directing effects of these ligands except that amines are the most strongly *cis*-directing and ethylene the most strongly *trans*-directing [see Chatt and Williams, *J.*, 1951, 3061; Hel'man and Karandashova, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, (4), 597]. Work now in progress also indicates that the *trans*-directing effects of organic phosphines are greater than those of sulphides and selenides (see Ahrland and Chatt, *Chem. and Ind.*, 1955, 96).

The series of compounds actually examined were of the type *trans*-[L, $amPtCl_2$] where " am " is a primary or secondary amine. The problem thus resolves itself into finding the change in electron distribution in the Pt–N bond from one compound to another in the above series. It was solved by measuring the N–H stretching frequencies (ν_{N-H}) by observation of the infrared spectra of the above series of compounds in dilute carbon tetrachloride solution. In the piperidine series the band intensities were also measured. The sizes of the alkyl groups, R, were chosen so as to render the complexes containing them sufficiently soluble in carbon tetrachloride for this investigation.

It was found that most of the complexes containing primary amines are associated in carbon tetrachloride solution by intermolecular hydrogen bonding through the N–H bonds. The degree of association depends on the ligand represented by L. The nature of the association and a detailed description of typical spectra will be given in another communication (for a preliminary note see Chatt, Duncanson, and Venanzi, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **17**, 120) but the approximate association constants, $K_{ass.}$, for bimolecular association are relevant to the present discussion. These and the spectroscopic data are listed in the Tables.

In Tables 1(*A*) and 1(*C*) the ligands, L, are the only variables and are listed in increasing order of electronegativity. It is difficult to place ethylene in this series, because it does not contain a donor atom with a lone pair of electrons; nevertheless, there seems little doubt that its correct position is near the nitrogen end of the series. The first ionisation potential of the π-electrons is 10·5 ev (Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207), about the same as that of the lone pair of ammonia, 10·8 ev, and higher than those of the common amines, 9·6 ev (Sugden, Walsh, and Price, *Nature*, 1941, **148**, 372; Price and Walsh, *Proc. Roy. Soc.*, 1947, *A*, **191**, 22), which suggests that ethylene might occupy a position even lower in the tables than the amines. On the other hand, carbon has about the same electronegativity as sulphur and so ethylene has been placed tentatively between the amines and sulphides.

Independently of any interpretation of the spectroscopic data the following conclusions can be drawn from the measurements listed in the Tables.

(1) The sizes of the alkyl groups, R, in the ligands, L, do not affect the N–H stretching frequencies within the limits of experimental error, *e.g.*, see the homologous series *trans*-[PR_3,p-CH_3·C_6H_4·NH_2,$PtCl_2$] (R = Et, Pr^n, and Bu^n) in Table 1(*C*). Evidently the large mass of the platinum atom effectively insulates the co-ordinated amines so that their high-frequency modes of vibration are independent of the masses and shapes of the various ligands L.

(2) The frequencies decrease and intensities increase with increasing electronegativity of L [Tables 1(*A*) and 1(*C*)]. Ethylene and ligands containing phosphorus do not quite fit into their places in the sequence, but nevertheless the correlation between the electronegativities of L and the spectroscopic data is sufficiently good to show that the effects of the ligands, L, on the N–H bonds are in the main inductive.

(3) Although the different ligands, L, produce definite changes in the N–H stretching frequencies [Tables 1(*A*) and 1(*C*)], the groups, X, in *trans*-[PPr^n_3,p-X·C_6H_4·NH_2,$PtCl_2$] [Table 1(*D*)] have negligible effect throughout the series, X = H, CH_3, C_6H_5, Cl, NO_2, and OCH_3. Evidently the electrical effects which influence the N–H bonds and are transmitted across the platinum atom are much stronger than those transmitted across the aromatic nucleus. The quaternary nitrogen atom, like the saturated carbon atom, would not be expected to transmit mesomeric effects, except perhaps rather weakly by hyperconjugation; and the absence of any dependence of the N–H frequencies on X is evidence of this.

(4) Although the N–H frequencies are insensitive to a change in X they are very sensitive to changes in small hydrocarbon groups attached to the nitrogen atom. In these circumstances the inductive, steric, and mass effects of the small groups are all able to exert their influence directly on the nitrogen atom and changes of up to 35 cm.$^{-1}$ are observed {*e.g.*, compare *trans*-[PPr^n_3,Et_2NH,$PtCl_2$] and *trans*-[PPr^n_3,MePhNH,$PtCl_2$] in Table 1(*B*)}.

