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(Physical Chemistry)
THE INFRARED ABSORPTION SPECTRA OF
METAL AMMINE COMPLEXES AND RELATED COMPOUNDS

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Doctor of Philosophy

by
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ABSTRACT.

The infrared absorption spectra of many metal ammine complexes of differing stabilities and steric configurations have been studied in the frequency range 4000 to 400 cm\(^{-1}\).

The use of deuteration techniques has provided a direct means of identifying the nitrogen-hydrogen vibrations, and by comparing the spectra of the ammines with those of simple molecules whose frequency assignments are definitely known, it has been possible to assign all the observed absorption bands to fundamental vibrations of the molecule. The metal-nitrogen vibration frequencies proved difficult to detect as the absorption bands produced were extremely weak, but these frequencies have now been identified for several of the more stable ammines, the assignment being confirmed by comparison with the Raman spectra of the same compounds.

The variations in the absorption frequencies found for the ammines have been compared with their stabilities and it has been shown that with a few exceptions the two properties show similar trends. The metal-nitrogen stretching frequencies are directly related to the strength of bonding of the ammonia group, and the effect of other substituents in the molecule on this bond has been examined. In this way it has been shown that some groups weaken the bonding of an ammonia molecule in the trans position, and this may
contribute to the increased ease of substitution of the group.

Other ligands where an almost complete frequency assignment of the absorption bands has been made include the nitro group and ethylene, the same method being used as for the metal ammines, i.e. comparison of the spectra of the complexes with those of simple molecules. Insufficient compounds of this type have been examined to observe any regularities in the spectra obtained. A preliminary study has also been made of ethylenediamine complexes.
ACKNOWLEDGEMENTS.

The author wishes to thank Dr. Norman Sheppard of the University of Cambridge for providing facilities for the infrared spectroscopy, when no other instrument was available, for his introduction to the spectroscopic techniques and for his guidance throughout this research.

Thanks are also due to colleagues at the Sir John Cass College for many helpful discussions and particularly to Mr. D.W. Wilson, Senior Lecturer in Inorganic Chemistry. The microanalyses have been carried out by Mr. P. Wood of this college and have proved of great value in establishing the identity and purity of the compounds used.

In conclusion it is a great pleasure to record sincere thanks to Dr. J.W. Smith, for his unfailing help and kindness throughout the long period involved in this work.
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Spectra of metal ammines

\[
\begin{align*}
\text{[Pt(NH}_3\text{)}_4]\text{Cl}_2 & \quad \text{80} \\
\text{[Pd(NH}_3\text{)}_2\text{Cl}_2] & \quad \text{81} \\
\text{[Co(NH}_3\text{)}_6]\text{Cl}_3 & \quad \text{82} \\
\text{[Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2 & \quad \text{83} \\
\text{[Co(NH}_3\text{)}_4\text{Cl}_2]\text{Cl} & \quad \text{84} \\
\text{[Rh(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2 & \quad \text{85} \\
\text{[Zn(NH}_3\text{)}_4]\text{Cl}_2 & \quad \text{86} \\
\text{Hg(NH}_3\text{)}_2\text{Cl}_2 & \quad \text{87} \\
\text{[Co(NH}_3\text{)}_6]\text{Cl}_2 & \quad \text{88} \\
\end{align*}
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Spectra of metal-nitro complexes

cis-[Pd(NH$_3$)$_2$(NO$_2$)$_2$],
trans-[Pd(NH$_3$)$_2$(NO$_2$)$_2$] and

$K_2[Pd(NO_2)_4]$

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cis-[Pt(NH$_3$)$_2$(NO$_2$)$_2$] and $K_2[Pt(NO_2)_4]$

