762. *A Study of the* NH *Stretching Bands and the Conformations of Some Amine Complexes of Platinum*(II).

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The NH stretching bands of *trans*-[L,R·NH$_2$,PtCl$_2$] (I; L = C$_2$H$_4$, PEt$_3$, R = Me, Et, Pr^i, Bu^t) have been recorded, and differences between them and between reported [1,2] spectra for the analogues (I; R = *p*-Me·C$_6$H$_4$) have been interpreted in terms of conformational changes which arise from restricted rotation of the amine about the Pt–N bond. The results indicate that the potential barriers responsible for this rotational isomerism originate from (i) steric repulsion between R and the chlorine atoms, (ii) intermolecular hydrogen-bonding, and (iii) interaction similar to an intramolecular hydrogen bond, or proton screening, between *N*-hydrogen atoms and the non-bonding *d*-electrons of the metal. A combination of factors (i) and (iii) explains why complexes of the type *trans*-[L,RR′NH,PtCl$_2$] show little, if any, tendency to form intermolecular hydrogen bonds.[2] The frequencies of the NH stretching bands of monomeric (I) decrease in the order R = Me > primary alkyl > secondary alkyl > tertiary alkyl.

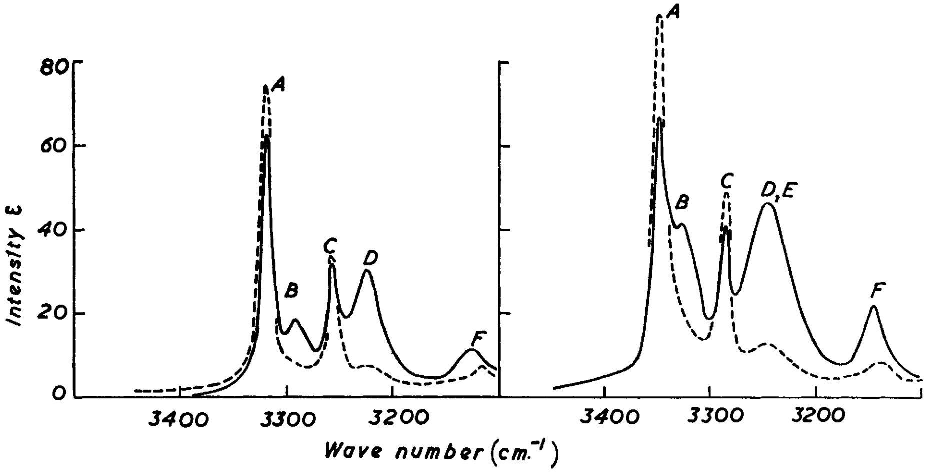
INFRARED spectra have shown [1,2] that complexes *trans*-[L,am,PtCl$_2$] (I; L = uncharged ligand, am = amine) of primary amines have a strong tendency to associate through intermolecular hydrogen bonds, but that those of secondary aliphatic amines have little, if any, such tendency. This is true whether the electron-donor for hydrogen-bond formation is another molecule of the complex itself (*i.e.*, giving N–H · · · Cl bonds) or a solvent molecule such as dioxan (*i.e.*, giving N–H · · · O bonds). Also the relative intensities of the NH stretching bands of associated primary amine complexes differ characteristically according to whether the co-ordinated amine is aliphatic or aromatic.[2] For instance, Figs. 4 and 5 of reference 2 show that associated molecules of (I; am = primary amine) have three broad NH stretching bands. The relative intensity of the highest-frequency band of these three is greater when the amine is aliphatic than when it is aromatic. The gain in intensity of the highest-frequency band appears to be achieved predominantly at the expense of the intensity of the lowest-frequency band. A suggested explanation [2] of this difference between aromatic and aliphatic primary amine complexes postulates rotational isomerism due to restricted intramolecular rotation of the amine about the Pt–N bond as axis, and requires that in intermolecularly hydrogen-bonded complexes *trans*-[L,R·NH$_2$,PtCl$_2$] the conformation of the amine relative to the plane of the complex is sensitive to the size of the hydrocarbon group R. Thus when R is the comparatively

[1] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.
[2] Chatt, Duncanson, and Venanzi, *J.*, 1956, 2712.

flat phenyl group the N–R bond can more easily lie in the plane of the complex (*i.e.*, R, Cl eclipsed) than when R is alkyl. This implies further that the eclipsed conformation is stabilised by stronger intermolecular hydrogen bonds than can be formed by molecules in other conformations.