TABLE 1. *The* N–H *frequencies* ν (*cm.*$^{-1}$), *band intensities B* (*cm.*$^{-2}$ *molecules sec.*$^{-1}$), *and association constants,* $K_{ass.}$, *for the compounds* trans-[L,am$PtCl_2$] *at* 25°.

(*A*) " am " = Piperidine.

L	ν_{N-H} (± 1)	10^7B (± 2·5%)	L	ν_{N-H} (± 1)	10^7B (± 2·5%)
$SbEt_3$	3235	—	Et_2S	3223	1·66
$AsPr^n_3$	3232	1·41	C_2H_4	3230	1·59
PPr^n_3	3237	1·35	Piperidine	3222	3·36 *
$P(OMe)_3$	3233	1·43	4-*n*-Pentylpyridine	3217	1·82
Et_2Te	3230	1·49	(Cf. also free piperidine †)	3350	~0·1
Et_2Se	3224·5	1·60			

* This figure must be halved for comparison with the others since the complex contains two independent but identical N–H groups.

† Russell and Thompson, *J.*, 1955, 483.

(*B*) " am " = Other secondary amines.

L	" am "	ν_{N-H} (±1)	L	" am "	ν_{N-H} (±1)	L	" am "	ν_{N-H} (±1)
PPr^n_3	Diethylamine	3237	PPr^n_3	*N*-Methylaniline	3261	C_2H_4	Dimethylamine	3261

(*C*) " am " = *p*-Toluidine

L	$\nu_{asym.}$ (±1)	$\nu_{sym.}$ (±1)	$K_{ass.}$ (±10%)
$SbPr^n_3$	3346	3275	40
$AsPr^n_3$	3342	3271	24
PEt_3	3347	3277	18
PPr^n_3	3348	3277	18
PBu^n_3	3348	3276	15
$P(OEt)_3$	3344	3275	—
Pr^n_2Te	3337	3270	—
Pr^n_2Se	3330	3264	—
Pr^n_2S	3329	3262	77
Bu^n_2S	3328	3263	77
C_2H_4	3331	3265	115
Cf. also *trans*-[PPr^n_3,*p*-$CH_3\cdot C_6H_4\cdot NH_2$,$PtCl_4$]	3330	3268	—
trans-[PPr^n_3,*p*-$CH_3\cdot C_6H_4\cdot NH_2$,$PdCl_2$]	3365	3291	2
Free *p*-toluidine	3471	3390	—

(*D*) " am " = Other primary amines

L	" am "	$\nu_{asym.}$ (±1)	$\nu_{sym.}$ (±1)
PPr^n_3	Methylamine	3347	3284
PEt_3	Ethylamine	3336	3271
PPr^n_3	Benzylamine	3332	3268
PPr^n_3	Aniline	3347	3277
PPr^n_3	*p*-Phenylaniline	3345	3275
PPr^n_3	*p*-Chloroaniline	3346	3274
PPr^n_3	*p*-Nitroaniline	3348	3276
PPr^n_3	*p*-Anisidine	3347	3277
PPr^n_3	2 : 6-Dimethylaniline	3346	3267
Bu^n_2S	2 : 6-Dimethylaniline	3329	3249
C_2H_4	2 : 6-Dimethylaniline	3324	3253
4-*n*-Nonylpyridine	2 : 6-Dimethylaniline	3268	3199
C_2H_4	Methylamine	3334	3277
C_2H_4	Ethylamine	3324	3263

(5) The association constants, $K_{ass.}$, show little correlation with the other properties tabulated in Table 1(*C*).

Interpretation of the Spectroscopic Data in Terms of the Electron Distribution in the L–Pt–N–H *Bonds.* All the spectroscopic data concern the N–H bonds and so must be interpreted in terms of electron distribution in the Pt–N bond to obtain information relevant to the operation of the *trans*-effect.

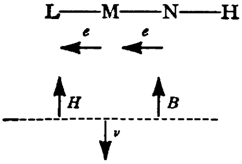
The change in intensity of the N–H band with change in electron distribution in the Pt–N bond is not easily predictable. Russell and Thompson (*loc. cit.*) have found, however, that the intensities of the fundamental N–H stretching bands of secondary amines increase with the acidity of the N–H groups, and so increasing intensity corresponds to increasing positive charge on the nitrogen atom.