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$Na_3[Co(NO_2)_6]$ and

trans-[Co(NH$_3$)$_4$(NO$_2$)$_2$]Cl

140

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Spectra of platinum-ethylene complexes

trans-[Pt(NH$_3$)(C$_2$H$_4$)Cl$_2$],

$K[Pt(C_2H_4)Cl_3] \cdot H_2O$ and

trans-[Pt(NMe$_3$)(C$_2$H$_4$)Cl$_2$]

154

Spectra of metal-ethylenediamine complexes

$[Co(en)_3]Cl_3$ and $[Ni(en)_3]Cl_2$

159

trans-[Co(en)$_2$Cl$_2$]Cl and $[Cu(en)$_2$][PtCl$_4$]$^2$

160
CHAPTER I.

GENERAL INTRODUCTION.

Valency bonding in Coordination Compounds.

The latter part of the nineteenth century brought great advances in preparative chemistry; among these were the isolation of many complex compounds of metal salts with other stable molecules such as ammonia, metal cyanides and oxalates, and even ethylene. Many of the preparative methods described are still of value today, but from a theoretical point of view these compounds provided difficulties to contemporary valency theories, since the valencies of the atoms concerned appeared to be quite unusual and could only be satisfied by very complex structures. The German chemist, Werner, and his co-workers not only discovered many new compounds of this type, but put forward a comprehensive theory to account for their existence. Werner, without making any assumptions as to the nature of valency forces, suggested that the molecules or groups concerned were grouped round the central metal ion in a "coordination sphere of attraction", the number of groups concerned being termed the coordination number. On this basis Werner was able to make great progress in the study of the arrangement, or stereochemistry, of the coordinated
groups, and by following the effect of substitution reactions was able to show the existence of cis/trans isomerism and optical activity in these compounds. The extent of Werner's achievement is seen in the fact that, without knowing anything of the electronic theory of valency, his structural determinations of octahedral cobaltic complexes are generally valid today, in spite of the fact that as late as 1920 some authors considered Werner's views to be incorrect. The coordination number of four gave more difficulty owing to the existence of two structural forms, planar and tetrahedral, and it was not until the period 1935 to 1939 that platinous complexes were definitely shown to have the planar square configuration.

The development of the electronic theory of valency offered an explanation of the structures suggested by Werner, the idea of coordinate or dative covalency providing the means by which coordinated groups, or ligands as they are now called, are bound to the central metal atom. Further progress followed from the idea of atomic and molecular orbitals of known steric orientation, which determine the stereochemistry of the coordination compounds.

Physical methods in the study of coordination compounds.

Use of physical methods provides valuable
information concerning the structure of complexes and the nature of the bonding and it is in this way that most recent progress in this subject has been made. There are four main aspects of the chemistry of coordination compounds where physical methods are of value: (1) in deciding the steric arrangement of the groups, (2) in determining the stability of the complex to dissociation, particularly in aqueous solution, (3) in measuring the strength of bonding of the groups, (4) in the examination of the nature and causes of reaction undergone by the compound, particularly the substitution of one group by another.

X-ray diffraction measurements often enable different steric arrangements, such as planar and tetrahedral, to be distinguished, but cannot generally locate individual atoms more precisely. Dipole moment measurements will often distinguish cis and trans forms and in some cases the polarity of the bonding can be determined, giving some idea of its character. This method is limited by the necessity for the substance to be soluble in a non-polar solvent. Magnetic measurements can establish the number of unpaired electrons in the molecule, and this fact will often indicate the combination of atomic orbitals of the metal which have been used in the bonding. In a few cases magnetic measurements show the reason for the weak bonding
of some ligands, where outer "d" orbitals are used. Study of the equilibria established in solution gives a measure of the stability of the compound to dissociation and the free energy change during its formation. For the simultaneous estimation of the different molecular species present in the solution, absorption spectra measurements in the visible and ultra violet regions are extremely valuable. This method is also useful in kinetic studies of the course of reactions in solution.

While all these physical methods are valuable in the study of coordination compounds, none give any direct measure of the strength and nature of the bonds concerned, and it is in this respect that spectroscopic measurements should be useful as they have been with many other simple and complex molecules.
CHAPTER II.