This communication records new data relevant to this rotational isomerism theory and extends the theory to explain why secondary differ from primary aliphatic amine complexes by not undergoing association through intermolecular hydrogen bonds.

FIG. 1*a*. FIG. 1*b*.



trans-[PEt_3,Bu^t·NH_2,$PtCl_2$]
——— 0·0978M in CCl_4
– – – – 0·00958M in CCl_4

trans-[PEt_3,Me·NH_2,$PtCl_2$]
——— 0·0928M in CCl_4
– – – – 0·00858M in CCl_4

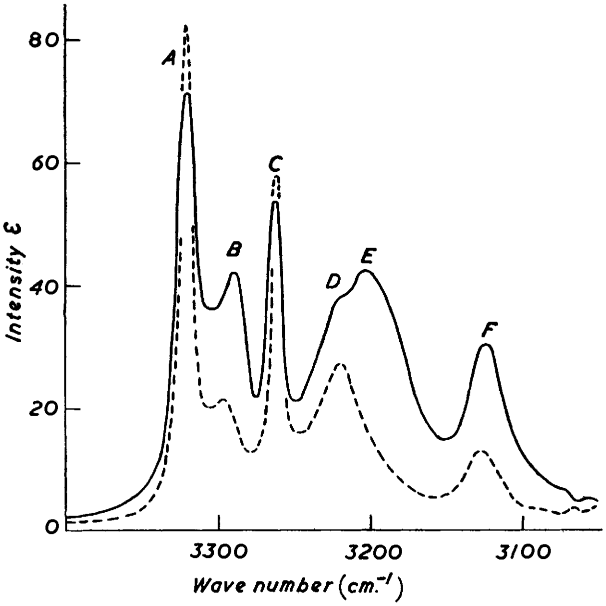


FIG. 2.

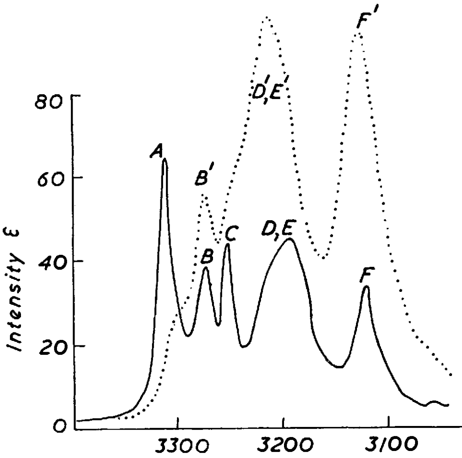
——— *trans*-[C_2H_4,Et·NH_2,$PtCl_2$] (0·00994M in CCl_4)
– – – – *trans*-[C_2H_4,Bu^t·NH_2,$PtCl_2$] (0·00940M in CCl_4)
(curve displaced 13 cm.⁻¹ to higher frequency)

The NH stretching bands of solutions of *trans*-[L,R·NH_2,$PtCl_2$] (L = C_2H_4, PEt_3, R = Me, Et, Pr^i, Bu^t) in carbon tetrachloride and carbon tetrachloride–dioxan have been measured, and differences between them correlated with the bulkiness of R. These measurements have incidentally provided data which show that the effects of different alkyl groups R upon the NH stretching frequencies of the complexes are dependent only upon the substitution pattern at the carbon atom attached directly to the nitrogen atom.

RESULTS

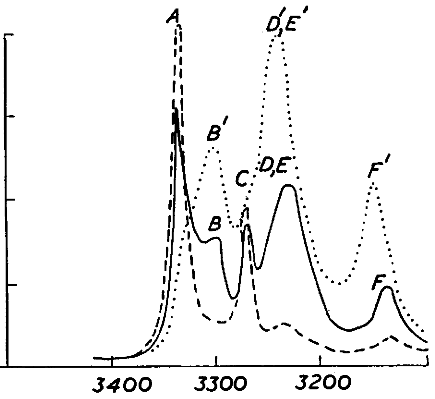
Observations of the NH stretching bands of amine complexes of platinum which we have reported in this and previous papers[1,2] can be roughly classified under two headings

