

535. *An Infrared Spectroscopic Investigation of Absorption Due to the N-H Stretching Modes of Vibration in Co-ordination Compounds of Ammonia and Amines. Hydrogen Bonding (N-H...Cl) in a Series of Amine Complexes of Platinous Chloride.*

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The infrared spectra of about 30 complex compounds of the type *trans*-[L,amPtX<sub>2</sub>] have been examined in the solid state, in solution in an inert (CCl<sub>4</sub>), and in an electron-donor solvent (CCl<sub>4</sub>-dioxan). In these compounds L is one of the following uncharged ligands: ethylene, 4-*n*-pentylpyridine, piperidine, a di-*n*-alkyl sulphide, selenide, or telluride, or a tri-*n*-alkyl-phosphine, -arsine, or -stibine, or a tri-*n*-alkyl phosphite; "am" is ammonia or a primary or secondary amine, and X is a halogen atom, usually chlorine. The spectra were examined in the 3000—3500 cm.<sup>-1</sup> region.

Generally, the spectra of the ammines and primary amine complexes were complicated by hydrogen bonding involving the *N*-hydrogen atoms. This bonding is intermolecular, to the halogen atom of another molecule, N-H...X, when the complexes are in the solid state and in carbon tetrachloride solution. In the presence of dioxan, however, it also occurs to the oxygen atoms of the solvent, N-H...O. The spectra of the primary amine complexes in dilute carbon tetrachloride have been interpreted in terms of the dimerisation equilibrium:  $2 \text{ trans-}[\text{L,R}\cdot\text{NH}_2\text{PtCl}_2] \rightleftharpoons (\text{trans-}[\text{L,R}\cdot\text{NH}_2\text{PtCl}_2])_2$ , and association constants, *K*, were determined for a series of *p*-toluidine complexes (Table 1).

The complexes in which "am" is a sterically hindered primary amine, *e.g.*, 2:6-dimethylaniline, or a secondary amine have less complicated spectra in the 3000—3500 cm.<sup>-1</sup> region. If any hydrogen bonding occurs it is very weak in the solid state and in solution, even in the presence of dioxan.

The electronic and steric effects of the various ligands "L," "am," and "X" on the spectra and association constants are discussed and a structure is proposed for the dimeric primary amine complex (Fig. 9).

THE value of infrared spectroscopic methods in the study of co-ordination compounds has become generally apparent during the last few years.<sup>1,2</sup> The method has the serious limitation that complex compounds are usually crystalline and insoluble in the solvents most

<sup>1</sup> See, *e.g.*, (a) Mizushima, Nakagawa, and Quagliano, *J. Chem. Phys.*, 1955, **23**, 1367; (b) Nyholm and Short, *J.*, 1953, 2670; (c) Chatt and Duncanson, *J.*, 1953, 2939; (d) Bellamy and Branch, *J.*, 1954, 4491.

<sup>2</sup> Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

suitable for infrared work. Most investigations have therefore been carried out upon the powdered crystalline complex suspended in some medium such as mineral oil or compressed in potassium bromide discs.<sup>3</sup> In such circumstances the subtle changes in the frequency, intensity, and width of the absorption bands caused, *e.g.*, by changing the metal or ligands in the complex, are interfered with or masked by lattice and other effects associated with the solid state.

In order to investigate the electronic effects which might control the position of substitution in platinous complexes, we<sup>2,4</sup> prepared a number of amine complexes of the type *trans*-[L,amPtX<sub>2</sub>]. In these compounds "am" is ammonia, or a primary or secondary amine, "X" a halogen atom, and "L" is ethylene, a tertiary-*n*-alkyl-phosphine, -arsine, or -stibine, or a di-*n*-alkyl sulphide, selenide, or telluride. The above non-ionic complexes, containing only one molecule of ammonia or amine, are soluble in most organic solvents. They are thus ideal for a systematic infrared spectroscopic investigation and comparison of the N-H absorption bands in various solvent media and in the solid state. We now

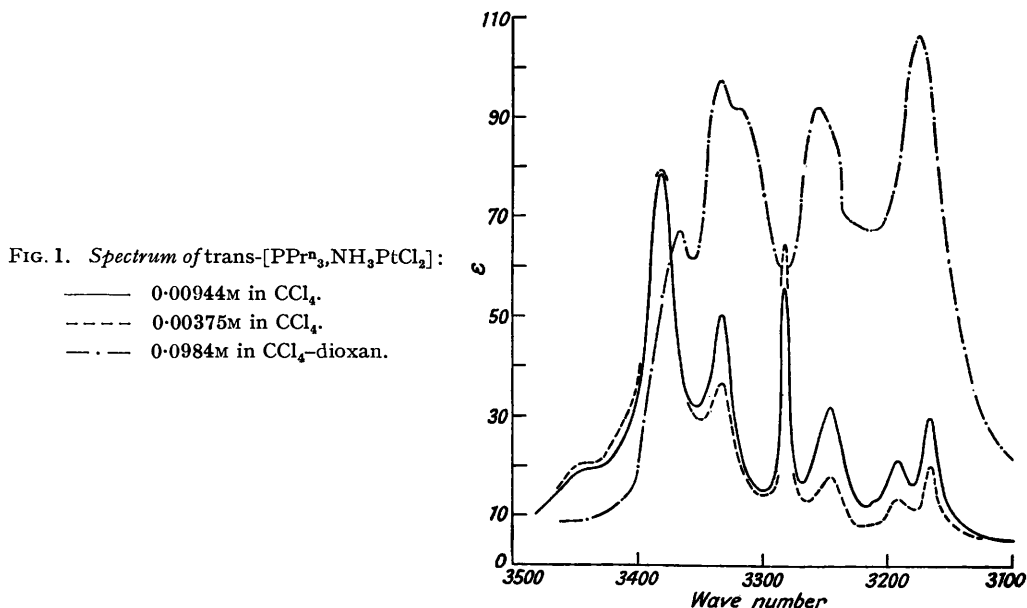


FIG. 1. Spectrum of *trans*-[PPr<sub>n</sub><sub>3</sub>,NH<sub>3</sub>PtCl<sub>2</sub>]:

- 0.00944M in CCl<sub>4</sub>.
- - - 0.00375M in CCl<sub>4</sub>.
- · - 0.0984M in CCl<sub>4</sub>-dioxan.

record the results of such an investigation in the hope that they will help in the interpretation of the spectra of solid complexes and guide future investigators in their choice of amino-complexes for investigation. We found that the spectra of the above monoamino-complexes in the 3000—3500 cm.<sup>-1</sup> region are not so simple as might be expected, because many of the compounds in the solid state and in concentrated carbon tetrachloride solution form intermolecular hydrogen bonds involving the hydrogen of the amine. The extent of the hydrogen bonding is greatly affected by the nature of the amine. The tendency to form hydrogen bonds is very strong in ammonia and primary amine complexes, except when the NH<sub>2</sub> group of the amine is sterically hindered. In secondary amine complexes the tendency is very slight. We are thus able to classify the complexes for the purpose of describing their spectra and general behaviour in solution according to the type of amine which they contain.

We use this classification to describe the spectra of the various complexes below. The N-H bands of the complexes in the crystalline state, in carbon tetrachloride solution, and in an electron-donor solvent are described, and interpreted in terms of hydrogen bonding. The extent of hydrogen bonding depends on the physical state of the complex, whether it

<sup>3</sup> Lane, Sen, and Quagliano, *J. Chem. Phys.*, 1954, 22, 1855.