GENERAL INTRODUCTION.

The Application of Spectroscopic Methods to Structural Determination.

The study of the absorption spectra and Raman spectra of molecules has proved one of the most useful methods for the determination of their structures and for the interpretation of the types of bonding which are present. These methods have been particularly applied to organic molecules and to the simple inorganic molecules, but it was hoped that the examination of the absorption spectra of coordination compounds of metal ions would provide useful information.

Basically the methods for the measurement of absorption spectra in the various spectral regions are similar in that they involve the use of a source of radiation, a dispersing unit and a detector, the sample being introduced at some point into the light beam and the amount of light absorption measured by the detector.

The materials which are usually used as sources, as dispersing prisms and sample cells, and as detectors are summarised as follows:
<table>
<thead>
<tr>
<th>Spectral region</th>
<th>Prism and cell material</th>
<th>Source</th>
<th>Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 - 400 mµ</td>
<td>Quartz</td>
<td>Hydrogen lamp</td>
<td>(Photocell or Photomultiplier.</td>
</tr>
<tr>
<td>350 - 1000 mµ</td>
<td>Glass</td>
<td>Tungsten lamp</td>
<td></td>
</tr>
<tr>
<td>1 - 3 mµ</td>
<td>Glass</td>
<td>Tungsten lamp</td>
<td>Lead sulphide cell</td>
</tr>
<tr>
<td>2 - 6 mµ</td>
<td>LiF</td>
<td>(Nernst fila- Thermopile</td>
<td></td>
</tr>
<tr>
<td>5 - 15 mµ</td>
<td>NaCl</td>
<td>(ment or</td>
<td></td>
</tr>
<tr>
<td>10 - 25 mµ</td>
<td>KBr</td>
<td>(heated SiC</td>
<td></td>
</tr>
<tr>
<td>15 - 40 mµ</td>
<td>CsBr</td>
<td>(rod</td>
<td></td>
</tr>
</tbody>
</table>

Gratings can also be used as dispersing units in many spectral regions but have not yet been used to a large extent in the long wave length region as the available light energy emitted from the usual sources is low, and light losses are greater with gratings than with prisms. The choice of materials for use as prisms is governed by the two factors of transparency and dispersing power for light of the wave length concerned and these two factors are interrelated as a substance has the greatest dispersing power near to the region where it begins to absorb light.

The changes in internal energy of the absorbing molecules which produce the absorption spectra are related to various types of internal change in the molecule; thus, in the ultra violet and visible spectra it is electronic
energy changes which are primarily involved, in the infrared region from 3.5 μ to 40 μ, it is changes in the vibrational energy states of the molecule, and at still longer wavelengths rotational energy changes in the molecules which are concerned. With the exception of the rotational energy changes these effects do not occur singly and the electronic transitions have superimposed vibrational and rotational effects, and the vibrations are always associated with smaller rotational energy changes, giving "fine structure" to vibrational bands. Furthermore, these approximate limits for these properties tend to overlap and although there appears to be a gap between the upper limit of electronic transitions near 1 μ and the start of vibrational wave lengths at 3.5 μ, the region is filled with the overtones of the vibrational changes, which may even extend below 1 μ (e.g. water shows an overtone of the 3 μ stretching vibration at 950 mμ).

Consideration of these factors makes it possible to obtain an idea as to the possible application of spectral methods to the study of coordination compounds, in the two main divisions of ultra violet and visible spectra, and infrared spectra.
Ultra violet and visible spectra of coordination compounds.

The marked changes in colour of transition metal ions on the coordination of colourless ligands is one of the most striking features of coordination compounds, and the absorption spectra which give rise to these colours have been examined since the beginning of this century. The use of modern instrumental techniques has greatly improved the accuracy of these measurements and has extended the range of spectral examination from the visible region well into the ultra violet region, the limit with most modern photo-electric instruments being about 200 mµ. Most of these spectra have been examined in aqueous solution and as the absorption bands are usually strong, dilute solutions can be employed.