FIG. 3*a*.



trans-[C_2H_4,Pr^i·NH_2,$PtCl_2$]
——— 0·00946M in CCl_4
– – – – 0·132M in CCl_4–dioxan

FIG. 3*b*.



trans-[PEt_3,Et·NH_2,$PtCl_2$]
——— 0·0970M } in CCl_4
– – – – 0·00897M }
. . . . 0·112M in CCl_4–dioxan

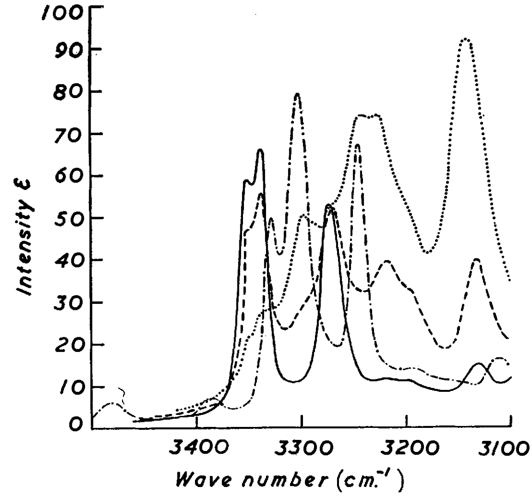


FIG. 4.
trans-[PBu^n_3,*o*-iodoaniline,$PtCl_2$]
– · – · (0·00926M in CCl_4)
trans-[PBu^n_3,*o*-toluidine,$PtCl_2$]
——— 0·00906M } in CCl_4
– – – – 0·0802M }
········· 0·0944M in CCl_4–dioxan

according as they concern steric or electronic effects. Steric effects cause changes in the general form of the NH stretching bands of the complexes (*i.e.*, the *relative* intensities and the numbers of the bands are altered by steric effects); electronic effects only cause changes in the frequencies and *absolute* intensities of the bands. However, this classification, although convenient for discussion, is somewhat arbitrary, because steric effects become intimately connected with electronic effects when the rôle played by non-bonding electrons of the metal atom is considered.

Steric Effects of Bulky Alkyl Groups.—One effect of increasing the bulkiness of the alkyl group (R) in *trans*-[L,R·NH_2,$PtCl_2$] is to reduce the amount of association through intermolecular hydrogen bonds. Fig. 1 (*a* and *b*) for *trans*-[PEt_3,R·NH_2,$PtCl_2$] (R = Me and Bu^t shows that, at comparable concentrations, the intensities of bands due to associated molecules (*B*, *D*, and *F*) are greater when R = Me than when R = Bu^t, *i.e.*, demonstrates steric hindrance of the amino-group by the bulky alkyl group. The same steric effect is observed in the presence of a large excess of dioxan. Another correlation between the bulkiness of the alkyl group (R) and the NH stretching bands of associated amine complexes is shown in Fig. 2, where the spectra of *trans*-[C_2H_4,R·NH_2,$PtCl_2$] (R = Et and Bu^t) have been superimposed. The spectrum of the ethylamine complex includes four bands (*B*, *D*, *E*, and *F*) due to associated molecules, as required by our original hypothesis,[2] although two of them (*D* and *E*) are only just resolvable. The spectrum of the t-butylamine complex has, on the other hand, only three bands due to associated molecules: *B*, *F*, and one other which may consist of bands *D* and *E* unresolved. The bands *D* and *E* for the complex *trans*-[PEt_3,R·NH_2,$PtCl_2$] are not resolvable except when R = Pr^i (see Table 2), but it is noteworthy that dilution of its solutions in carbon tetrachloride shifts the lowest-frequency bands (*F*) significantly to longer wavelengths (Fig. 1), suggesting that *F* is made up of two, nearly overlapping, bands.

