649. *The Transmission of Electronic Effects through a Palladium Atom.*

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

The N–H stretching frequencies and band intensities of a series of palladous complexes *trans*-[L,amPtCl$_2$] [L = PR$_3$, P(OR)$_3$, AsR$_3$, R$_2$S, R$_2$Se, R$_2$Te, piperidine, and *n*-octylamine; " am " = piperidine, *n*-octylamine, and *p*-toluidine] have been measured. The effects transmitted from the ligand L across the palladium atom to the N–H bond are mainly electrostatic. There appears to be direct interaction between the *N*-hydrogen atom and filled *d*-orbitals of the metal. The frequency–intensity relationship and the half-band widths of the piperidine complexes are discussed.

The N–H stretching frequencies of a series of complexes of the general type *trans*-[L,amPtCl$_2$] (" am " = primary or secondary amine) show that differences between the electronic effects transmitted through the platinum atom from ligands L such as MR$_3$ (M = N, P, As, Sb) and R$_2$Q (Q = S, Se, Te) to the amine are mainly inductive.[1] Nevertheless, anomalies, which are just significant in the phosphine (L = PR$_3$) and marked in the ethylene complexes (L = C$_2$H$_4$), indicate that there is a second mode of transmission. This second mode is probably mesomeric, owing to the interaction of the filled orbitals of d_{xy}-type (or *dp*-hybrid) of the metal atom with vacant low-energy orbitals of suitable symmetry in the ligands L, and with the *N*-hydrogen atoms of the amine.

We now describe a similar study of an analogous series of palladium complexes. Since, in general, palladium(II) is not so easily oxidised to palladium(IV) as platinum(II) to platinum(IV), it seems that the electrons in the *d*-orbitals of palladium lie at a rather lower energy level and would not be so readily available for double bonding and so transmitting mesomeric effects. Thus anomalies due to mesomeric effects should be smaller in the palladium series of complexes. Unfortunately, the ligand ethylene (L = C$_2$H$_4$) which gave the largest anomalies in the platinum series would not form a palladium compound, *trans*-[C$_2$H$_4$,amPdCl$_2$], suitable for similar investigations. Nevertheless, the slight anomalies of the triethylphosphine complexes are smaller in the palladium series.

Table 1. N–H *Stretching frequencies* ν (*cm.*$^{-1}$), *band intensities* B (*cm.*$^{-2}$ *molecules sec.*$^{-1}$), *and apparent half-band widths* $\Delta\nu_{\frac{1}{2}}{}^{a}$ (*cm.*$^{-1}$), *of the compounds* trans-[L,pipPdCl$_2$] *in carbon tetrachloride solution.*

L	ν	10^7B	$\Delta\nu_{\frac{1}{2}}{}^{a}$
Piperidine ...	3237	3·14 *	19·8
Et$_2$S	3238	—	—
Et$_2$Se	3240	—	—
Et$_2$Te	3249	—	—
AsEt$_3$	3252	1·12	17·5
PEt$_3$	3254	1·13	17·0
PPr$^n_3$	3254	1·14	17·5
PPh$_3$	3247	1·49	20·1
P(OMe)$_3$ ...	3250	1·27	17·2
P(OPh)$_3$ ...	3247	1·30	17·3

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

Table 2. N–H *Stretching frequencies* ν (cm.$^{-1}$) *of the monomeric complexes* trans-[L,amPdCl$_2$] *in carbon tetrachloride solution.*

L	am = *n*-Octylamine		am = *p*-Toluidine	
n-Octylamine...	3335	3271	—	—
Pr$^n_2$S	3339	3274	3348	3281
Pr$^n_2$Se	3340	3276	3350	3281
Pr$^n_2$Te	3345	3280	3359	3286
AsPr$^n_3$	3348	3283	3362	3289
PPr$^n_3$	3351	3285	3365	3291
P(OMe)$_3$	3348	3280	3362	3286
PPh$_3$	3348	3279	3360	3285
P(OPh)$_3$	3345	3280	3358	3286

The compounds examined, together with the relevant spectroscopic data, are listed in Tables 1 and 2. It was not possible to measure the band intensities or half-band widths

