865. *Infrared Spectra of Metal Ammines and Related Compounds. Part II.** *The* trans-*Effect in Platinous Complexes.*

By D. B. Powell.

Infrared spectra of a number of platinous ammine complexes in the potassium bromide region show the effect of the *trans*-directive ligands Cl, Et_2S, and C_2H_4 on the frequencies of the νPt–N vibration. The value of this frequency is directly related to the strength of bonding of the NH_3 group, and the results indicate that whereas *trans*-Cl has little effect on the strength of the Pt–N bond, diethyl sulphide and ethylene cause an appreciable bond weakening. The possible significance of this factor in consideration of the *trans*-effect is discussed.

On the basis of substitution reactions in metal complexes it is possible to arrange ligands in a series of increasing *trans*-effect, though in some cases the exact order may be doubtful. Russian authors quoted by Chatt, Duncanson, and Venanzi [1] give the following order: $H_2O < OH < NH_3 < R{\cdot}NH_2 < \text{pyridine} < Cl < Br < CNS \sim I \sim NO_2 \sim SO_3H \sim PR_3 \sim R_2S \sim SC(NH_2)_2 < NO \sim CO \sim C_2H_4 \sim CN$.

Examples of the *trans*-effect have been reviewed by Quagliano and Schubert,[2] and more recently Chatt *et al.*[1] have discussed the cause of the effect. They consider that bond weakening of the *trans*-group, favouring dissociation of the complex, which had generally been assumed to be responsible, was not an important factor. It is suggested that the more strongly *trans*-directive ligands are able to form a π bond with the metal in addition to the normal σ bond; this will withdraw electrons from the metal orbitals and favour substitution in the *trans*-position through an S_N2 mechanism.

This view of the mechanism of the substitution in platinum complexes is supported by studies of the rate of exchange of Cl, Br, I, or CN in platinum complexes of the type K_2PtX_4,

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* The paper by Powell and Sheppard, *J.*, 1956, 3108 is regarded as Part I.

[1] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.

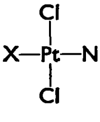
[2] Quagliano and Schubert, *Chem. Revs.*, 1952, **50**, 201.

where it is found that the more rapid exchange takes place with the more stable complex; this would not be expected if the substitution took place through a dissociative type of mechanism.[3]

Chatt, Duncanson, and Venanzi [4] give spectroscopic data on the infrared N–H stretching frequencies of several amines when *trans* to groups of varying *trans*-directive strength in platinum complexes. Their results show that the apparent weakening of the Pt–N bond, as indicated by changes in the spectra due to the N–H stretching vibrations, does not follow the same order as the *trans*-directive strengths of the ligands. It is therefore concluded that bond weakening is not the main factor in determining the directive properties of a ligand.

The study of N–H vibrations can only give indirect evidence as to the nature of the M–N bond, and no estimate can be made on this basis of the numerical values of bond-strength differences. The identification of the M–N skeletal frequencies for a number of different metal ammines [5] affords a means of obtaining a more direct comparison of bond strength when an NH_3 group is *trans* to various ligands. NH_3 is a useful group on which to examine the directive effect of other groups as it is itself unlikely to show an appreciable tendency to form a double bond with the metal ion.

As a first approach to the problem, the infrared spectra of *cis*- and *trans*-isomers of $Pt(NH_3)_2Cl_2$ have been compared, as in the *cis*-compound each NH_3 is *trans* to Cl, whereas in the *trans*-compound each NH_3 is *cis* to Cl. Examination of the results showed that there is difficulty in the interpretation of the νM–N frequencies observed, since two infrared-active frequencies would be expected for the *cis*-compound, but only one for the *trans* [in practice only one frequency was detected for *cis*-$Pt(NH_3)_2Cl_2$, though both frequencies were found for the corresponding palladium compound [6]]. A group of compounds where this difficulty does not arise, and in which the *trans*-effect can be examined directly, are those of the type (I), where only one infrared-active skeletal stretching frequency would be expected. From a chemical point of view *trans*-$Pt(NH_3)_2Cl_2$ is the first member of this series and, in addition, the compounds containing Et_2S and C_2H_4 in position X have now been examined.



$$\begin{array}{c} Cl \\ | \\ X—Pt—NH_3 \\ | \\ Cl \end{array}$$

(I)

Spectra have been obtained in the potassium bromide region for all these compounds, together with similar compounds not containing an NH_3 group to confirm the identification of the Pt–N frequency. Spectra in the rock-salt region have also been obtained in a number of cases, either to confirm the purity of particular isomers or where the low-frequency spectra show features of particular interest. The frequencies observed are contained in the Table.