In none of the solutions of aliphatic amine complexes in a carbon tetrachloride–dioxan mixture could the bands *D* and *E* be resolved and, the case of *trans*-[C_2H_4, Pr^iNH_2,$PtCl_2$] illustrated in Fig. 3*a* being taken as typical, it seems that this may be due to a diminution in intensity of band *E* relative to band *D* in this solvent mixture. It is also possible that the bands are closer in frequency and unresolved under these conditions. A further observation is pertinent to the subsequent interpretation of these spectra, namely, that changing the ligand (L) in *trans*-[L,R·NH_2,$PtCl_2$] from PEt_3 to C_2H_4 causes an increase in the intensity of band *F* relative to *D*, *E* as is shown most clearly by comparison of the dotted line curves in Figs. 3*a* and 3*b*.

The NH stretching bands of the primary arylamine complex *trans*-[PBu^n_3,*o*-toluidine,$PtCl_2$] are shown in Fig. 4. This compound, and its *o*-iodoaniline analogue, are the only two primary amine complexes investigated which exhibit more than two NH stretching bands due to monomers. Thus, in the *o*-toluidine complex the band (*A*) due to the antisymmetric NH_2 stretching mode is split into two components, at 3352 and 3339 cm.$^{-1}$, and the band (*C*) (3273 cm.$^{-1}$) due to the corresponding in-phase vibration is fairly broad and may consist of two, unresolved components. The remaining four bands (*B*, *D*, *E*, and *F*) are due to associated molecules and are all easily resolvable in the carbon tetrachloride–dioxan solvent.

The effects of changing R upon the NH stretching frequencies of the complexes *trans*-[L,R·NH_2,$PtCl_2$] (L = C_2H_4, PEt_3; R = Me, Et, Pr^n, Pr^i, Bu^t, Bu^n, Bu^i, Bu^s) are shown in Tables 1 and 2. For a given ligand (L), the NH stretching frequencies of the monomeric complexes decrease in the order R = Me > n-alkyl > s-alkyl > t-alkyl. It should be noted that this sequence is not always followed by the bands due to associated molecules in solution, the sequence being R = Me > n-alkyl > t-alkyl > s-alkyl, both in pure carbon tetrachloride and in carbon tetrachloride–dioxan.

DISCUSSION

To explain the above observations we assume that the complexes undergo rotational isomerism, the Pt–N bond being the axis of intramolecular rotation concerned. This presupposes that intramolecular rotation of the amine about the Pt–N axis is restricted to some extent, and we must now consider the possible factors which contribute to the hindering potential.

Factors hindering Intramolecular Rotation of the Amine.—There appear four possibilities, namely, (i) steric repulsion between the groups attached to the nitrogen atom and the chlorine atoms in *cis*-positions to the amine, (ii) intermolecular hydrogen-bond formation, (iii) double bonding between the co-ordinated nitrogen atom and the platinum atom, and (iv) an intramolecular hydrogen-bond type of interaction between the *N*-hydrogen atoms and the non-bonding 5*d*-electrons of the platinum atom. These factors will be discussed for each class of amine complex.

The conformations of primary amine complexes have already been discussed to some extent[2] but we can now draw some firmer conclusions about their relative stabilities. So far as associated molecules are concerned, we conclude that the intermolecular hydrogen bonds tend to hold the molecules in the R,Cl eclipsed conformation (Fig. 5*a*), whereas the steric repulsions oppose this effect, being at a minimum when the N–R bond lies in a plane at right angles to that of the complex (Fig. 5*b*). The resultant of these effects naturally depends upon their individual magnitudes. The intermolecular hydrogen bonding presumably exerts a predominating influence in primary aromatic amine complexes, steric repulsion being more important in primary aliphatic amine complexes containing bulky alkyl groups (R). This is indicated by the changes in the relative intensities of the bands due to associated molecules of *trans*-[L,R·NH_2,$PtCl_2$] as the bulkiness of R increases.

TABLE 1. NH *stretching frequencies* (*cm.*$^{-1}$) *of the compounds* *trans*-[C_2H_4,NH_2R,$PtCl_2$].