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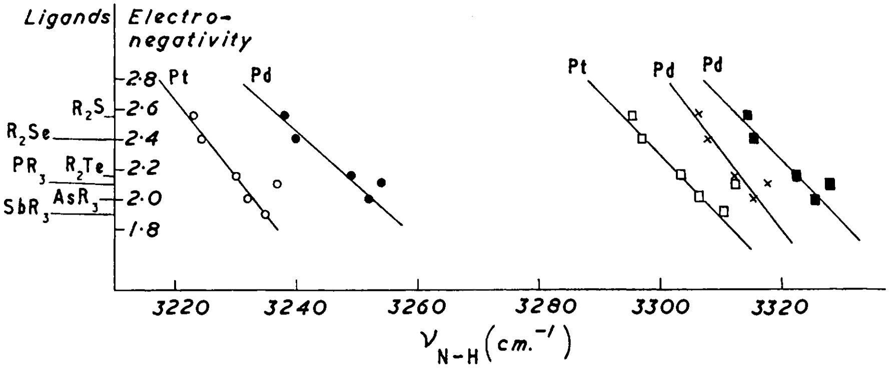
[1] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

of the piperidine complexes with L = Et_2S, Et_2Se, or Et_2Te, because the complexes were too unstable to be isolated. The *n*-octylamine series of complexes analogous to the *p*-toluidine complexes was examined to provide a complete series of secondary amine complexes, including a diamino-complex soluble in carbon tetrachloride. In the platinous complexes this requirement was met by the compound *trans*-[pepy,tolPtCl_2] (pepy = *n*-pentylpyridine; tol = *p*-toluidine). We could not prepare the palladous analogue or other mixed amine complexes in the palladous series, and resorted to *n*-octylamine complexes because the alternative, *trans*-[tol_2PdCl_2], is insoluble in carbon tetrachloride. Amino-palladous complexes containing trialkylstibines or ethylene were too unstable to be obtained, even in solution.

Useful information about electronic interactions in the complexes is obtained first from a consideration of frequencies alone and then from the relation between the frequencies and square-roots of the intensities of the N–H stretching bands of the piperidine complexes: the square-roots of the intensities were plotted as being the more fundamental property since they are proportional to the rate of change of the dipole moment of the bond during the vibration. Over the short range of intensities and frequencies available the plot of frequency against intensity is also linear. Our conclusions are as follows:

Fig. 1. *Relation between the electronegativity of the ligand atom in* L *and the* N–H *stretching frequencies* ν_{N-H} *of the complexes* trans-[L,amMCl_2] *in carbon tetrachloride at* 20° (M = Pt or Pd).



Round symbols: Piperidine complexes.
Square symbols: *p*-Toluidine complexes. The mean of N–H stretching frequencies is plotted.
Crosses: *n*-Octylamine complexes.
Electronegativities are Pritchard and Skinner's " best values " (*Chem. Rev.*, 1955, **55**, 767).

(1) The influence of the ligands L on the N–H stretching frequencies (ν_{N-H}) is largely electrostatic. The plot of the frequencies against the electronegativities of the donor atoms in the closely similar alkyls gives a good straight line (Fig. 1), but the phosphines are anomalous, as in the platinous series.* However, as was expected, the phosphine points lie nearer to the lines in the case of palladium than of platinum, supporting the view that the anomalies are due to a mesomeric interaction. Nevertheless, the correspondence between the palladium and platinum plots is very close.

(2) The frequencies ν_{N-H} in the palladous series of complexes are generally 15—20

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* A. L. Allred and F. Basolo have suggested personally that the anomalous position of the phosphines may be due to an error in the value assigned to the electronegativity of phosphorus. This had occurred to us and been rejected because no single value of the electronegativity of phosphorus would remove the anomaly from both plots. To bring the phosphine point to the palladium line would require phosphorus to have an electronegativity of 1·95, between that of arsenic (2·0) and antimony (1·9), in accordance with the suggestion of Allred and Rochow (*J. Inorg. Nuclear Chem.*, 1958, **5**, 264; 269). This is a possibility. If this value for the electronegativity of phosphorus were adopted, some anomaly would still remain in the case of platinum, and this we consider to be due to double bonding to phosphorus. To bring the phosphine point to the platinum line, phosphorus would have to be assigned an electronegativity of 1·8, even lower than that of antimony.

cm.$^{-1}$ higher than in their platinous analogues. This is consistent with the commonly-accepted view that palladium(II) is a poorer acceptor of electrons from its ligands than is platinum(II), so causing the nitrogen atoms to be more negatively charged than in the platinum analogues and ν_{N-H} to be higher.[1]