<sup>4</sup> Chatt and Venanzi, *J.*, 1955, 3858.

be solid, or in solution, and on the nature of the solvent; it also depends on intramolecular, steric, and electronic factors. How all these factors affect the hydrogen bonding is discussed after the following general description and interpretation of the spectra.

(1) Ammonia complexes such as *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtCl<sub>2</sub>] are associated by intermolecular hydrogen bonds in the solid state and in solution. The spectrum of *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtCl<sub>2</sub>] in carbon tetrachloride solution (Fig. 1) contains six distinct NH stretching bands at 3383, 3336, 3281, 3243, 3197, and 3167 cm.<sup>-1</sup>, together with a shoulder near

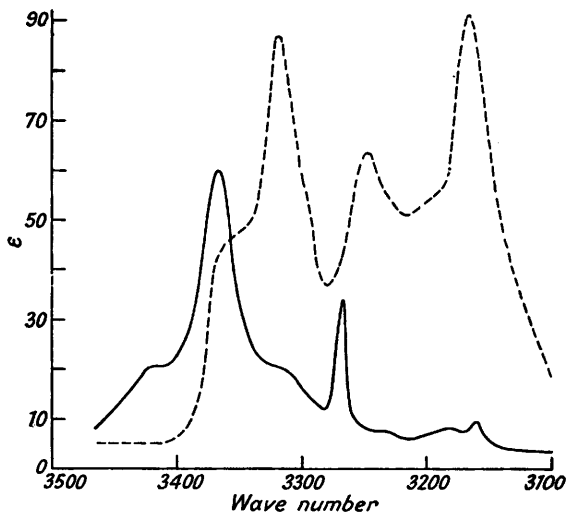
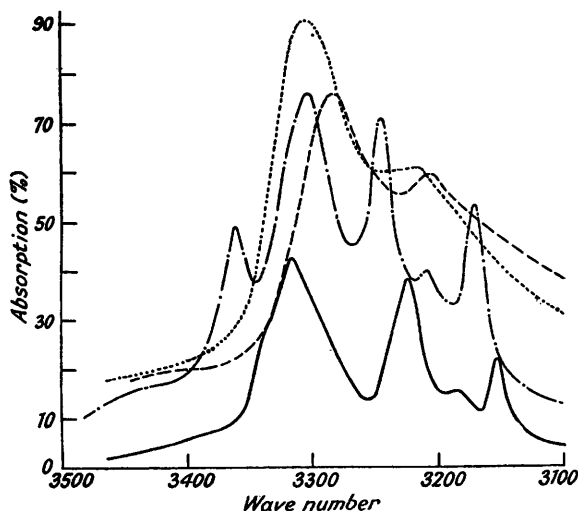


FIG. 2. Spectrum of *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtI<sub>2</sub>]:

— 0.00936M in CCl<sub>4</sub>.  
 - - - 0.0851M in CCl<sub>4</sub>-dioxan.

FIG. 3. Spectra of solid complexes:

— *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtI<sub>2</sub>].  
 - - - *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtCl<sub>2</sub>].  
 . . . *trans*-[(NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>].  
 - - - *cis*-[(NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>].

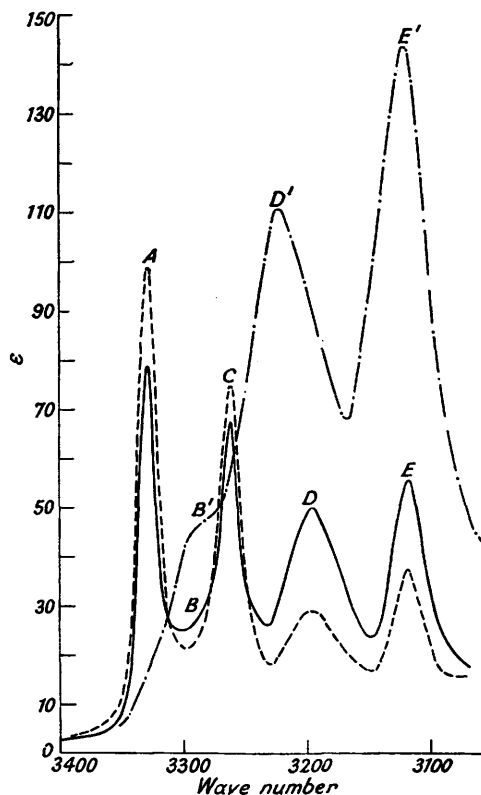


3450 cm.<sup>-1</sup>. The relative intensities of these bands vary with the concentration of the solution as is shown in Fig. 1, enabling us to assign those at 3383 and 3281 cm.<sup>-1</sup> to the monomeric complex because they increase in intensity as the concentration decreases. The band at 3281 cm.<sup>-1</sup> is much sharper than any of the others and is attributed to the symmetric NH<sub>3</sub> stretching mode, while the highest-frequency band (3383 cm.<sup>-1</sup>) is assigned to the anti-symmetric stretching modes of the NH<sub>3</sub> group. The latter band presumably overlaps a band due to associated molecules, since its intensity increases more slowly than that of the 3281 cm.<sup>-1</sup> band on dilution. The comparative broadness of the 3383 cm.<sup>-1</sup> band and the shoulder near 3450 cm.<sup>-1</sup> are probably due to splitting of the degenerate levels of the free ligand by co-ordination in a planar complex. The remaining four bands

in this region of the spectrum are assigned to the NH stretching bands of molecules which are associated, to various extents, through hydrogen bonds. These assignments were confirmed by observing the spectrum of the carbon tetrachloride solution of *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtI<sub>2</sub>] (Fig. 2) where the degree of association is much smaller than in the corresponding chloro-complex. There are only two strong NH bands, one at 3368 cm.<sup>-1</sup> (broad, with shoulder near 3410 cm.<sup>-1</sup>) and the other at 3267 cm.<sup>-1</sup> (sharp), together with four much weaker bands due to associated molecules.

The NH stretching bands of these two complexes in the solid state are shown in Fig. 3 together with those of the insoluble complexes *cis*- and *trans*-[(NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>]. These spectra are shown in order to demonstrate how difficult is their interpretation. Difficulty in

FIG. 4. Spectrum of  
*trans*-[Pr<sup>n</sup><sub>2</sub>S,*p*-Me·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>PtCl<sub>2</sub>]:  
— 0.00754M in CCl<sub>4</sub>.  
- - - 0.00259M in CCl<sub>4</sub>.  
- · - 0.564M in CCl<sub>4</sub>-dioxan.



assigning the bands is, in some cases, due to the complexity of the spectra caused by hydrogen bonding in the crystal, but even where the spectra are not complicated, *e.g.*, cf. *cis*- and *trans*-[(NH<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>] (Fig. 3), there must be considerable doubt about how large and how variable is the perturbing effect of hydrogen bonding on the vibration frequencies. With the above diammino-complexes either the hydrogen bonding is of a different type from that present in the monoammino-complexes or else the broadness of the bands masks any structure which may be present. The spectrum of a suspension of powdered crystalline *trans*-[PPr<sup>n</sup><sub>3</sub>,NH<sub>3</sub>PtCl<sub>2</sub>] in compressed potassium bromide discs was found to be identical with that of its suspension in paraffin oil.