	Solutions in CCl_4		Solutions in CCl_4–$C_4H_8O_2$	Solid
	Bands due to:			
R	monomer	associated molecules		
Me ...	3334	3307	3307	3261
	3276	{ 3230(sh)	3234	3218
		3210	3141	3147w
		3133		
Et ...	3322	3289	3289	3259
	3263	{ 3220(sh)	3223	3221
		3204	3132	3135w
		3124		
Bu^n...	3322	3290		3243
	3264	{ 3220(sh)	n.i.*	3198
		3204		3105vw
		3124		
Pr^i...	3313	3273	3274	3257
	3252	{ 3215(sh)	3213	3208
		3195	3126	3114w
		3120		
Bu^i...	3324	3294		3260
	3267	{ 3220(sh)	n.i.	3206
		3197		3127
		3124		
Bu^s...	3313	3274		3257
	3251	{ 3215(sh)	n.i.	{ 3231
		3195		3218(sh)
		3119		3183
				3113
Bu^t...	3309	3284	3282	3235
	3249	3207	3211	3205
		3116	3125	3123

(sh) = shoulder on the side of the other band contained in the long bracket.

For the solid state w (= weak) and vw (= very weak) refer to the relative intensities. Other bands are of moderate to strong intensity.

* n.i. = not investigated.

FIG. 5.

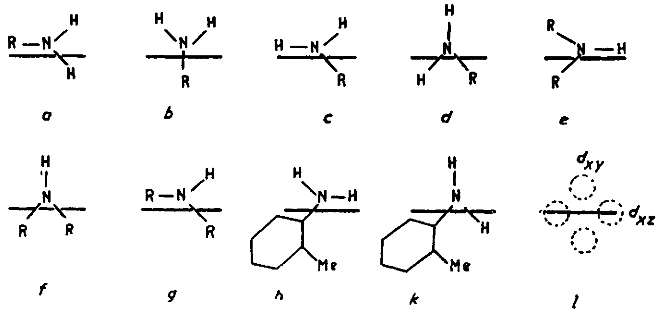


Diagram illustrating some possible conformations of amine complexes of platinum(II). *In each case the heavy horizontal line represents the plane of the complex, and only those configurations in which the* PtNR *or* PtNH *bonds lie in planes making angles of* 0°, 30°, 60°, *and* 90° *with the plane of the complex are drawn. a—d, primary amine complexes*; *e—g, secondary amine complexes*; *h and k,* o-*toluidine complexes*; *l, regions of high* d-*electron density of the metal atom available for intramolecular hydrogen-bond type of interaction with the* N-*hydrogen atoms.*

Thus when R = phenyl there are two strong bands due to associated molecules (*e.g.*, *D* and *E* in Fig. 4 of ref. 2) and only a weak third band (*ibid.*, *B*). It is assumed that the two strong bands are largely due to associated molecules in the R,Cl eclipsed conformation (Fig. 5*a*). When R = Et, four bands due to associated molecules are apparent (Fig. 2; *B*, *D*, and *F*) and ultimately when R = t-butyl three remain (Fig. 2; *B*, *D*, and *F*),* these last being attributable to associated molecules in conformations other than the R,Cl eclipsed one (*i.e.*, Fig. 5, *b*, *c*, and *d*). Of the latter conformations, that represented by Fig. 5*b* will suffer the least steric repulsions but those represented by Fig. 5*c* and *d* may be stabilised by intramolecular hydrogen bonding (factor iv, above). It is not clear how great is the influence of the intramolecular hydrogen-bond type of interaction in determining the relative stabilities of conformations of these complexes but it may exert a deciding effect when the opposing influences of steric repulsion and intermolecular hydrogen bonding are closely balanced.