These differences in frequency cannot be due to the difference between atomic masses of the two metals. We can consider the hypothetical non-linear triatomic molecules Pt-N-H and Pd-N-H to obtain an approximate measure of the effect of changing the mass of the metal atom upon the N-H stretching frequencies. If a valence-force field [2] is assumed there is no mass effect of the metal atom upon the N-H frequency. Even if we go to the other extreme and assume a force-field which would allow the mass of the metal atom to play a large part in determining the N-H stretching frequency (*i.e.*, by postulating a strong Pt-H or Pd-H bond and a weak N-H bond), the change in mass of the metal from 195 to 107 atomic mass units cannot raise the stretching frequency of the bond to the hydrogen atom by more than about 5—6 cm.$^{-1}$. This being an extreme case it is safe to assume that the principal causes of the lower frequencies of the N-H stretching bands of an amine in its platinous as compared with its analogous palladous complexes are electronic in origin.

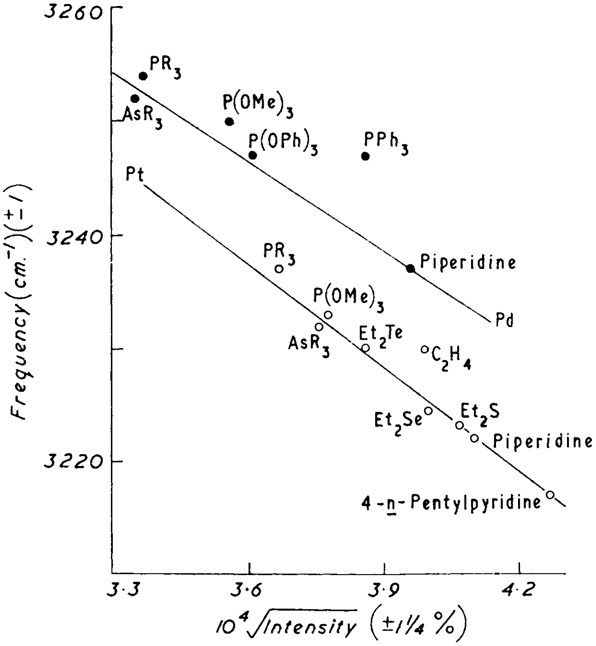

FIG. 2. N-H *Stretching frequencies and band intensities of complexes* trans-[L,pipPtCl$_2$] *and* trans-[L,pipPdCl$_2$].

(3) In the piperidine complexes *trans*-[L,pipPtCl$_2$] we found a linear relation between the frequencies and square roots of the intensities of the N-H bands, except for the phosphine and ethylene complexes.[1] Unfortunately, data relating to the palladous analogues are not nearly so complete. However, if we plot the relation and draw a line through the points relating to palladous complexes in a position corresponding to the best line through the platinous points we probably have comparable graphs for both series of complexes (Fig. 2).

It is noteworthy that these two graphs do not coincide so that one becomes an extension of the other, but instead the palladium graph is displaced to the side of higher intensity relative to the platinum graph. To explain why the point relating to *trans*-[C$_2$H$_4$,pipPtCl$_2$] lies significantly to the side of the higher intensity, we suggested that in all the platinous

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[2] Lechner, *Monatsh.*, 1932, **61**, 385.

piperidine complexes the proton or N–H bond interacts with the electrons in the d_{xy}-type of orbitals on the platinum atom.[1] This was necessary because the frequency and intensity of N–H vibration vary independently, and we need two routes from the ligand L across the platinum atom to the hydrogen atom to allow this. The first and obvious route is inductive through the nitrogen atom. The second can only be mesomeric, directly through a d_{xy}-type of orbital of the metal interacting with suitable orbitals in the ligand L and the N–H bond. This interaction might be a type of hyperconjugation if the electron drift is from the N–H bond towards the platinum atom, which has a vacant p_z orbital to receive electrons, or an intramolecular hydrogen bond if the drift is from the *d*-orbitals of the metal to the proton. We consider the latter more likely in the case of platinum since its *d*-orbitals are all filled and it tends to form dative π-bonds better than most metals in their normal valency states. This intramolecular hydrogen bond can also be looked upon as orbital-following of the N–H stretching vibration, or screening of the proton by electrons in a non-bonding *d*-orbital of the metal.