(2) (i) Primary amine complexes of the type *trans*-[L,R·NH<sub>2</sub>PtCl<sub>2</sub>] (L = uncharged ligand, R = alkyl or aryl) also form intermolecular hydrogen bonds in solution and in the solid state. The effects of this association on their NH stretching bands can be seen in Figs. 4—6. The spectra shown in Fig. 4 are typical of all the aniline and *p*-substituted aniline complexes which we have examined (see Table 3). In dilute solution (~0.005—0.01M) four bands are apparent; two sharp bands (A and C) within the ranges 3348—3328

and 3272—3262  $\text{cm}^{-1}$ , together with two broader ones (*D* and *E*) in the regions 3210—3220 and 3120—3130  $\text{cm}^{-1}$ , respectively (for precise frequencies see Table 3). The sharp bands increase in intensity at the expense of the broad ones as the concentration is diminished, and their origins are doubtless the antisymmetric (*A*) and the symmetric (*C*) NH stretching modes of the monomeric complexes. At higher concentrations (especially  $>0.02\text{M}$ ) another region of absorption (*B*) becomes apparent, extending from about 3330  $\text{cm}^{-1}$  to lower frequencies. This band is very broad in the spectra of the complexes

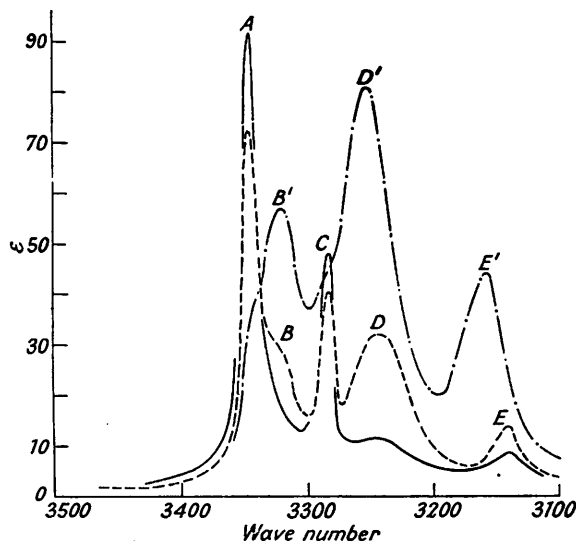


FIG. 5. Spectrum of  $\text{trans-}[\text{PPr}^n_3, \text{Me-NH}_2\text{PtCl}_2]$ :

— 0.00871M in  $\text{CCl}_4$ .  
 - - - 0.0519M in  $\text{CCl}_4$ .  
 - · - 0.0195M in  $\text{CCl}_4$ -dioxan.

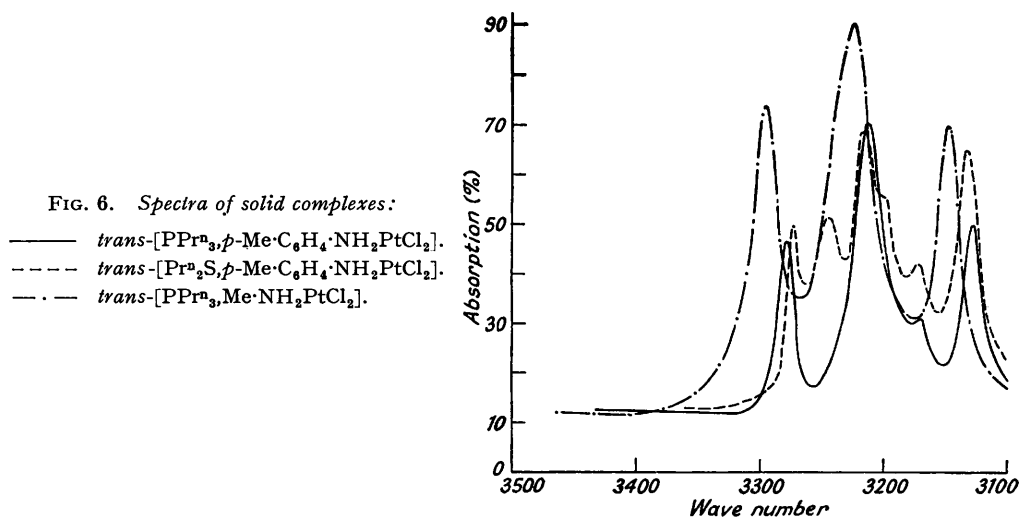


FIG. 6. Spectra of solid complexes:

—  $\text{trans-}[\text{PPr}^n_3, p\text{-Me-C}_6\text{H}_4\text{-NH}_2\text{PtCl}_2]$ .  
 - - -  $\text{trans-}[\text{Pr}^n_2\text{S}, p\text{-Me-C}_6\text{H}_4\text{-NH}_2\text{PtCl}_2]$ .  
 - · -  $\text{trans-}[\text{PPr}^n_3, \text{Me-NH}_2\text{PtCl}_2]$ .

of aromatic primary amines and its exact position is, therefore, somewhat indefinite. It is, however, sharper and more pronounced in the spectra of aliphatic primary amine complexes, e.g.,  $\text{trans-}[\text{PPr}^n_3, \text{alkyl-NH}_2\text{PtCl}_2]$ . The greater prominence of this band (*B*) is the most marked difference between the spectra in carbon tetrachloride solutions of the complexes containing aromatic and aliphatic primary amines and a possible reason for this will be discussed later. Otherwise, apart from differences in NH frequencies, the spectra of these two classes of complexes are very similar. For example, the spectrum of  $\text{trans-}[\text{PPr}^n_3, \text{Me-NH}_2\text{PtCl}_2]$  in carbon tetrachloride solution (Fig. 5) has bands at 3347 and 3284

$\text{cm}^{-1}$  (*A* and *C*, monomer) and 3325, 3242, and 3140  $\text{cm}^{-1}$  (*B*, *D*, and *E*, associated molecules). Comparison of Figs. 4 and 5 clearly shows the greater distinctness of the highest-frequency band (*B*) due to associated molecules in the spectrum of the methylamine complex as compared with the corresponding band in the spectrum of the *p*-toluidine complex.

FIG. 7. Spectrum of  $\text{trans}[\text{PPr}^n_3, 2 : 6\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2\text{PtCl}_2]$ :

— 0.0832M in  $\text{CCl}_4$ .  
 - - - - 0.116M in  $\text{CCl}_4$ -dioxan.

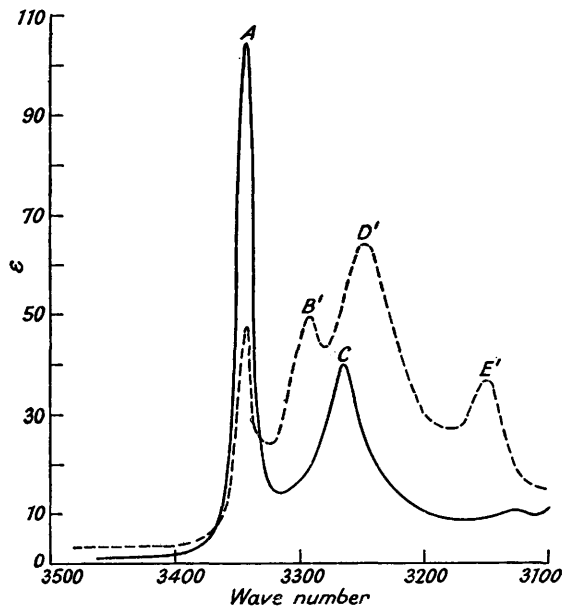
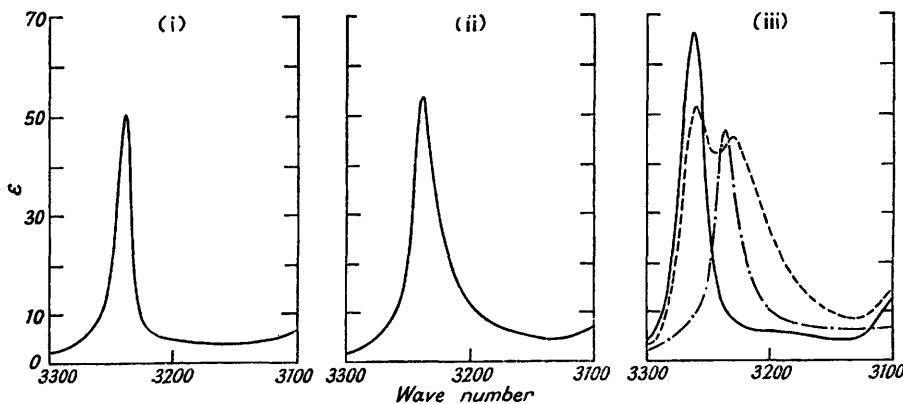