The spectra in this region arise from three main types of electronic transition: (1) absorption bands characteristic of the ligands as modified by the coordination bonding to the metal, (2) internal "d" electron transitions of the metal ion, due to perturbation of the energy levels by the electric field of the ligand, and (3) "charge transfer" transitions in which an electron is transferred from the metal ion to the ligand or vice versa. Absorption bands due to (1) will not be considered further as many of the ligands concerned have no absorption in the
region considered and direct interpretation of the effect of coordination on such absorption bands is usually difficult. Bands due to (2) or (3) are easily distinguished as the latter usually have extinction coefficients at least 100 times as large as the former and lie well into the ultraviolet region of the spectrum. However, most useful work on the nature of coordination compounds has been obtained from bands arising from (2). The absorption bands in the visible region which are responsible for the colour of these compounds clearly show wide changes with different ligands and when this effect is examined quantitatively results are obtained such as the following for cobaltic complexes, the wave length in mμ of the absorption band of longest wavelength being given below:

* \( \text{Co}_2(\text{SO}_4)_3 \) (in N₂H₂SO₄) \[\text{Co(NH}_3\]6\]Cl₃ \[\text{K}_3[\text{Co(NH}_6\]6\]  
615 \hspace{1cm} 490 \hspace{1cm} < 200 mμ

It is tempting to equate the wave length shifts in this absorption band with the stability of the complexes which in this case follow the same order, but if the effect of the replacement of the water molecule by chlorine in the compound \[\text{Co(NH}_3\]5\]H₂O\]Cl is examined, a shift of the absorption band to longer wave lengths is observed, although the chlorine atom is undoubtedly more strongly bound than

* These figures were obtained during some preliminary experiments in this work.
FIG. I.

ABSORPTION SPECTRA OF COBALTIC NITROAMMINES.
FIG. I
ABSORPTION SPECTRA OF COBALTI
NITROAMMINES

WAVELENGTH mμ

450
400
350

6NH₃ 5NH₃ 4NH₃ 3NH₃ 2NH₃ O NH₃
ONO₂ 1 NO₂ 2NO₂ 3NO₂ 4NO₂ 6NO₂

COMPOSITION

Cis
Trans
the water molecule. Tsuchida has found that the second absorption band (i.e. that at shorter wave lengths) gives a better measure of stability, but difficulties often arise in detecting this shorter wave length band in the presence of charge transfer bands. Basalı has used this relationship in the study of the stereochemistry of cobaltic complexes, since the mutual weakening of the bonding of trans groups should result in a longer wave length absorption band for the trans compound compared with its cis isomer. Willis and Mellor have been able to distinguish planar and tetrahedral nickel II complexes on the basis of a strong absorption band occurring near 400 m\(\mu\) for all complexes having the planar configuration as shown by magnetic measurements.

In some preliminary experiments to the work reported here an interesting relationship was observed with the wave lengths of the first absorption bands of a series of cobaltic nitroammines. The results are shown in Fig. 1, where the wave lengths of the absorption bands of longest wave length are shown plotted against composition. It is observed that a straight line relationship is observed for four of these complexes, but with cis-[Co(NO\(_2\))]\(_2\)(NH\(_3\))\(_4\)]\(^+\), [Co(NO\(_2\))]\(_3\)(NH\(_3\))\(_3\)] and [Co(NO\(_2\))]\(_4\)(NH\(_3\))\(_2\)]\(^-\) the absorption band is at longer wave lengths. The only structural feature
common to these compounds is the tendency for the nitro groups to be *cis* in a plane; with \([\text{Co(NO}_2\text{)}_4(\text{NH}_3)_2]^{-}\), where the deviation from a straight line is greatest, all four nitro groups are planar and *cis* to each other. Similar results were obtained with a series of cobaltic aquoammines, though the differences in wavelength observed were much smaller.