The similarity of the νM–N frequencies observed for *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ as reported previously [6] indicates that Cl has no appreciable bond-weakening effect on the Pt–N bond, but it is observed that where diethyl sulphide and ethylene are ligands, they cause a significant weakening of the Pt–N bond *trans* to them, since the skeletal frequencies found (493 cm.$^{-1}$ for diethyl sulphide and 481 cm.$^{-1}$ for ethylene) are considerably smaller than those for *trans*-$Pt(NH_3)_2Cl_2$ (507 cm.$^{-1}$) or $[Pt(NH_3)_4]Cl_2$ (511 cm.$^{-1}$).[5] In view of the great mass of the platinum atom, it is very probable that the stretching frequency of the Pt–N bond does not interact with other vibrations of the rest of the molecule. We shall assume that the νPt–N vibration of the Pt–NH_3 system can be treated as that of an effectively diatomic molecule. In such a case the frequency ν is related to the force constant, k, by the relation $\nu = [k(1/M_1 + 1/M_2)]^{\frac{1}{2}}/2\pi$. It follows that, if ν_1 and ν_2 are the vibration frequencies of the same group in two different complexes, $k_1/k_2 = \nu_1^2/\nu_2^2$. Inserting the values quoted above for the νPt–N frequency in *trans*-$Pt(NH_3)_2Cl_2$ and *trans*-$Pt(NH_3)(C_2H_4)Cl_2$, we find that the force constant in the latter is 10% less than in the former.

The order of the bond weakening for the groups examined is the same as that reported by Chatt, Duncanson, and Venanzi,[4] based on the N–H stretching frequencies, but the extent of the weakening is greater than might have been expected on those results: for

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[3] Grinberg and Nikol'skaya, *Zhur. priklad. Khim.*, 1951, **24**, 893, reported in *Ann. Reports*, 1953, **50**, 49.

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

[5] Powell and Sheppard, *J.*, 1956, 3108.

[6] Powell, *Chem. and Ind.*, 1956, 314.

the effect of various *trans*-groups on the N–H stretching frequencies of the compounds *trans*-[Pt L, piperidine, Cl_2] in dilute solution, Chatt gives the following values: L = piperidine, 3222 cm.$^{-1}$; L = Et_2S, 3223 cm.$^{-1}$; L = C_2H_4, 3230 cm.$^{-1}$. For indications of bond strength based on band intensity, the effect appears rather greater, and for the same complexes the values of 10^7B are given as 1·68, 1·66, 1·59, respectively. Several factors may account for the lack of exact correlation between these methods of assessing M–N bond strengths, the most obvious being that the first ligand of the series in the present work is NH_3, whereas Chatt *et al.* used piperidine. In addition there are effects which may modify the actual vibration frequencies measured: hydrogen bonding of the ammines in the solid state may indirectly affect the νM–N value, but it is probable that changes in frequency due to this cause are very small. This effect was avoided in the νN–H values given by Chatt *et al.*[4] by the use of dilute carbon tetrachloride solutions. It has also been observed by Chatt and his co-workers that there is an interaction of the proton of the N–H bond with a *d* orbital of the platinum and that this will affect the absorption band due to the N–H vibration.

Main infrared absorption frequencies of platinum complexes * (cm.$^{-1}$).

trans- $Pt(NH_3)_2Cl_2$ †	*cis*- $Pt(NH_3)_2Cl_2$	*cis*- $Pt(NH_3)_2(NO_2)Cl$	*cis*- $Pt(NH_3)_2(NO_2)_2$
507 ‡ w.	508 ‡ w.	*ca.* 510 ‡ v.w.	—
828 m.	805 m.	533 s.	No ν Pt–N frequency detected due to very strong NO_2 absorption.
1288 s. (1305)	1300 s.	545 s.	
	1317 s.		
1538 w.	1536 w.		
1638 w.	1630 w.	Not examined in rock salt region.	
3170 m.	3270 m. (3200)		
3270 m.	—		

trans- $(Et_2S)_2PtCl_2$	*cis*- $(Et_2S)_2PtCl_2$	*trans*- $(Et_2S)(NH_3)PtCl_2$	$K[Pt(C_2H_4)Cl_3]H_2O$	*trans*- $(C_2H_4)(NH_3)PtCl_2$
—	—	493 ‡ w.	500 } v.s. broad	481 ‡ w.
677 m.	677 m.	679 m.	550 } (H_2O)	
726 w.	725 w.	727 w.	620 w.	617 w.
		789 s.	717 m.	735 m.
		835 w.	—	820 w.
		975 m.	1011 s.	1010 s. (1023)
Not examined in rock-salt region.		1037 w.	1023 s.	—
		1045 w.	1240 w.	1255 s.
		1245 w.	—	1267 s.
		1284 s.	1245 s.	1422 m.
		1317 w.	1612 s.	1610 m.
		1631 m.	3480 m.	3300 s.
		3170 w.	3540 m.	—
		3260 w.	—	—

* These spectra were determined on Nujol mulls of unknown concentration, and so band strengths are only comparative for a particular spectrum. Weaker bands have been omitted except below 600 cm.$^{-1}$

† These frequencies have been recorded previously.[5]

‡ Due to νPt–N vibration.

cis-$Pt(NH_3)_2Cl(NO_2)$ gave apparently a very weak absorption band at *ca.* 510-cm.$^{-1}$, but no detectable lower-frequency absorption. This seems to indicate that the nitro-group, like Cl, exerts no bond-weakening effect, though the band is too weak to allow a definite conclusion to be reached.