All chemical evidence points to the electrons in the *d*-orbitals of palladium(II) being less available for double bonding than those in platinum(II), and so weaker interaction between the proton and electrons should occur in palladous complexes. The displacement of the palladium line to the high-intensity side of the platinum line is consistent with this view, since the interaction would tend to neutralise dipole changes in the N–H bond and so lower the intensity of the N–H stretching band. The scatter of the points relating to palladous complexes containing phosphorus as ligand atoms (Fig. 2) suggests that the interaction is significant even in palladous complexes.

The very close correspondence between the platinum and palladium plots in Fig. 1 and the very slight effects of the difference between the atomic weights of the metal atoms on the N–H vibration being considered it is perhaps surprising that the graphs in Fig. 2 are not more closely similar. Generally the points relating to the palladous complexes are more scattered. They cover a wider range of frequency corresponding to the differences in slope of the graphs in Fig. 1 (piperidine complexes). Also the points relating to phosphorus complexes are all displaced to lower frequencies and to higher intensities than would be expected from the corresponding points in the platinum graph. In the palladous complexes the N–H vibration is more sensitive to the electronic effects of the ligands, L, than in their platinous analogues. The greater number of electrons in the platinum atom appears to neutralise to a greater extent the electronic effects during transmission through it, and it may also be that the N–H vibration in the palladous complexes takes place in a region of more rapidly changing *d*-electron density so that the intensity of infrared absorption is more sensitive to changes in the mesomeric effect of L. Whatever the cause of the slight differences between the two series of complexes the exceptional position of triphenylphosphine should be noted.

The apparent half-band widths of the N–H stretching bands in the spectra of the piperidine complexes *trans*-[L,pipPdCl$_2$] have been recorded. They fall mainly in the range 16—18 cm.$^{-1}$ in both the palladous and platinous [1] series, but there are two notable exceptions. The narrowest band occurs in *trans*-[C$_2$H$_4$,pipPtCl$_2$] (13·8 cm.$^{-1}$), where we expect the direct Pt–H interaction to be least amongst the platinous complexes, and the widest occurs in *trans*-[pip$_2$PtCl$_2$] (22·6 cm.$^{-1}$).

There are probably many factors which affect band width in these molecules and they are not fully understood but it seems possible that the large width of the band in *trans*-[pip$_2$PtCl$_2$] is at least partly due to coupling of the two N–H bonds. This coupling is unlikely to be mechanical because of the large mass of the platinum atom and also because it appears to be less in the corresponding palladium complex. However, the difference in band width between the dipiperidine complexes of PtCl$_2$ and PdCl$_2$ is consistent with the orbital-following hypothesis of the interaction between the N–H bonds and the non-bonding *d*-orbitals of the metal atoms. Thus in these complexes the two N–H bonds can couple electronically through a *d*-orbital of the metal and such coupling should be weaker in palladium than in platinum complexes. This explanation of variations in the band widths must, however, be treated with some reserve as the complex *trans*-[PPh_3,piperidine$PdCl_2$] has an exceptionally large half-band width of the same magnitude as that of *trans*-[pip_2PdCl_2] and this explanation could not apply here.

EXPERIMENTAL

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

The compounds *trans*-[L,am$PdCl_2$] were obtained by the reaction of the amine, am, with the bridged compound, $L_2Pd_2Cl_4$.[3] The mixed complexes containing R_2S, R_2Se, and R_2Te could not be isolated, but their spectra were obtained by dissolving the appropriate solid bridged compound together with its equivalent of amine in carbon tetrachloride and examining the spectrum of the solution. All the measurements where am is *n*-$C_8H_{17}\cdot NH_2$ were carried out by this method, and the pure complexes were not isolated.

trans-*Bis*-n-*octylaminedichloropalladium*.—Ammonium dichloropalladite (1 g.) and *n*-octylamine (2 c.c.) were warmed until a white solid formed. The mixture was cooled, and concentrated hydrochloric acid added. The yellow-orange solid formed was filtered off, dried, and recrystallised twice from ethanol and once from ether, m. p. 113—114° (Found: C, 44·0; H, 8·6; N, 6·6. $C_{16}H_{38}N_2Cl_2Pd$ requires C, 44·1; H, 8·8; N, 6·4%).

The spectra were measured at 25° ± 1° exactly as described in ref. 1.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

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[3] Chatt and Venanzi, *J.*, 1957, 2445.