FIG. 8. Spectra of  $\text{trans}[\text{PPr}^n_3, \text{RR}'\text{NH}\text{PtCl}_2]$ : (i)  $\text{R} = \text{R}' = \text{Et}$ ; 0.00691M in  $\text{CCl}_4$ ; (ii)  $\text{R} = \text{R}' = \text{Et}$ ; 0.125M in  $\text{CCl}_4$ -dioxan; (iii) —  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ; 0.00732M in  $\text{CCl}_4$ ; - - - -  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ; 0.0121M in  $\text{CCl}_4$ -dioxan; - · - · -  $\text{RR}'\text{NH} = \text{piperidine}$ ; 0.0662M in  $\text{CCl}_4$ -dioxan.



There is again little to be learned by observation of the NH frequencies of the solid complexes, mainly because of their multiplicity. Of the spectra of solid primary amine complexes shown in Fig. 6, that of  $\text{trans}[\text{PPr}^n_3, \text{Me}\cdot\text{NH}_2\text{PtCl}_2]$  is the simplest and contains three NH stretching bands. The other two spectra in Fig. 6 are of complexes containing *p*-toluidine with, in one case, di-*n*-propyl sulphide as the ligand in *trans*-position to the amine, and in the other case, tri-*n*-propylphosphine. It can be seen that any attempt to correlate the NH frequencies with the donor properties of sulphur and phosphorus, in the manner successfully applied with dilute solutions,<sup>2</sup> would fail. For example, the frequency shift of the shortest-wavelength band, in passing from the sulphide to the phosphine complex,

is in the opposite sense to that of the longest-wavelength band. Especially noteworthy of the difference between the spectra of solid complexes and their solutions is the existence of a band at  $3243\text{ cm.}^{-1}$  in the spectrum of solid *trans*-[Pr<sup>n</sup><sub>2</sub>S, *p*-Me·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>PtCl<sub>2</sub>], which has no counterpart in the spectrum of solid *trans*-[PPr<sup>n</sup><sub>3</sub>, *p*-Me·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>PtCl<sub>2</sub>] or in solutions of any of the primary amine complexes which we examined. The differences between the spectra of the solids render it doubtful whether bands due to corresponding modes of vibration can be identified in their spectra.

(ii) Hindered primary amine complexes, as would be expected, are much less associated by hydrogen bonding than are complexes of non-sterically hindered primary amines. This is clearly demonstrated in the spectrum of *trans*-[PPr<sup>n</sup><sub>3</sub>, 2 : 6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·NH<sub>2</sub>PtCl<sub>2</sub>] in carbon tetrachloride solution (Fig. 7). It has only two NH stretching bands ( $3347$  and  $3268\text{ cm.}^{-1}$ ) at concentrations where the spectrum of the corresponding *p*-toluidine complex exhibits bands due to both the monomer and associated molecules. The spectra of the complexes of 2 : 6-dibromo-4-*n*-dodecylaniline also show only two NH bands in solution. The bands attributed to the symmetric NH<sub>2</sub> stretching modes of these hindered amine complexes are appreciably broader and of lower peak height than the corresponding bands of non-hindered amine complexes. This may be caused by some interaction of the NH<sub>2</sub> group with the *ortho*-substituents.

(3) Secondary amine complexes of the type *trans*-[PPr<sup>n</sup><sub>3</sub>, RR'NH<sub>2</sub>PtCl<sub>2</sub>] have little, if any, tendency to form intermolecular hydrogen bonds in solution. A small deviation of the NH absorption band from Beer's law indicates that complexes of the type *trans*-[C<sub>2</sub>H<sub>5</sub>, RR'NH<sub>2</sub>PtCl<sub>2</sub>] may be slightly associated in solution but at concentrations under 0.01M the amount of association is negligible. Even in the spectra of more concentrated solutions only a single sharp NH stretching band can be seen. Furthermore, intermolecular forces involving NH groups in the solid state must be small; for example, in the spectrum of solid *trans*-[PPr<sup>n</sup><sub>3</sub>, Et<sub>2</sub>NH<sub>2</sub>PtCl<sub>2</sub>] the NH frequency is only  $14\text{ cm.}^{-1}$  lower than that found in the spectrum of its carbon tetrachloride solution ( $3240\text{ cm.}^{-1}$ ) (Fig. 8). The spectrum of the analogous complex of *N*-methylaniline (Fig. 8) also has only one NH band in carbon tetrachloride solution ( $3261\text{ cm.}^{-1}$ ) but its tendency to form hydrogen bonds with dioxan is somewhat greater than that of the dialkylamine complexes, as will be described later. (The precise frequencies and intensities of the NH stretching bands of 13 complexes of this class are listed in Tables 1A and 1B of reference 2; those of 10 piperidine complexes are also listed in Table 2 of this paper.)

*Effects of the Ligands L and X on the Tendency of trans*-[L, amPtX<sub>2</sub>] *to form Hydrogen Bonds.*—Changing the ligands (L) and the halogens (X) causes more subtle changes in the association of the complexes of a given amine than does changing the type of amine. For this reason, quantitative estimates of the extent of association have been made with a series of complexes of the type *trans*-[L, *p*-toluidinePtX<sub>2</sub>]. By measuring the deviation of the monomer NH bands from Beer's law and assuming that at low concentrations dimerisation is the principal associative step, an approximate association constant (*K*) for the dimerisation can be obtained (Table 1).

TABLE 1. Association constants, *K*, for the dimerisation by hydrogen bonding of a series of complexes *trans*-[L, *p*-toluidinePtX<sub>2</sub>] at  $25^\circ \pm 1^\circ$ .

L	C <sub>6</sub> H <sub>4</sub>	Pr <sup>n</sup> <sub>2</sub> S	Bu <sup>n</sup> <sub>2</sub> S	SbPr <sup>n</sup> <sub>3</sub>	AsPr <sup>n</sup> <sub>3</sub>	PEt <sub>3</sub>	PPr <sup>n</sup> <sub>3</sub>	PBu <sup>n</sup> <sub>3</sub>	PPr <sup>n</sup> <sub>3</sub>	Bu <sup>n</sup> <sub>2</sub> S	PPr <sup>n</sup> <sub>2</sub>
X	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Br	Br	I
K	115	77	77	38	24	18	18	15	7.5	23	—

Cf. also: *trans*-[PPr<sup>n</sup><sub>3</sub>, *p*-toluidinePdCl<sub>2</sub>] has *K* = 2; *trans*-[PPr<sup>n</sup><sub>3</sub>, *p*-NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>ClPtCl<sub>2</sub>] has *K* ~ 24.

It is evident that the sizes of the alkyl groups in the ligands, L, have little effect on the extent of association by hydrogen bonding, but the nature of the donor atom in the ligand, L, has a marked effect. Evidently the differences in association are largely due to electronic effects. The effect of changing the electron affinity of the central metal atom has also been demonstrated by substituting palladium for platinum; this results in a lower association constant.