It would be useful to obtain some quantitative measure of the effect in terms of the stability constants of the ammines. It is appreciated that stability constants are not directly related to the bond strengths as indicated by vibration frequencies, but previous work [5] has shown that, though there is not an exact correlation, the vibration frequencies and the logarithms of the stability constants show a similar trend.

Unfortunately, there are insufficient data, on both stability constants and infrared-active skeletal vibrations of the less stable ammines, since these are expected to lie mainly below 420 cm.$^{-1}$. However, if Raman frequencies are used, some rough idea of the size of the effect can be obtained; thus, for $[Pt(NH_3)_4]^{2+}$ no stability figures are available, but it is generally regarded as being slightly more stable than $[Co(NH_3)_6]^{3+}$, for which log $k_{average}$ is 5·9. This is supported by the νM–N frequency of 511 cm.$^{-1}$ as compared with 501 cm.$^{-1}$ found for $[Co(NH_3)_6]Cl_3$. For the less stable ammines such as $[Cu(NH_3)_4]^{2+}$ (log $k_{average}$ 3·3), a Raman frequency of 419 cm.$^{-1}$ has been reported,[7] and as this ammine has the same symmetry as the platinous tetrammine with Raman frequencies of 538 and 526 cm.$^{-1}$,[8] it would not be unreasonable to expect an infrared-active frequency near 400 cm.$^{-1}$. This is supported by examination of the infrared spectrum of $[Cu(NH_3)_4]Cl_2$, which shows evidence of an absorption band just below 400 cm.$^{-1}$ but which could not be identified more definitely as it is below the range of the potassium bromide prism. On this basis 110 cm.$^{-1}$ would correspond to a change of about 3 in the value of log $k_{average}$, and the 26 cm.$^{-1}$ change in frequency when NH_3 is replaced by C_2H_4 would correspond to a change in log k of about 0·7.

From these considerations it is clear that, in these cases, notably that of ethylene, and to a lesser extent of diethyl sulphide, the bond weakening produced is sufficient to have a significant effect on the tendency of the *trans*-NH_3 group to dissociate. This does not imply that dissociation is the controlling factor in determining the extent of the *trans*-directive power of ligands, but that in such cases the possibility of its having a contributory effect should be considered.

EXPERIMENTAL

Most of the spectra in the potassium bromide region from 720 to 450 cm.$^{-1}$ were obtained by using a modified Hilger D 209 spectrometer as a single-beam instrument. For the spectra of $[Co(NH_3)_6]Cl_3$ and $[Cu(NH_3)_4]Cl_2$ a Hilger H 800 spectrometer was used to extend the region examined to 400 cm.$^{-1}$. The compounds were all examined as very concentrated Nujol mulls, since the ν M–N absorption frequencies are extremely weak. The spectra in the rock-salt region were obtained by using a Perkin-Elmer double beam spectrometer.

Preparation of Compounds.—*cis*-$Pt(NH_3)_2Cl_2$ was prepared by Jörgensen's method. Its spectrum showed no indication of the absorption peaks at 1288 and 828 cm.$^{-1}$ found for the *trans*-isomer.

cis-$Pt(NH_3)_2(NO_2)Cl$ was precipitated by addition of aqueous ammonia to $K[Pt(NO_2)Cl_3]$ [Found: N, 13·65. Calc. for $Pt(NH_3)_2(NO_2)Cl$: N, 13·5%]. *cis*-$Pt(NH_3)_2(NO_2)_2$ was prepared by addition of aqueous ammonia to a solution of $K_2Pt(NO_2)_4$. $K[Pt(C_2H_4)Cl_3],H_2O$ was obtained as described by Chatt *et al.*[9] and was converted into *trans*-$Pt(C_2H_4)(NH_3)Cl_2$ by addition of aqueous ammonia.

cis- and *trans*-$(Et_2S)_2PtCl_2$ were prepared as described by Angell, Drew, and Wardlaw.[10] The *cis*-isomer on treatment with Na_2PtCl_4 produced the bridged compound described by Chatt and Venanzi;[11] this was then converted into *trans*-$Pt(Et_2S)(NH_3)Cl_2$ by addition of the theoretical amount of ammonia in 95% alcohol. The identity of the product was confirmed by measurement of the infrared spectra in the rock-salt and the potassium bromide region. These spectra indicated the presence of co-ordinated NH_3 and Et_2S groups, and the frequency due to the Pt–N vibration is smaller than for the platinous chloroammines [Found: C, 12·7; H, 3·6. Calc. for $Pt(Et_2S)(NH_3)Cl_2$: C, 12·8; H, 3·5%].

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[7] Hibben, "The Raman Effect and its Chemical Applications," Reinhold, New York, 1939, p. 462.
[8] Mathieu, *J. Chim. phys.*, 1939, **36**, 308.
[9] Chatt and Duncanson, *J.*, 1953, 2939.
[10] Angell, Drew, and Wardlaw, *J.*, 1930, 349.
[11] Chatt and Venanzi, *J.*, 1955, 2787, 3858.