The factors affecting the N–H stretching frequencies of amines have been investigated by Richards (*Trans. Faraday Soc.*, 1948, **44**, 40), Flett (*ibid.*, p. 767), and Fuson *et al.* (*J. Chem. Phys.*, 1952, **20**, 145). The results of these investigations are not directly applicable to our problem because in the free amines the hybridisation of the nitrogen atom may, in theory, vary from p^3 to sp^3, and sp^2. However, the above work, and that of Linnett (*Trans. Faraday Soc.*, 1945, **41**, 223; see also Longuet-Higgins, *ibid.*, p. 233) leads to the general conclusion that, for a given N–H bond type, increasing negative charge on the nitrogen atom increases the force constant of the N–H bond and decreases the acidity of the amine. Large changes in bond type are not likely in our complexes; with four groups attached to the nitrogen atom, its hybridisation must always approximate to sp^3, and so the above generalisation should apply. It is known that only small changes in hybridisation of the tetrahedral carbon atom are caused even by very large changes in electronegativities of the groups attached (*e.g.*, Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46).

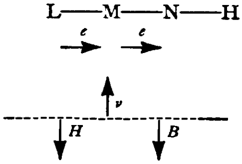
We have two pieces of supporting evidence from complex chemistry that the generalisation does apply. (*a*) In *trans*-$[PPr^n_3,p\text{-}CH_3\cdot C_6H_4\cdot NH_2,PtCl_4]$, where the metal is more positively charged than in its platinous analogue, the greater electron affinity of the metal causes a decrease of some 13 cm.$^{-1}$ in the N–H stretching frequencies [see Table 1(*C*)]. (*b*) Palladous complexes have the same general electronic structure as their platinous analogues but are as a rule less stable. Rightly or wrongly, this fact has commonly been interpreted as an indication that the electron-acceptor properties of palladium(II) are not so great as those of platinum(II). In agreement with this view we now find that the N–H stretching frequencies of *trans*-$[PPr^n_3,p\text{-}CH_3\cdot C_6H_4\cdot NH_2,PdCl_2]$ are some 12 cm.$^{-1}$ higher than those of its platinous analogue. The lower acidity of the *N*-hydrogen atoms in the palladous than in the platinous complex is also evident from its low association constant [see Table 1(*C*)].

A weakening of the Pt–N bond, *i.e.*, a displacement of the bonding electrons from the platinum atom towards the nitrogen atom, would cause the nitrogen atom to become more negatively charged. The above evidence indicates that such a change would be accompanied by an increase in N–H stretching frequency and a decrease in band intensity. Our experimental data interpreted according to this scheme give a very simple general picture of the electron drifts in the L–Pt–N–H bond system as follows:

The least electronegative ligands, L, by donating their electrons more completely to the metal atom, M, cause it in turn to release electrons to the nitrogen atom. This as a consequence binds its hydrogen atoms more firmly and increases its N–H stretching frequency. These relations between electron drifts (*e*), M–N bond strength (*H*) and spectroscopic data (frequency, ν, and intensity, *B*) are summarised in the following diagram.*



Effect of increasing electronegativity of L



Effect of decreasing electronegativity of L

Although this scheme is essentially correct as shown by the correlation between electronegativities of the donor atoms in L and the observed N–H frequencies, it is not yet complete. It does not explain the slightly anomalous positions of the phosphorus-containing ligands and ethylene.

Complexes containing phosphorus have higher N–H frequencies than those of the other members of the phosphorus triad, and not lower ones as would be expected from the electronegativity of phosphorus. Also, ethylene gives complexes with greater N–H frequencies

---

* The authors thank a Referee for suggesting the inclusion of this diagram.

than would be expected. We must conclude that there is a factor which influences the N–H frequencies, and is not inductive. This factor apparently raises the N–H frequencies above the values to be expected empirically on the basis of the electronegativities of the donor atoms in the ligands, L. It does not appear to be significant except in the ethylene- and phosphorus-containing complexes. Consequently, if the ligands, L, are arranged in order of decreasing N–H frequencies of their complexes, *trans*-[L,amPtCl$_2$] [*i.e.*, PR$_3$ > SbR$_3$ > P(OR)$_3$ > AsR$_3$ > R$_2$Te > C$_2$H$_4$ > R$_2$Se > R$_2$S > Piperidine > 4-*n*-Pentylpyridine] the order must be close to that of increasing strength of the Pt–N bonds, and of decreasing tendency of L to donate electrons to platinum. Two interesting conclusions may be drawn .