The extent of association also depends greatly on the nature of the halogen atoms, decreasing rapidly in the order  $X = \text{Cl} > \text{Br} > \text{I}$ . The rapid decrease in association with decreasing electronegativity of the halogen  $X$  is to be expected if the association occurs through  $\text{N-H} \cdots \text{X}$  bonds. This mechanism of association is also supported by the fact that the absorption due to hydrogen-bonded  $\text{NH}_2$  groups is increased when *trans*-[4-*n*-pentylpyridine]<sub>2</sub>PtCl<sub>2</sub>] (A) is added to a solution of *trans*-[C<sub>2</sub>H<sub>4</sub>, *p*-toluidinePtCl<sub>2</sub>] (B) in carbon tetrachloride. By measuring the residual monomer N-H intensity, the constant for the equilibrium,  $A + B \rightleftharpoons AB$ , was estimated to be  $62 \pm 10$  at 25°.

*Effect of an Electron-donor Solvent.*—The effects on the spectra of adding an electron donor (dioxan) to carbon tetrachloride solutions of the complexes were investigated in an attempt to relate the acidities of the NH group of the amine complexes to the tendencies to form hydrogen bonds. The absorption bands due to hydrogen-bonded NH groups were, however, too broad and frequency differences from one complex to another too small to allow us to do this. However, different types of complex behaved rather differently in presence of the dioxan. The solvent used consisted of 5 vol. of carbon tetrachloride to 1 vol. of dioxan and the concentrations of the complexes were of the order of 0.02–0.05M.

(1) Ammonia complexes in the presence of a relatively high concentration of an electron-donor solvent such as dioxan exhibit neither of the two bands (*A* and *C*) assigned to the monomeric complexes (Figs. 1 and 2). The spectra are again complicated, that of *trans*-[PPr<sup>n</sup><sub>3</sub>, NH<sub>3</sub>PtCl<sub>2</sub>] being more so than that of *trans*-[PPr<sup>n</sup><sub>3</sub>, NH<sub>3</sub>PtI<sub>2</sub>]. This fact, taken in conjunction with the spectroscopic data obtained from pure carbon tetrachloride solutions, indicates that, while the platinumous iodide complex is to a great extent hydrogen-bonded to the dioxan, the corresponding solution of the platinumous chloride complex contains a significant proportion of molecules which are self-associated. It can be seen from the diagrams, in which extinction coefficients are plotted, that the total absorption due to NH stretching fundamentals is greater in carbon tetrachloride–dioxan than in pure carbon tetrachloride as solvent. Russell and Thompson's observations of the effect of a change of solvent on band intensity<sup>5</sup> indicate that a change of this magnitude cannot be due to a change in the refractive index of the solvent, and we conclude that hydrogen-bond formation ( $\text{N-H} \leftarrow \text{X}$ ) increases the absorption intensity of the NH stretching modes. The same effect has been observed in the spectra of organic amides.<sup>6</sup>

(2) Primary amine complexes of the type *trans*-[L, *p*-Me-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>PtCl<sub>2</sub>] in carbon tetrachloride–dioxan solutions exhibit no band which can be attributed to non-hydrogen-bonded NH<sub>2</sub> groups (Fig. 4). Two broad bands (*D'* and *E'*) are observed some 100–150 cm.<sup>-1</sup> lower in frequency than the bands due to the monomeric complex in carbon tetrachloride solution and there is also a weak shoulder (*B'*) near 3300 cm.<sup>-1</sup> which is most clearly apparent in concentrated solutions. This shoulder in the spectra of *p*-toluidine complexes is replaced by a well-defined band near 3320 cm.<sup>-1</sup> (*B'* in Fig. 5) in the spectrum of the corresponding methylamine complex, and this parallels the difference between the bands due to associated molecules in carbon tetrachloride solutions. Steric hindrance of the NH<sub>2</sub> group of the aromatic amine, by *ortho*-substituents, reduces but does not completely prevent hydrogen bonding to dioxan. Thus the spectrum of *trans*-[PPr<sup>n</sup><sub>3</sub>, 2 : 6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-NH<sub>2</sub>PtCl<sub>2</sub>] in carbon tetrachloride–dioxan solution (Fig. 7) has both bonded (3293, *B'*; 3244, *D'*; and 3143 cm.<sup>-1</sup>, *E'*) and non-bonded (3344 cm.<sup>-1</sup>, *A*) NH stretching bands. The symmetric NH stretching band of the monomer (*C*) is evidently masked by the broad bands (*B'*) and (*D'*).

Different halogen atoms attached to the platinum do not markedly affect the tendency of the NH<sub>2</sub> groups to form hydrogen bonds to dioxan. Even *trans*-[PPr<sup>n</sup><sub>3</sub>, *p*-Me-C<sub>6</sub>H<sub>4</sub>-NH<sub>2</sub>PtI<sub>2</sub>], which has little tendency to self-association, has no monomer NH bands in the spectrum of its carbon tetrachloride–dioxan solution.

(3) Secondary amine complexes, where both of the groups attached to the nitrogen atom are aliphatic, have a single fairly sharp NH stretching band in carbon tetrachloride–dioxan solutions (Fig. 8) which is close in frequency to that observed in their carbon tetrachloride solutions. For example, the NH frequency of *trans*-[PPr<sup>n</sup><sub>3</sub>, Et<sub>2</sub>NHPtCl<sub>2</sub>] in carbon

<sup>5</sup> Russell and Thompson, *J.*, 1955, 479.

<sup>6</sup> Davies, Evans, and Jones, *Trans. Faraday Soc.*, 1955, 51, 761.



tetrachloride solution ( $3240 \text{ cm.}^{-1}$ ) is shifted by only  $2 \text{ cm.}^{-1}$  on the addition of dioxan. However, the addition of dioxan does cause some broadening of the band on its low-frequency side (Fig. 8) which may indicate some interaction with the solvent. As can be seen from the diagram, this broadening is less marked in the case of the corresponding piperidine complex. The corresponding complex of the alkylarylamine, *N*-methylaniline, while showing no tendency for self-association in carbon tetrachloride solution ( $\nu_{\text{NH}} = 3262$ ; Fig. 8), has two bands ( $3257$  and  $3228 \text{ cm.}^{-1}$ ) in carbon tetrachloride-dioxan solution (Fig. 8), showing that some bonding to the solvent occurs. As a rule, however, the complexes of dialkylamines show only a slight tendency to associate with dioxan in carbon tetrachloride solution.

We see from the above that if values of NH frequencies have to be obtained from solid complexes because of their insolubility in suitable solvents, it is safest to use secondary alkylamine complexes for the purpose. However, if the unperturbed NH frequency has to be known accurately to within a few wave-numbers, as for example in our studies of inductive and mesomeric effects in platinum complexes,<sup>2</sup> even measurements on solid secondary amine complexes are unsatisfactory. For example, the NH stretching frequencies of the complexes *trans*-[L,piperidinePtCl<sub>2</sub>] in solution and in the powdered crystal are listed in Table 2 in order of increasing NH frequency in solution.

TABLE 2. NH stretching frequencies ( $\text{cm.}^{-1}$ ) of the compounds *trans*-[L,pipPtCl<sub>2</sub>] in carbon tetrachloride ( $\nu$ , soln.) and in the solid state ( $\nu$ , solid).