The situation arising when factor (ii) above (*i.e.*, intermolecular hydrogen bonding) does not occur must also be considered; *i.e.*, what are the most stable conformations of the monomeric primary amine complexes? It is in connection with this question that the spectrum of *trans*-[PBu^n_3,*o*-toluidine,$PtCl_2$] (Fig. 4) is of most interest. If it is assumed that steric repulsions usually outweigh the effect of the intramolecular hydrogen-bond type of interaction between the NH group and the metal, then the configuration in which the N–R bond lies in a plane perpendicular to that of the complex (Fig. 5*b*) will be the most stable irrespective of whether R is alkyl or aryl. This, however, will not necessarily be so when R is an unsymmetrical group such as *o*-Me·C_6H_4, and steric repulsion will, in this case, tend to decrease the stability of the conformation in which the N–R bond lies in a plane perpendicular to that of the complex (Fig. 5: this is because the *ortho*-substituent would find itself directly against one of the chlorine atoms bound to the platinum) relative to those in which an N–H bond lies respectively in planes parallel and perpendicular to that of the complex (Fig. 5, *h* and *k*). This means that the group R = *o*-Me·C_6H_4 is tending to stabilise the two conformations in which an N–H bond can interact most strongly with the non-bonding *d*-electrons of the metal. As these two conformations are not equivalent to each other (and probably even more so when L is a ligand of good π-bonding ability such as PBu^n_3) we can understand how a solution containing both of them exhibits more than two NH stretching bands due to monomeric molecules. The effect is even more apparent in the spectrum of *trans*-[PBu^n_3,*o*-iodoaniline,$PtCl_2$] (Fig. 4) where the band due to the antisymmetric NH_2 stretching mode is split into two components, 25 cm.$^{-1}$ apart, of markedly different intensities. On the basis of the above arguments, the difference between the intensity ratios of these two components as the size of the *ortho*-substituent is altered (*i.e.*, from Me to I) may indicate a change in the relative equilibrium concentrations of the two rotational isomers represented in Fig. 5, *h* and *k*. The two weak bands in the spectrum of the *o*-iodoaniline complex at 3482 and 3385 cm.$^{-1}$ are due to a small amount of free amine produced by dissociation in solution. We conclude that the energetically preferred conformations of monomeric primary amine complexes are usually those in which minimal steric repulsions are attained.

The preferred conformations of secondary amine complexes of the general type *trans*-[L,RR′NH,$PtCl_2$] (R = alkyl; R′ = alkyl or aryl) are primarily determined by steric repulsion between the hydrocarbon groups and the chlorine atoms. This is to be expected as (*a*) there are now two hydrocarbon groups attached to the nitrogen atom and (*b*) intermolecular hydrogen bonding seems to play little part in the behaviour of the complexes.

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* At this point we must modify our original interpretation [2] of the bands due to associated molecules because band *F* does not disappear concurrently with band *E* but merely becomes much weaker. The concentration-dependence of the frequency of band *F* in some of these complexes (cf. Fig. 1) suggests that it is multiple and that its components originate from more than one conformation of associated molecules. Its decrease in intensity as the bulkiness of R increases is hence caused by the disappearance of one of its components, namely, that originating from molecules in the R,Cl eclipsed conformation.

When R = R′, both being alkyl, steric repulsions between them and the chlorine atoms will be least when projections of the two N–R bonds on to a plane through the two chlorine atoms, and perpendicular to the plane of the complex, make angles of approximately 60° with the Pt–Cl bonds (Fig. 5*e*). This steric effect puts the NH bond into the plane of the complex (*i.e.*, in the plane of the non-bonding d_{xy}-orbital) and interaction between the *N*-hydrogen atoms and the *d*-electrons can occur most favourably. The next most stable staggered conformation is that obtained by rotation of the amine about the Pt–N axis through 90° (Fig. 5*f*), and here the N–H bond lies in the plane of the d_{xz}-orbital with which, again, a hydrogen-bond type of interaction can occur. Now in both these conformations, which are the most stable from the point of view of steric repulsions, conditions are favourable for maximal interaction between the non-bonding 5*d*-electrons of the metal atom and the *N*-hydrogen atom. We therefore infer that these complexes show little tendency to form intermolecular hydrogen bonds because the *N*-hydrogen atoms participate in an intramolecular hydrogen-bond type of interaction. In other words, factors (i) (steric repulsion) and (iv) (proton screening) co-operate to prevent the operation of factor (ii) (intermolecular hydrogen-bonding). This situation cannot, of course, arise in primary amine complexes because in such cases, even if the conformation is such that one N–H bond lies eclipsed to a non-bonding *d*-orbital of the platinum atom (*e.g.*, Fig. 5, *h* and *k*), the second N–H bond must lie near one of the minima of *d*-electron density.

The behaviour of *trans*-[PPr^n_3,NHPhMe,$PtCl_2$] shows that the intramolecular hydrogen-bond type of interaction is in itself not sufficiently strong to prevent intermolecular association completely. This compound, while showing little if any tendency towards self-association through N–H ··· Cl bonds, does form intermolecular hydrogen bonds in the presence of a large excess of dioxan. The inference from this is that, when the stimulus for intermolecular hydrogen-bond formation is sufficiently strong, intramolecular rotation can occur so that the flat phenyl group lies eclipsed to a chlorine atom and the N–H bond lies staggered to the maxima of *d*-electron density (Fig. 5*g*), thereby permitting intermolecular hydrogen-bond formation.