While many empirical relationships of this type can be obtained, it is clearly difficult to obtain from such results any real information as to the nature of bonding of the coordinated group. One particular difficulty in complexes where more than one ligand is concerned is that the absorption spectrum can only represent the overall perturbation effect of all the ligands, and the effects due to individual ligands are not separated. In view of these considerations and the publication of further work on these compounds it became clear that additional experimental evidence would be of little value without a mathematical treatment to relate the results to the nature of the bonding in these compounds. Some progress along these lines has now been made, notably by Orgel and his collaborators⁶, but it was at this time decided to concentrate the main emphasis of this work on the infrared spectra of these compounds. As these are concerned with
the vibration of the atoms themselves, they should give more direct results as to the nature of the bonding in these compounds.
The Infrared Spectra of Coordination Compounds.

The absorption of light in the infrared region is associated mainly with vibrational changes in the molecules; rotational changes in such large molecules would only show effects at very low frequencies and need not be considered here except in so far as they may modify the vibrational frequencies. Examination of the vibrational infrared spectra of these molecules can give a much more direct indication of the nature and strength of the bonding of the coordinated groups than can be obtained by other methods.

As a first approximation the metal ion can be regarded as a static centre during the vibration of the surrounding groups; this is certainly true of atoms not directly bound to the metal ion, providing the masses of the atoms of the coordinated groups concerned are not too great. Where the vibrations of groups directly bonded to the metal ion are considered, the mass of the metal ion must have an appreciable effect even where light groups or atoms are concerned. The only exception to this is the totally symmetric or "breathing" frequency, which is not active in the infrared spectrum, but which can be
identified in the Raman spectrum.

It is important to consider the regions of the spectrum where the fundamental vibrations of these molecules might be expected, and so, for example, with a coordinated ammonia group we can say, by analogy with ammonia itself, that the $\mathrm{N-H}$ stretching vibrations ($\nu \mathrm{N-H}$) will probably be near $3000 \text{ cm}^{-1}$, and the $\mathrm{N-H}$ bending frequencies ($\delta \mathrm{N-H}$) near $1000-1500 \text{ cm}^{-1}$. The metal-nitrogen stretching frequencies will have much lower values, for methyl iodide, $\mathrm{CH}_3\mathrm{I}$ the $\mathrm{C-I}$ stretching frequency is near $500 \text{ cm}^{-1}$ and we might expect the metal-nitrogen stretching frequency, in a compound of the type metal-$\mathrm{NH}_3$, to be in this region, say within the range $400-600 \text{ cm}^{-1}$. If the strength of the bond is lower than that of a normal covalent bond, the frequency will be still smaller. These figures imply that if the vibrations of atoms directly bound to the metal ion are to be examined there is a limit to the masses of the atoms that can be used, as infrared spectroscopy becomes experimentally much more difficult at low frequencies. The experimental difficulties are twofold; there is first the problem of finding suitable materials that will transmit the radiation at low frequencies and so can be used for making the dispersing prism and for cell windows. In the frequency
region from 4000 to 760 cm$^{-1}$ rock salt (crystalline sodium chloride) can be used and from 1000 cm$^{-1}$ to 400 cm$^{-1}$ potassium bromide prisms can be used, but below 400 cm$^{-1}$ the only suitable materials so far discovered have been caesium bromide and iodide; these can extend the frequency range to 200-250 cm$^{-1}$ but are extremely expensive and not readily available. At the time this work was carried out only rock salt and potassium bromide prisms were available and so the effective frequency range examined was from 4000 to 400 cm$^{-1}$. The second difficulty with work at low frequencies is the small energy available from the available infrared sources, usually a Nernst filament. These sources have a maximum energy in the rock salt region and while it is possible to move the energy maximum to lower frequencies by lowering the temperature of the source, the total energy emitted is also reduced and the net gain in energy in the low frequency region is not great. This method does, however, reduce the amount of scattered light reaching the thermopile of the instrument and so improve its performance. Scattered light in infrared instruments working at low frequencies reaches very considerable proportions, and in the caesium bromide region it may be as much as 30-50% of the total energy reaching the detector. Some experiments have been tried using an f-centred crystal
as a filter; these filters absorb the higher frequency radiation but do not greatly reduce the low frequency energy, thus it is possible to reduce greatly the proportion of scattered light. The actual value of the lower frequency reached reliably, depends to some extent on the instrument used, such factors as the light energy loss within the instrument and the sensitivity of the detector having appreciable effects. In practice, with a potassium bromide prism in the Hilger D 209 spectrometer, used in the earlier stages of this work, no reliable results could be obtained below 450 cm\(^{-1}\). With a modern Hilger H 800 spectrometer 400 cm\(^{-1}\) could just be reached, and with a new Perkin Elmer Model 22 instrument the range could be extended to 380 cm\(^{-1}\).