L *	pepy	pip	Et <sub>2</sub> S	Et <sub>2</sub> Se	Et <sub>2</sub> Te	C <sub>2</sub> H <sub>4</sub>	AsPr <sup>n</sup> <sub>3</sub>	P(OMe) <sub>3</sub>	SbEt <sub>3</sub>	PPr <sup>n</sup> <sub>3</sub>
$\nu$ , soln. ...	3217	3222	3223	3224.5	3230	3230	3232	3233	3235	3237
$\nu$ , solid ...	3189	3174	3200	3186	3193	3209	3235	3214	3203	3238

\* pepy = 4-*n*-pentylpyridine, pip = piperidine.

It can be seen that the sequence followed by the values for solutions is different from that for solids. The difficulty of measuring unperturbed NH frequencies of the solid complexes is not overcome by using the KBr disc technique, as we have not found significant differences between the spectra measured by this method and those measured when using powdered suspensions in paraffin oil.

## DISCUSSION

Our experiments indicate that in many amines and primary amine complexes of type *trans*-[L,amPtCl<sub>2</sub>] there is strong intermolecular hydrogen bonding in the solid state and in solution. In inert solvents it occurs between the *N*-hydrogen atoms of the co-ordinated ammonia or amine and a chlorine atom of another molecule. That the hydrogen bonding is intermolecular is shown by the way the intensities of the NH stretching bands change with changes in the concentrations of the solutions (Figs. 1, 4, and 5), and by the fact that the addition of *trans*-[(4-*n*-pentylpyridine)<sub>2</sub>PtCl<sub>2</sub>] to a carbon tetrachloride solution of *trans*-[C<sub>2</sub>H<sub>4</sub>,*p*-toluidinePtCl<sub>2</sub>] increases the amount of hydrogen-bonded NH in the solution. This suggests that the acceptor atom is the halogen, a conclusion which would also explain the rapid decrease in the association constants in the halide series, *trans*-[L,amPtX<sub>2</sub>], when Cl is replaced by Br and Br by I (Table 1). It is unlikely that this decrease in the tendency to associate as one halogen is replaced by another is due primarily to the steric effects of the halogens or to the electronic effects transmitted from the halogen to the N-H bond through the platinum atom, because the *trans*-[PPr<sup>n</sup><sub>3</sub>,*p*-toluidinePtI<sub>2</sub>] appears to form hydrogen bonds to dioxan just as completely as does the corresponding chloro-complex.

The NH frequencies of the complexes *trans*-[L,amPtX<sub>2</sub>] decrease as the halogen atoms X are changed from chlorine to bromine to iodine (see Table 3). This change in frequency is in the opposite sense to that to be expected from the relative electronegativities of the halogens (cf. ref. 2). This means either (a) that dative  $\pi$ -bonding from the platinum atom to the halogens increases markedly in the order Cl < Br < I, so that there is increasing electron drift from the platinum atom to the halogen atoms in the same order, or (b) that there is some intramolecular interaction between the NH bonds of a co-ordinated amine

and the adjacent halogen atom. A rapid increase in dative  $\pi$ -bonding from the platinum atom to the halogen atom would be in agreement with the sequence of the halogens in the *trans*-effect series, where iodine is known qualitatively to have a high *trans*-effect, about equal to that of the nitro-group.<sup>7</sup> In an attempt to resolve this point, we are now investigating similarly the complexes of other metals where dative  $\pi$ -bonding will be less strong.

The influence of the ligand, L, on the association and spectroscopic quantities is almost entirely electronic in origin. It is mainly inductive and is transmitted across the platinum atom, so changing the acidity of the NH group. The evidence for this and its relation to other spectral changes has already been discussed fully.<sup>2</sup> Steric effects of the ligands, L, on the association are small and close to the limits of error in measurement of the association constants (cf. the homologous series of phosphine complexes in Table 1). That electronic effects are important in determining the tendency of these complexes to associate is shown by the great reduction in association which occurs when platinum is replaced by palladium. This replacement has no effect on the size or shape of the molecule but the presumably weaker electron affinity of palladium(II) decreases the acidity of the NH group. Interaction between the filled *d*-orbitals of the metal atom and hydrogen atoms of the N-H bond and also lone-pair repulsion between the *d*-electron pair of the metal and *p*-electron pairs of the hydrogen-bonded halogen atom may be significant factors opposing association (see ref. 2).

Attempts to interpret the NH stretching bands of the hydrogen-bonded complexes have led us to certain conclusions concerning the manner in which association of the primary amine complexes takes place in solution. The two lowest-frequency NH stretching bands (e.g., *D* and *E*, Fig. 4) observed in the spectra of carbon tetrachloride solutions of primary amine complexes have been assigned to symmetric and antisymmetric  $\text{NH}_2$  stretching modes of hydrogen-bonded molecules.<sup>8</sup> If this assignment is correct the frequency separation of the bands requires that the two bonds of the  $\text{NH}_2$  group maintain their equivalence or near equivalence in the associated molecules. Furthermore, the lack of any appreciable drift in the association constants with concentration indicates that dimerisation is the principal associative process at low concentrations ( $<0.01\text{M}$ ). A possible mode of association in which these requirements are fulfilled is shown in Fig. 9 for *trans*- $[\text{PEt}_3, p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{PtCl}_2]$ . However, the third region of absorption near  $3325\text{--}3300\text{ cm}^{-1}$  (*B*, Figs. 4 and 5), which is observed with higher optical path lengths and is particularly marked in solutions of primary alkylamine complexes, is not accounted for. This band (*B*) gives the spectrum of a  $0.1\text{M}$ -solution of *trans*- $[\text{PPr}_3, \text{Me}\cdot\text{NH}_2\text{PtCl}_2]$  (Fig. 5) a certain resemblance to that of a dilute solution of acetamide.<sup>9</sup> Thus the NH stretching bands of monomeric acetamide in carbon tetrachloride solution are separated by a band due to associated molecules. This has been assigned<sup>10</sup> to a vibration of the free NH bond of an  $\text{NH}_2$  group which forms only one hydrogen bond. It is unlikely, however, that the similar band (*B*, Fig. 5) in the spectrum of the platinum complex can be so assigned. Here it is a broad band, which also occurs in presence of dioxan and so is more likely to be caused by a

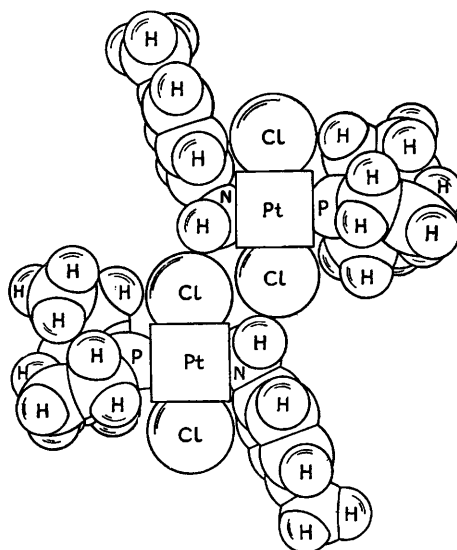


FIG. 9. *trans*- $[\text{PEt}_3, p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\text{PtCl}_2]$ :  
Postulated stable configuration of the hydrogen-bonded dimer.

<sup>7</sup> See Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.

<sup>8</sup> *Idem*, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat.*, 1954, 17, 120.

<sup>9</sup> Davies and Hallam, *Trans. Faraday Soc.*, 1951, 47, 1170.

<sup>10</sup> Badger and Rubaclava, *Proc. Nat. Acad. Sci.*, 1954, 40, 12.