We conclude that three factors, namely, steric repulsion, intermolecular hydrogen bonding, and an intramolecular hydrogen-bond type of interaction between the NH groups and the *d*-electrons of the metal, are sufficient to account for most of the observed differences between the forms of the NH stretching bands of various types of primary and secondary amine complexes of platinum(II). Steric repulsion and intermolecular hydrogen bonding seem to be the most important factors in determining the conformations of the complexes, whereas the intramolecular hydrogen-bond type of interaction appears to play a significant part in preventing intermolecular association, particularly in the cases of secondary amine complexes. Other, purely electronic, effects which can be transmitted through the platinum atom and primarily affect the frequencies and intensities of the NH stretching bands of monomeric complexes without altering their character, have already

TABLE 2. NH *stretching frequencies* (*cm.*$^{-1}$) *of the compounds* *trans*-[PEt_3,NH_2R,$PtCl_2$].

	Solutions in CCl_4		Solutions in CCl_4–$C_4H_8O_2$	Solid		Solutions in CCl_4		Solutions in CCl_4–$C_4H_8O_2$	Solid
	Bands due to:					Bands due to:			
R	monomer	associated molecules			R	monomer	associated molecules		
Me ...	3347	3327	3321	3323	Pr^i ...	3325	3285	3286	3286
	3284	3246	3252	3244		3258	3235(sh)	3233	3226
		3144	3158	3150			3221	3146	3130
							3133		
Et ...	3336	3300	3303	3308	Bu^t ...	3319	3292	3290	3283
	3271	3232	3242	3236		3256	3224	3231	3221
		3137	3149	3136			3125	3140	3129

been fully discussed.[1] There remains for comment another effect which has been observed during the present work.

The effect of the alkyl group (R) in *trans*-[L,R·NH_2,$PtCl_2$] upon the NH stretching frequencies has been discussed earlier. Our results show that for a comparative study of NH stretching frequencies in this type of compound (*e.g.*, for investigating the *trans*-effect)[1] it is permissible to use complexes containing different alkylamines, to suit particular preparative purposes or solubility criteria, provided that they all contain the same *type* of alkyl group (*i.e.*, Me or n-alkyl, etc.). It has previously been shown[1] that the NH stretching frequencies of *para*-substituted aniline complexes of platinum(II) are not significantly affected by the nature of the *para*-substituent.

EXPERIMENTAL

(Microanalyses by Messrs. W. Brown and G. Olney, of these laboratories.)

Preparations.—The complexes of type *trans*-[PEt_3,am,$PtCl_2$] (am = amine) were prepared from the binuclear complex $(PEt_3)_2Pt_2Cl_4$, and the corresponding amine by the method of Chatt and Venanzi[6] who also describe the preparations of *trans*-[PBu^n_3,*o*-toluidine,$PtCl_2$] and *trans*-[PEt_3,NH_2Et,$PtCl_2$].

trans-*Methylaminetriethylphosphinedichloroplatinum* recrystallised from methanol as greenish-yellow prisms, m. p. 85—86° (approx. 60%) (Found: C, 20·2; H, 4·7; N, 3·45. $C_7H_{20}NCl_2PPt$ requires C, 20·2; H, 4·85; N, 3·4%).

trans-*Isopropylaminetriethylphosphinedichloroplatinum* recrystallised from light petroleum (b. p. 60—80°) as greenish-yellow prismatic needles, m. p. 98—100° (approx. 70%) (Found: C, 24·3; H, 5·4; N, 3·3. $C_9H_{24}NCl_2PPt$ requires C, 24·4; H, 5·5; N, 3·2%).

trans-*t-Butylaminetriethylphosphinedichloroplatinum* recrystallised from light petroleum (b. p. 40—60°) as greenish-yellow prismatic needles, m. p. 98—99° (approx. 75%) (Found: C, 26·35; H, 6·2; N, 3·1. $C_{10}H_{26}NCl_2PPt$ requires C, 26·3; H, 5·7; N, 3·1%).