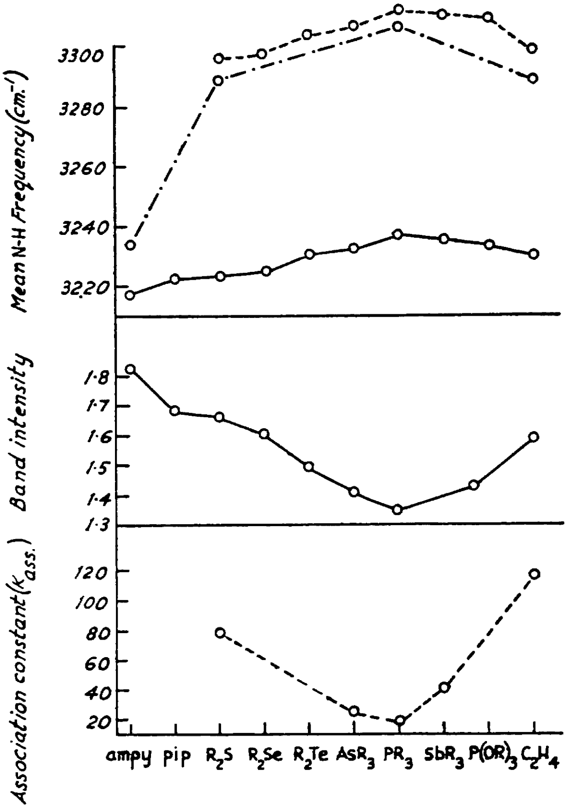


FIG. 1. *Plots of spectroscopic data and association constants against the unique order of ligands* " ampy " * *to* C$_2$H$_4$.

* " ampy " = 4-*n*-Pentylpyridine.
" pip " = Piperidine.

— — — *p*-Toluidine complexes.
——— Piperidine complexes.
– · — · – 2 : 6-Dimethylaniline complexes.

(1) If previous investigators are correct in supposing that ethylene has the greatest *trans*-directing effect of the uncharged ligands in the above series (see Part I, *loc. cit.*), the *trans*-effect cannot operate by *trans*-bond weakening, because this implies that the ethylene complexes have the weakest Pt–N bonds. The strength of the Pt–N bond in the ethylene complexes appears to be slightly greater than that of the telluride complexes. It may be even greater than its position in the above series indicates, because the unknown factor has the effect of placing ethylene too high in the series. Certainly, the olefin complexes do not contain the weakest Pt–N bonds.

(2) The completeness of donation of electrons to platinum from widely different donor atoms which occurs in the various ligands, L, does not determine the qualitatively observed general stabilities of their complexes. The latter may be classified as : very stable (L = PR$_3$ and R$_2$S), stable (L = AsR$_3$ and amines), and rather unstable (L = C$_2$H$_4$, SbR$_3$, R$_2$Te, and R$_2$Se). This series bears no relation to the above sequence of decreasing donor capacities of the ligands, L.

The relationship between the positions of the donor atoms in the Periodic Table and the stabilities of their platinous complexes is very interesting and shows an inversion between the fifth and the seventh group of donor atoms in the Periodic Table. In the fifth group it runs $NR_3 \ll PR_3 > AsR_3 > SbR_3 > BiR_3$ (Chatt, *J.*, 1951, 652). In the sixth group it is $R_2O \lll R_2S \gg R_2Se < R_2Te$ (Chatt and Venanzi, *J.*, 1955, 2787), and in the seventh group $F^- \lll Cl^- < Br^- < I^-$ (Leden and Chatt, *J.*, 1955, 2936). Platinous complexes with tertiary bismuthines, ethers, or the fluoride ion co-ordinated to platinum(II) are unknown.

Arrangement of Ligands in a Series according to Their Inductive and Mesomeric Effects.—So far we have considered in detail only the N–H frequencies and band intensities and have shown that the differences caused by changing the ligands, L, are due almost entirely to the inductive effects of the ligands. We have also drawn attention to two obvious though minor anomalies involving ethylene and ligands containing phosphorus. Other less obvious anomalies also exist; for example, ethylene cannot be fitted into any definite place in the series of ligands according to the properties listed in the tables. The N–H frequency of its piperidine complex places it with the tellurides, but its band intensity and the N–H frequencies of its *p*-toluidine complex place it beside the selenides. Its association constant, $K_{\text{ass.}}$, is exceptionally large.