The difficulties of work at low frequencies places a restriction on the ligands that can be examined by means of the direct vibration of the metal-ligand bond, as the vibration frequencies will be much smaller with the heavier ligands. For this reason much of the work described here is concerned with the metal-ammonia complexes (ammines) as the ammonia group is one of the lightest common ligands and one which is often strongly bound to the metal ion. Other ligands have also been examined in some cases either incidentally or where they are likely to show features of
particular interest; these include the nitro group, NO₂, ethylene and ethylenediammine.

The first stage in the examination of the spectrum of a compound is to assign the frequencies to particular fundamental vibrations in the molecule. In most cases the systems examined here are too complex to apply calculation methods, but it is usually possible to obtain a reliable assignment of the frequencies by comparison with the spectra of simple molecules of similar symmetry whose assignment is known unequivocally; for example, the comparison of the spectrum of a metal-nitro complex with the spectrum of Cl—N=O, nitryl chloride; or the comparison of the metal-ethylene complexes M—CH₂ with S—CH₂, ethylene sulphide. When the fundamental vibrations have been related to absorption frequencies it is then possible to elucidate variations in the bond character with different metal ions and to examine the effect of different substituent groups on the bonding of the group in question.

Several previous workers have examined metal ammines in the "rock-salt" region, but have generally only considered a limited number of compounds, principally the cobaltic and chromic ammines. These workers often disagreed as to the assignment of some of the absorption frequencies to particular vibrations of the molecules.
The present work on ammines was undertaken so as to reach
definite conclusions as to the assignment of the
frequencies, to extend the range of compounds to cover as
many metal ions as possible, and to extend the spectro-
scopic examination to lower frequencies using a potassium
bromide prism. Most of the following results on nitro
complexes, ethylene complexes and the "trans effect"
arose out of an extension of the results obtained on
simple ammines.
EXPERIMENTAL Techniques used in the Determination of Infrared Spectra.

Spectra have been obtained using both rock salt and potassium bromide prisms, but the choice of instrument was limited by the consideration of availability, which did not always allow the most useful instrument to be used for a particular spectrum. Ideally all potassium bromide region spectra would have been taken using the Perkin-Elmer instrument, but in practice this was only available on a very few occasions with this prism.

Most of the earlier work was done using a Hilger D 209 double beam spectrometer. This instrument has a number of disadvantages, the most important being that it depends on a D.C. system of amplification using a double arrangement of galvanometers and thermopiles to amplify the primary signal. The instrument is very sensitive to vibration and has a considerable tendency for the zero to "drift" during the running of a spectrum. It is, however, quite convenient in use as a single beam instrument in the potassium bromide region of the spectrum, as the degree of amplification can easily be varied over a wide range, thus assisting in the magnification of weak absorption peaks.
FIG. 2.