The complexes of type *trans*-[C_2H_4,am,$PtCl_2$] were prepared from Zeise's salt, K[C_2H_4,$PtCl_3$],H_2O and the corresponding amine by Chatt's method.[7] The preparations of *trans*-[C_2H_4,Me·NH_2,$PtCl_2$] and *trans*-[C_2H_4,Et·NH_2,$PtCl_2$] have already been described.[1]

Pure trans-*n-propylamine-ethylenedichloroplatinum* was obtained in small yield by treating a solution of Zeise's salt in 0·1N-hydrochloric acid with n-propylamine, filtering off the precipitate, and adding further n-propylamine to the ice-cold mother-liquor. This gave yellow needles, m. p. 77·5—78° (Found: C, 17·1; H, 3·8; N, 4·0. $C_5H_{13}NCl_2Pt$ requires C, 17·0; H, 3·7; N, 4·0%).

Pure trans-*isopropylamine-ethylenedichloroplatinum* was obtained by recrystallisation from light petroleum (b. p. 60—80°) as yellow prismatic needles, m. p. 94—95° (approx. 35%) (Found: C, 17·3; H, 3·7; N, 4·35%).

trans-*n-Butylamine-ethylenedichloroplatinum* was obtained in poor yield analogously to the n-propylamine complex and purified further by recrystallisation from light petroleum (b. p. 40—60°); it formed yellow needles, m. p. 51—53° (Found: C, 19·8; H, 4·05; N, 4·0. $C_6H_{15}NCl_2Pt$ requires C, 19·6; H, 4·1; N, 3·8%).

trans-*Isobutylamine-ethylenedichloroplatinum* was obtained in 50% yield as yellow needles [from light petroleum (b. p. 60—80°)], m. p. 69—70° (Found: C, 19·75; H, 4·2; N, 3·8%).

trans-*s-Butylamine-ethylenedichloroplatinum,* yellow needles obtained (approx. 50%) by recrystallisation from light petroleum (b. p. 60—80°), had m. p. 56—57° (Found: C, 19·6; H, 4·1; N, 3·9%).

trans-*t-Butylamine-ethylenedichloroplatinum* was obtained in approx. 40% yield as yellow needles, m. p. 120—130° (decomp.), recrystallised from light petroleum (b. p. 60—80°) (Found: C, 20·2; H, 4·1; N, 3·8%).

trans-o-*Iodoanilinetri-n-butylphosphinedichloroplatinum* was prepared (67%) analogously to the triethylphosphine complex and purified by recrystallisation from light petroleum (b. p.

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[3] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.
[4] Chatt and Gamlen, *J.*, 1956, 2371.
[5] Chatt, Duncanson, and Venanzi, *J.*, 1958, 3203.
[6] Chatt and Venanzi, *J.*, 1955, 3858.
[7] Chatt, *J.*, 1949, 3340.

60—80°); it formed greenish-yellow needles, m. p. 70—71° (Found: C, 31·3; H, 4·9; N, 2·2. $C_{18}H_{33}NCl_2IPPt$ requires C, 31·45; H, 4·8; N, 2·0%).

Infrared Spectra.—These were measured with a Grubb–Parsons S3A spectrometer fitted with a lithium fluoride prism. The estimated slit widths were of the order of 5 cm.$^{-1}$ and the frequency calibration was checked regularly by using the 3μ NH band, giving an accuracy of ± 1 cm.$^{-1}$. The extinction coefficients [$\varepsilon = (cl)^{-1} \log (T_0/T)$, where T_0 and T are the intensities of the incident and transmitted radiation respectively, c is the molar concentration, and l is the cell thickness in cm.] are plotted for certain compounds in Figs. 1—4. The values of T_0 were obtained by measuring transmitted energy as a function of frequency when the absorption cell contained pure solvent. A 1-cm. fused silica cell was used for the more dilute solutions (<0·01M) in carbon tetrachloride, and a permanent rocksalt cell of thickness 0·031 cm. (measured interferometrically) was used for the more concentrated solutions (0·1M) in carbon tetrachloride and in a carbon tetrachloride–dioxan (5 : 1 v/v). The carbon tetrachloride was distilled from phosphorus pentoxide before use, and reagent-grade dioxan was used without further purification.

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