Taken singly, these anomalies are of doubtful significance. Together they allow us to sort the ligands into a series such that the magnitudes of all the properties listed in the tables, even the association constants, run in a regular and similar manner. They rise or fall from the amines to phosphines, then fall or rise respectively to ethylene. The series is: 4-*n*-alkylpyridine, piperidine, R_2S, R_2Se, R_2Te, AsR_3, PR_3, SbR_3, $P(OR)_3$, and C_2H_4. Fig. 1 shows how all listed properties fit into this sequence. It is not possible to take any ligand from the right-hand side of the phosphines and place it in a definite position on the other side without destroying the similarity of the various graphs in Fig 1. The correlation is sufficiently good to suggest that all the anomalies have one ultimate cause. The position given to the stibines is not definite but is based solely on the value of the association constant of *trans*-$[SbPr^n{}_3,p\text{-}CH_3\cdot C_6H_4\cdot NH_2,PtCl_2]$.

FIG. 2. *How dative* π-*bonding to the group* L (i.e., *its mesomeric effect*) *may influence the* N–H *bond through a* d-*orbital.*

(I)
L has no double-bonding capacity.

(II)
L forms a strong dative π-bond.

The significance of the sequence seems clear. The ligands to the left of the phosphines exert their influence on all the properties we have measured, mainly through induction in the L–Pt bond.

Phosphines and those ligands to the right of the phosphines have imposed on the inductive effect the other factor which causes a slight irregularity. Since the phosphites and olefins are the most strongly double-bonding ligands in this series the anomaly is most probably caused by their mesomeric effects. Thus we have our most electronegative ligands to the left, and most strongly double-bonding to the right, of phosphorus in the sequence. To the left of phosphorus the ligands are in order of increasing electronegativity; to the right, probably of increasing tendency to form dative π-bonds.

There are two obvious interdependent ways in which the mesomeric effect resulting from the formation of a dative π-bond by the ligand, L, can affect the N–H vibration. (*a*) The increase in electron affinity of the platinum atom caused by the drift of electrons from its *d*-orbitals into the dative π-bond will strengthen the Pt–N bond and so decrease the N–H frequency. (*b*) The drift of electrons from the metal atom in the dative π-bond towards the ligand, L, will decrease the electron affinity of the donor group. This will enhance the donation of its lone pair in the L–Pt σ-bond, and so in turn reduce the electron affinity of the platinum atom. This will result in a weakening of the Pt–N bond and so increase the N–H frequency.

Doubtless both of these effects occur, and if they were the only factors, the effect of (*b*) must outweigh that of (*a*), but our observations cannot be accommodated on that basis alone; to obtain a complete explanation it is necessary to assume that there is some direct interaction between the N–H group and the *d*-orbitals of the platinum atom. One may picture such interaction as in Fig. 2, the interaction occurring between the N–H group and the antinodes, *aa'*, of a *d*-orbital; our evidence that it occurs is as follows :

In the piperidine complexes, with the single exception of the ethylene complex, we find empirically that there is a linear relation between the square-root of the band intensity and the N–H stretching frequency (Fig. 3). The band intensity of the ethylene complex is significantly greater than would be predicted from the N–H frequency, according to this linear relation. If the only factor affecting the N–H bond were the position of electrons in the Pt–N bond, as required by (*a*) and (*b*) above, it is difficult to see how that one cause could produce at one N–H frequency two different intensities. However, if the N–H bond is affected by L in two ways, both inductively through the Pt–N bond and mesomerically through weak interaction of the *d*-orbital with the proton or N–H bonding electrons, then these two ways may influence the N–H frequencies and band intensities differently. Different combinations of inductive and mesomeric effects might thus result in the same N–H frequency, but different band intensities, as happens, *e.g.*, in the telluride and ethylene complexes. It may be significant that the points corresponding to the phosphite and phosphine complexes in Fig. 3 are slightly displaced to the same side of the line as the point corresponding to the ethylene complex.