PRESLIT OPTICAL SYSTEM OF HILGER D 209 SPECTROMETER.
FIG. 2
PRESLIT OPTICAL SYSTEM OF HILGER D209 SPECTROMETER

ORIGINAL

MODIFIED
FIG. 3.

WATER VAPOUR CALIBRATION IN ROCK SALT REGION.
FIG. 3
WATER VAPOUR CALIBRATION IN ROCK SALT REGION
FIG. 4.

POTASSIUM BROMIDE REGION

WATER VAPOUR CALIBRATION
FIG. 4

POTASSIUM BROMIDE REGION
WATER VAPOUR CALIBRATION

ZERO

CO₂

INSTRUMENT CALIBRATION

2.74  2.86  2.98  3.10  3.22  3.34  3.46  3.58  10
The original optical system of the instrument was modified by means of an additional concave mirror, so as to provide a focus in the sample beam; this is shown in Fig. 2 and it is clear that although this system allows much smaller samples to be used, the disparity in the optical paths of the sample and reference beams partly destroys the double beam cancellation of the water vapour and carbon dioxide from the atmosphere. This, of course, is not important in the potassium bromide region where the instrument is used as a single beam system in any case. The instrument was calibrated in both the rock salt and potassium bromide regions using the atmospheric water vapour and carbon dioxide bands. Typical calibration spectra are shown in Figs. 3 and 4, and from these calibration curves for the prisms are prepared. Temperature variations of only one or two degrees centigrade produced appreciable changes in the calibration curves and the calibration was checked at least once a day.

Many of the spectra in the rock salt region were also obtained using a Perkin Elmer 21 double beam spectrometer from 4000 to 700 cm\(^{-1}\), and in some cases the same instrument was used with a potassium bromide prism; this extended the lower frequency limit to 400 cm\(^{-1}\), and in a few cases absorption bands could be detected at as low a
frequency as 380 cm⁻¹, though these results are less reliable as the energy available is very small. Unfortunately, this instrument was only occasionally available with this prism. A number of the more recent spectra were taken on a Hilger H 800 double beam spectrometer in the rock salt and potassium bromide regions. The characteristics of the spectra taken on these modern instruments were very similar and no instrumental modifications were required. The optical arrangement of the Hilger H 800 spectrometer is shown in Fig. 5; this is typical of modern instruments where an A.C. amplification system is used. In this system the beam passing through the sample and the reference beam are allowed to fall alternately on the thermopile, using an oscillating mirror, and the alternating potential produced operates a shutter in the reference beam until the energies of the two beams are equal. The change in the shutter aperture, which is then proportional to the absorption of the sample is measured in the deflection of the recorder. The great advantage of this method of double beam operation is that the A.C. amplification leads to much greater electronic stability. These instruments did not require frequent calibration checks as a temperature compensating bimetal strip is attached to the prism table. Occasional checks were
carried out using water vapour or thin polystyrene films as standard substances.

**Accuracy of measurements.**

The accuracy of measurement of the frequencies recorded requires some clarification, as published figures are generally reported to the nearest wave number (cm\(^{-1}\)), irrespective of the region being considered. Using the normal calibration of the instrument, it is very doubtful if such accuracy can be obtained, and calibration experiments in the 1600 cm\(^{-1}\) region, using the atmospheric water vapour bands as standards, showed that an accuracy of about \(\pm 5\) cm\(^{-1}\) is the best that can be expected. In many spectral regions much more accurate results can be obtained by using the spectrometer as a single beam instrument and using the atmospheric water vapour and carbon dioxide bands as internal calibration standards. The frequency of the absorption band due to the substance is then determined by direct interpolation between the absorption bands of known frequency. In this way errors are avoided due to the construction of the calibration curve as well as errors due to temperature changes during the course of the experiment. This method was used where accurate values for absorption frequencies were required in the consideration
of the trans effect (Chap. XI), the frequencies concerned being in the potassium bromide region, near 500 cm\(^{-1}\). Using this method the absorption peaks can be located with an accuracy of at least one cm\(^{-1}\). Difficulty arises in the detection of weak, broad absorption bands by the single beam method, as these may be obscured by water vapour absorption. Wherever possible a double beam spectrum is first obtained to locate the absorption bands, the frequency of which is then accurately determined by single beam operation.