TABLE 3. The frequencies ( $\text{cm}^{-1}$ ) of the NH stretching bands of some ammonia and primary amine complexes ( $\text{trans-[L,amPtX}_2\text{]}$ ) in solution.

L	X	am	Solution in $\text{CCl}_4$		Solution in $\text{CCl}_4 + \text{C}_4\text{H}_8\text{O}_2$
			Monomer bands	* Bands due to associated molecules	
$\text{PPrn}_3 \ddagger$ .....	Cl	$\text{NH}_3$	3383	3336	3365
			3281	3243	{ 3332
				3197	{ 3314 sh.
				3167	3254
					3172
$\text{PPrn}_3 \ddagger$ .....	I	$\text{NH}_3$	{ ~3420 sh.	~3322	{ ~3355 sh.
			3369	~3236	3321
			3269	3184	3249
				3162	3166
$\text{PPrn}_3 \ddagger$ .....	Cl	$\text{NH}_2\text{Me}$	3347	3325	3322
			3284	3242	3251
				3140	3153
$\text{PPrn}_3 \ddagger$ .....	Cl	2 : 6- $\text{Me}_2\text{C}_6\text{H}_3\cdot\text{NH}_2$	3346	—	3342
			3267 broad	—	3292
					3243
					3143
$\text{SbPrn}_3$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3346	3211	†
			3275	3127	
$\text{AsPrn}_3$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3342	3207	3229
			3271	3123	3134
$\text{PPrn}_3 \ddagger$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3348	3218	3232
			3277	3130	3138
$\text{PBun}_3$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3348	3217	†
			3276	3126	
$\text{Prn}_2\text{Te}$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3337	3205	†
			3270	3122	
$\text{Prn}_2\text{Se}$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3330	3194	†
			3264	3119	
$\text{Prn}_2\text{S}$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3329	3196	3225
			3262	3106	3124
$\text{Bun}_2\text{S}$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3328	3196	†
			3263	3118	
$\text{C}_2\text{H}_4$ .....	Cl	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3331	3196	3216
			3265	3117	3111
$\text{PPrn}_3$ .....	Br	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3339	3215	3230
			3270	3125	3137
$\text{PPrn}_3$ .....	I	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3328	—	3229
			3260	—	3133
$\text{Bun}_2\text{S}$ .....	Br	<i>p</i> - $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3321	3196	†
			3256	3118	
$\text{PPrn}_3$ .....	Cl	$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}_2$	3332	~3300	3306
			3268	3218	3234
				3120	3139
$\text{PPrn}_3$ .....	Cl	<i>p</i> - $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3345	3213	3231
			3275	3127	3137
$\text{PPrn}_3$ .....	Cl	<i>p</i> - $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3346	3215	3231
			3274	3129	3134
$\text{PPrn}_3$ .....	Cl	<i>p</i> - $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	3348	3208	3229
			3276	3125	3128
$\text{PEt}_3$ .....	Cl	$\text{NH}_2\text{Et}$	3336	~3300	†
				3230	
				3130	

\* The data for complexes with "am" = *p*-substituted anilines do not include the absorption bands (*B*) of associated molecules near  $3300 \text{ cm}^{-1}$  which are broad and difficult to locate in most cases.

† Not investigated.

‡ Frequencies in the solid state: *trans*- $[\text{PPrn}_3, \text{NH}_3, \text{PtCl}_2]$ , 3362, 3305, 3243, 3207, 3171; *trans*- $[\text{PPrn}_3, \text{NH}_3, \text{PtI}_2]$ , 3319, 3226, 3188, 3155; *trans*- $[\text{PPrn}_3, \text{Me}\cdot\text{NH}_2, \text{PtCl}_2]$ , 3296, 3226, 3184; *trans*- $[\text{PPrn}_3, 2 : 6\text{-Me}_2\text{C}_6\text{H}_3\cdot\text{NH}_2, \text{PtCl}_2]$ , 3276, 3234, 3139; *trans*- $[\text{PPrn}_3, p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2, \text{PtCl}_2]$ , 3278, 3213, 3174, 3129; *trans*- $[\text{Prn}_2\text{S}, p\text{-Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2, \text{PtCl}_2]$ , 3274, 3246, 3217, 3200, 3174, 3134.

TABLE 4. Association constants,  $K$ , for the dimerisation of  $\text{trans-[L, } p\text{-toluidine, PtX}_2\text{]}$  in  $\text{CCl}_4$  at  $25^\circ \pm 1^\circ$ .

L = $\text{C}_2\text{H}_4$ , X = Cl										
$c^*$	5.586	5.013	3.816	2.644	1.970	0.584	0.574	0		
$\epsilon$	66.2	69.0	74.9	83.1	88.2	106.5	104.7	117		
$\alpha$	0.566	0.590	0.640	0.710	0.754	0.911	0.895	—		
$K$	122	118	115	109	110	116	114	—	Mean	115
L = $\text{Bu}_2\text{S}$ , X = Cl										
$c$	5.46	3.28	2.73	2.18	1.64	1.37	1.09	0.55	0	
$\epsilon$	72.9	82.3	85.8	89.5	94.5	95.5	97.0	105.4	113	
$\alpha$	0.645	0.729	0.760	0.792	0.836	0.845	0.858	0.933	—	
$K$	78.2	78.0	78.1	76.0	71.6	79.4	88.3	70.0	—	Mean 77
L = $\text{Pr}_2\text{S}$ , X = Cl										
$c$	6.91	4.21	3.46	2.76	2.11	0				
$\epsilon$	68.6	79.3	81.7	86.0	90.2	113				
$\alpha$	0.607	0.685	0.724	0.761	0.799	—				
$K$	77.2	79.7	76.1	74.8	76.7	—			Mean	77
L = $\text{SbPr}_3$ , X = Cl										
$c$	5.76	4.89	4.29	3.24	2.84	2.60	2.19	0.775	0.516	0
$\epsilon$	79.2	81.0	82.4	86.8	87.2	88.9	91.1	97.9	99.6	103.7
$\alpha$	0.764	0.781	0.794	0.837	0.841	0.857	0.879	0.944	0.961	—
$K$	35.7	36.7	38.0	36.1	39.7	37.6	35.8	40.5	41.3	—
										Mean 38
L = $\text{AsPr}_3$ , X = Cl										
$c$	6.23	5.37	4.51	3.61	2.71	0.54	0			
$\epsilon$	83.6	86.7	88.1	90.3	93.2	101.3	103.8			
$\alpha$	0.806	0.835	0.849	0.870	0.898	0.976	—			
$K$	24.1	22.0	23.2	23.8	23.3	23.3	—			Mean 23
L = $\text{PPr}_3$ , X = Cl										
$c$	6.68	6.27	4.60	3.77	3.34	2.85	2.64	2.00	0	
$\epsilon$	85.1	86.3	91.2	91.2	93.1	93.6	95.1	95.9	103	
$\alpha$	0.826	0.838	0.885	0.885	0.904	0.908	0.923	0.931	—	
$K$	19.0	18.4	15.9	19.4	17.7	19.5	17.1	19.8	—	Mean 18
L = $\text{PEt}_3$ , X = Cl										
$c$	4.48	3.61	2.73	2.69	2.02	0.574	0			
$\epsilon$	90.3	93.3	96.0	96.6	98.9	102.7	104.7			
$\alpha$	0.862	0.891	0.917	0.922	0.945	0.981	—			
$K$	20.6	19.0	18.1	17.0	15.4	17.5	—			Mean 18
L = $\text{Bu}_2\text{S}$ , X = Br										
$c$	5.51	3.31	2.75	2.20	1.66	1.38	1.10	0.55	0	
$\epsilon$	97.6	101.0	103.6	104.7	105.5	108.3	108.4	112.8	115	
$\alpha$	0.849	0.878	0.901	0.910	0.917	0.942	0.943	0.981	—	
$K$	19	24	22	20	30	24	29	18	—	Mean 23
L = $\text{PPr}_3$ ; X = Br										
$c$	5.95	3.58	2.96	2.15	1.50	0				
$\epsilon$	93.9	96.6	97.8	98.2	99.2	101.5				
$\alpha$	0.9255	0.9520	0.9637	0.9677	0.9775	—				
$K$	7.31	7.40	6.61	7.99	7.85	—				Mean 7
L = $\text{PPr}_3$ , X = I										
$c$	5.87	3.52	2.94	2.35	1.76	1.47	1.17			
$\epsilon$	78.7	78.6	77.9	76.8	76.0	77.6	75.9			
										(no association)
Cf. also :										
$\text{trans-[PPr}_3, p\text{-toluidinePdCl}_2\text{]}$										
$c$	5.80	4.54	3.78	2.45	0.647	0				
$\epsilon$	78.45	78.97	79.74	79.69	80.20	80.5				
$\alpha$	0.9545	0.9810	0.9907	0.9900	0.9963	—				
$K$	2.32	2.18	1.26	2.08	2.29	—				Mean 2