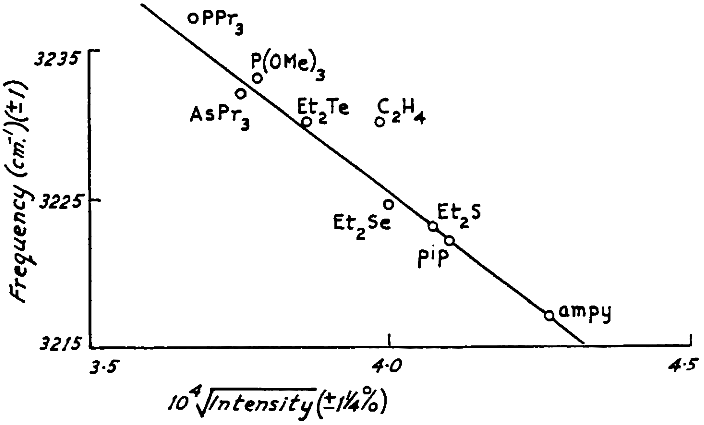


FIG. 3. *Plot of* N–H *frequency against the square-root of the band intensity of the complexes,* trans-[L, pip, $PtCl_2$].*

* " ampy " = 4-*n*-Pentylpyridine.
" pip " = Piperidine.

The " errors " define the limit of reproducibility.

The interaction between the N–H group and the *d*-orbitals of the platinum atom may occur either (*a*) by the interaction of the N–H bonding electrons with the vacant *dp*-hybrid, when L is strongly double bonding—a type of hyperconjugation—or (*b*) by the interaction of the proton with electrons in a filled *d*-orbital—a type of intramolecular hydrogen bonding. Further work with metals other than platinum(II) is in hand to determine the exact nature of the interaction, but preliminary results favour (*b*). Such interaction of the *N*-hydrogen atoms with filled *d*-orbitals may be a significant contributory cause of the low stability of tertiary alkylamine complexes of the transition metals, as compared with their ammines and primary and secondary amine complexes (*e.g.*, see Chatt and Wilkins, *J.*, 1952, 4300).

The rapid rise in the association constants of the complexes containing ligands to the right of the phosphines in our series may also be explained on the basis of electron withdrawal from the *d*-orbitals of the metal by L when it forms a π-type bond. The complexes *trans*-[L,am$PtCl_2$] associate through intermolecular N–H···Cl bonds. The formation of the hydrogen bond may be opposed by lone-pair repulsion between the *d*-electron pairs of the platinum atom and *p*-electron pairs of the chlorine atom, and also by interaction of the proton with the *d*-electrons. Association may thus be increased either by raising the electronegativity of the ligand, L, and so enhancing the acidity of the NH_2-group, or by increasing the strength of dative π-bonding to L, and so diminishing the lone-pair repulsion and proton interaction (cf. Fig. 2). Ethylene is one of the more electronegative ligands and has the greatest tendency to form double bonds; we should therefore expect its complexes to have high association constants, as we have observed. The association may be subject to steric factors other than lone-pair repulsion. The greater association of the ethylene complex may be partly due to the small bulk of the ethylene molecule, which might favour the formation of the dimer. On the other hand, the bulk of the ligand, L, does not appear to be of prime importance since all the phosphine homologues have about the same association constants [Table 1(*C*)]. Certainly steric effects of the ligands, L, are not likely to account for the different tendencies of the tri-*n*-propyl-phosphine, -arsine, and -stibine complexes to associate.

A complete series of association constants could not be obtained because the compounds of the type *trans*-[am,*p*-$CH_3 \cdot C_6H_4 \cdot NH_2$,$PtCl_2$] (am = an amine) which we prepared were not soluble in carbon tetrachloride, and the selenide and telluride compounds, *e.g.*, *trans*-[Pr^n_2Te,*p*-$CH_3 \cdot C_6H_4 \cdot NH_2$,$PtCl_2$], were too unstable to be isolated.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

Most of the compounds *trans*-[L,am$PtCl_2$] were obtained by the reaction of the amine, am, with the bridged compound $L_2Pt_2Cl_4$ and are described in previous publications (Chatt, *J.*, 1950, 2301; 1951, 652; Chatt and Venanzi, *J.*, 1955, 3858). *trans*-[Pr_2Se,*p*-$CH_3 \cdot C_6H_4 \cdot NH_2$,$PtCl_2$] and *trans*-[$Pr_2Te$,*p*-$CH_3 \cdot C_6H_4 \cdot NH_2$,$PtCl_2$] were too unstable to be isolated but their spectra were obtained by dissolving the appropriate solid bridged compound, *e.g.*, $(Pr_2Se)_2Pt_2Cl_4$ (*idem, ibid.*), together with its equivalent of solid *p*-toluidine in carbon tetrachloride and examining the spectrum of the solution. The following compounds were prepared by the reaction of the amine on $K[C_2H_4PtCl_3]$ in the same general manner as their *p*-toluidine analogue (Chatt, *J.*, 1949, 3340). trans-*Methylamine-ethylenedichloroplatinum*, yellow needles from carbon tetrachloride; decomp. 125—129° (Found: C, 11·1; H, 2·8. $C_3H_9NCl_2Pt$ requires C, 11·1; H, 2·8%). trans-*Ethylamine-ethylenedichloroplatinum*, yellow needles from light petroleum (b. p. 60—80°); decomp. 85—89° (Found: C, 14·9; H, 3·4. $C_4H_{11}NCl_2Pt$ requires C, 14·2; H, 3·3%). trans-2 : 6-*Dimethylaniline-ethylenedichloroplatinum*, deep yellow prisms from benzene; decomp. 150—155° (Found: C, 28·8; H, 3·7; N, 3·7. $C_{10}H_{15}NCl_2Pt$ requires C, 28·9; H, 3·6; N, 3·4%).

trans-*Dipiperidinedichloroplatinum*. The crude mixture of *cis*- and *trans*-bisdimethylsulphidedichloroplatinum (2 g.), prepared by reaction of dimethyl sulphide with aqueous K_2PtCl_4 (Enebuske, *J. prakt. Chem.*, 1888, **38**, 358), was suspended in dibutyl ether (50 c.c.); piperidine (0·5 c.c.) was added, and the mixture boiled under reflux for 15 min. The hot reaction mixture was filtered and the product separated in needles as the filtrate cooled. Recrystallised repeatedly from ethanol, the pure *complex* was obtained in 50% yield; decomp. 252—255° (Found: C, 27·6; H, 5·2. $C_{10}H_{22}N_2Cl_2Pt$ requires C, 27·5; H, 5·1%).

Spectra were measured at 25 ± 1° with a Grubb-Parsons S3A single-beam spectrometer fitted with a lithium fluoride prism. The 3μ ammonia and methane bands were used for frequency calibration, the accuracy of which was ± 1 cm.$^{-1}$. The carbon tetrachloride used as solvent was distilled over phosphoric oxide and stored over solid potassium hydroxide before use. The intensities, *B*, of the N–H stretching bands of the piperidine complexes were found by measuring the optical density at the frequency of minimum transmission and the band width at half this optical density. These quantities were substituted in the equation,

$$B = K(\log_e T_0/T)\Delta\nu^{a}_{\frac{1}{2}}\,(Ncl)^{-1}$$

where T_0 and T are respectively the measured incident and transmitted intensities, $\Delta\nu^{a}_{\frac{1}{2}}$ is the apparent half band-width in cycles per second, N is Avogadro's number, c is the concentration in moles per c.c., l is the cell thickness in cm., and K is a factor related to the band shape and the spectral slit width as calculated by Ramsay (*J. Amer. Chem. Soc.*, 1952, **74**, 72). The values of K were obtained from his table. T_0 was found by measuring the energy transmitted by the cell (1-cm., fused silica) containing pure solvent. This operation was repeated twice before and twice after the examination of each solution, and the mean value was taken as T_0. The N–H band of a given solution was measured five times to obtain mean values of the peak height and half-width. This procedure was repeated for three different concentrations of each complex in the range 0·006—0·009 M, and the deviations from the mean value were found to be no greater than ±2·5%, usually being of the order of 1%. The limits of ±2·5% can be taken as the accuracy of the relative intensities, although the absolute accuracy may be less owing to uncertainty about the true spectral slit width, the estimated value of which was 4 cm.$^{-1}$. The apparent band half-widths of the N–H stretching bands in the complexes *trans*-[L,piperidine,$PtCl_2$] for the various ligands L were: $AsPr^n_3$, 18·6; PPr^n_3, 17·7; $P(OMe)_3$, 16·4; Et_2Te, 17·8; Et_2Se, 17·5; Et_2S, 17·7; C_2H_4, 13·8; 4-*n*-pentylpyridine, 17·8; piperidine, 22·6 cm.$^{-1}$.

The authors are very grateful to Professor M. J. S. Dewar for useful discussion and to Mr. P. F. Todd for experimental assistance.

Akers Research Laboratories, Imperial Chemical Industries Limited,
The Frythe, Welwyn, Herts.
[*Received, June 13th*, 1955.]