\* All  $c$  in  $10^{-3}$  mole/l.

Intermolecular association of $\text{trans-[C}_2\text{H}_4, p\text{-toluidinePtCl}_2\text{]}$ and $\text{trans-[pepy}_2\text{PtCl}_2\text{]}$ .					
$C_A = 0.003225$ mole/l.	$K = 115$	$\epsilon_0 = 117$			
$C_B$ (mole/l. $\times 10^3$ ) .....	1.950	2.748	5.035	8.190	
$\epsilon$ .....	73.82	73.12	68.75	62.21	
$K'$ .....	68	55	59	66	Mean 62

hydrogen-bonded NH bond. In fact, the resemblance between the spectra of amides and of the primary amine complexes is probably only superficial; we think it more probable that the existence of this band (*B*) in the spectra of our complexes depends on the existence of more than one configuration of the complexes in solution. The different configurations arise from intramolecular rotation of the amine about the N-Pt axis. We assume that the configuration shown in Fig. 9 is that which permits the formation of the most stable hydrogen bonds. Replacement of the flat aromatic ring by a more bulky alkyl group would reduce the stability of this configuration relative to that obtained by rotation of the amine about the Pt-N bond through an angle of 90°. Hence, solutions of primary aliphatic amine complexes contain a higher proportion of molecules in the configuration which forms weaker hydrogen bonds than do solutions of corresponding primary aromatic amine complexes. Then if the symmetric  $\nu(\text{NH}_2)$  band of the weakly hydrogen-bonded dimer overlaps to some extent with the asymmetric  $\nu(\text{NH}_2)$  band of the strongly bonded dimer, so that the observed very broad band *D* (Figs. 4 and 5) is a composite band, the observed difference between the intensities of the bands due to associated molecules (*B*, *D*, and *E*) of the alkyl- and aryl-amine complexes can be explained. This interpretation of the absorption bands due to associated molecules implies that the effect of the alkyl group relative to the aryl group will be to increase the intensities of the two higher-frequency bands at the expense of the lower-frequency one. Comparison of Figs. 4 and 5 shows this effect clearly, both for self-association and for association with dioxan.

Our experience in the above work indicates that great caution is necessary when interpreting the spectra of ammine and primary amine complexes in the solid state, or in solution in electron-donor solvents. If it is impossible to make measurements with the compounds in dilute solution in inert solvents, the best alternative is to study the spectra of secondary alkylamine complexes in the solid state. Even under these conditions, however, lattice forces may produce spectral changes which are of similar magnitude to those due to the intramolecular electronic or steric effects about which information is required. We have but few data relating to octahedral complexes, but it seems probable that similar considerations will apply to them as to the planar complexes of platinum.

#### EXPERIMENTAL

The spectra of the carbon tetrachloride solutions of the complexes were measured as previously described<sup>2</sup> by using a Grubb-Parsons S3A spectrometer fitted with a lithium fluoride prism. The preparation of the complexes has also been described.<sup>2,4</sup> The spectra of solids were obtained from suspensions of the powdered specimens in mineral oil. A mixture of 5 vol. of dry carbon tetrachloride and 1 vol. of "AnalaR" dioxan was used as the solvent to obtain the spectra of the complexes in the presence of an electron donor, and solutions in this solvent mixture were examined in a cell of path length 0.031 cm. The accuracy of calibration was  $\pm 1 \text{ cm.}^{-1}$  for bands due to monomeric complexes in carbon tetrachloride solution and  $\pm 4 \text{ cm.}^{-1}$  for the broader bands due to associated molecules.

*Association constants.* These were estimated by measuring the deviations from Beer's law of the antisymmetric NH stretching bands of the monomeric complexes and assuming that at low concentrations ( $< 0.007M$ ) dimers are the principal associated species. In order to minimize the effect, which is small in the concentration range used, of interference by the absorption due to associated molecules near  $3300 \text{ cm.}^{-1}$ , the 100% transmission line was drawn as the common tangent to the energy curve at the transmission maxima immediately on each side of the absorption band. The extinction coefficients for a number of concentrations of a given complex were calculated from  $\epsilon = \log_{10} (T_0/T)/cl$ , where  $l$  is the cell length in cm.,  $c$  the molar concentration, and  $T_0$  and  $T$  are the incident and the transmitted light intensity respectively. Extrapolation of  $\epsilon$  to zero concentration gave the extinction coefficient of the monomeric complex ( $\epsilon_0$ ). Association constants were obtained from the expression  $K = (1 - \alpha)/2\alpha^2c$ , where  $\alpha = \epsilon/\epsilon_0$  = fraction of the total number of molecules present as the monomer.

The extent of association through hydrogen bonds between two different species of complex molecules was estimated by adding various amounts of *trans*-[(4-*n*-pentylpyridine)<sub>2</sub>PtCl<sub>2</sub>] (*B*) to a carbon tetrachloride solution of *trans*-[C<sub>2</sub>H<sub>4</sub>, *p*-Me·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>PtCl<sub>2</sub>] (*A*). By measuring the extinction coefficients of the residual monomer band ( $\epsilon$ ),  $[A]$  was obtained from  $[A] = C_A\epsilon/\epsilon_0$ , where  $C_A$  is the known initial concentration of *A*. The association reaction is  $A + B \rightleftharpoons AB$

and its equilibrium constant  $K'$  is given by  $K' = [\text{AB}][\text{A}]^{-1}[\text{B}]^{-1}$ . The constant  $K$  for self-association of A is given by  $K = [\text{A}_2][\text{A}]^{-2}$ .

Writing  $C_{\text{B}}$  as the known initial concentration of B, we have

$$C_{\text{A}} = 2K[\text{A}]^2 + [\text{A}] + [\text{AB}]$$

$$C_{\text{B}} = [\text{B}] + [\text{AB}]$$

and hence  $[\text{B}] = 2K[\text{A}]^2 + [\text{A}] - C_{\text{A}} + C_{\text{B}}$

$$[\text{AB}] = C_{\text{A}} - 2K[\text{A}]^2 - [\text{A}]$$

giving  $K' = (C_{\text{A}} - 2K[\text{A}]^2 - [\text{A}]) \{ [\text{A}](2K[\text{A}]^2 + [\text{A}] - C_{\text{A}} + C_{\text{B}}) \}^{-1}$

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