**Description of vibration frequencies.**

The terminology used to describe the vibrations generally follows the usage of Hersberg^9, and is summarised as shown below.

\[ \gamma \text{ stretching vibration concerned mainly with } \text{A—B bond} \]
\[ \delta \text{ deformation vibration concerned mainly with } \text{A—B bond} \]

- **Bending**
- **Wagging**
- **Twisting**
- **Rocking**

+ indicates vibration above plane of paper
- indicates vibration below plane of paper
Numbering of frequencies \( y_n \) is arranged so that lowest values of \( n \) correspond to vibrations of the highest symmetry. Frequencies of absorption bands shown in parentheses, e.g. 1545 (1555), are "shoulders" on the sides of the main absorption bands, or bands of subsidiary intensity. Frequencies bracketed together

\[
1545) \\
1555)
\]

represent two bands of similar intensity which are incompletely resolved.

The measured intensities of the absorption bands have no absolute significance as the spectra have been generally obtained on dispersions of unknown concentration. The relative intensities for a particular spectrum are indicated as follows:

- v.s. very strong
- s. strong
- m. medium
- w. weak
- v.w. very weak
- bd. broad.
CHAPTER V.

EXPERIMENTAL.

Preparation of Samples for Infrared Examination.

Most of the compounds examined were insoluble in organic solvents and so their spectra were usually determined in the solid state. A few of the compounds were also examined in concentrated aqueous solution, the cell being made by pressing a drop of the solution between two silver chloride plates and clamping them firmly. The spectra could only be examined in this way over a small portion of the spectrum, from about 800-1500 cm\(^{-1}\), owing to the strong absorption of the water itself. The spectra obtained did confirm the general similarity of the spectra in the solid state with those in aqueous solution, although only a few of the ammines were examined in solution, the most important being \([\text{Ag(NH}_3\text{)}_2\text{]}\text{SO}_4, [\text{Cu(NH}_3\text{)}_4\text{]}\text{SO}_4\cdot\text{H}_2\text{O}\) and \([\text{Co(NH}_3\text{)}_6\text{]}\text{Cl}_3\). The spectra taken in aqueous solution were also important in the deuteration experiments described later, as some of the ammines could not be isolated from the deuterium oxide used for the deuteration and had to be examined in that solution. It was therefore important to compare these spectra with those taken under similar conditions using water as solvent, so that comparison
FIG. 6.

SPECTRA OF METAL AMMINES IN VARIOUS MEDIA
SPECTRA OF METAL AMMINES IN VARIOUS MEDIA

- Nujol Mull
- Aqueous Solution
- KBr disc
could be made of the ammines and deuterammines in the same physical state.

The majority of the spectra were taken by the standard methods for solid samples, either as dispersions in "Nujol ("Nujol mulls") or as potassium bromide discs. In Fig. 6 the spectra taken by these three standard methods can be compared. It is observed that the spectra generally are very similar, there being no evidence of such effects as crystal interactions causing the splitting of absorption bands into several components, or of completely new bands appearing in the spectrum. There is, however, an appreciable difference in frequency of some of the absorption bands obtained in aqueous solution as compared with those taken in the solid state. For \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3 the absorption band which occurs at 1329 cm\(^{-1}\) in the Nujol mull occurs at 1331 cm\(^{-1}\) in the potassium bromide disc, but at 1342 cm\(^{-1}\) in aqueous solution. The band near 800 cm\(^{-1}\) is much less sensitive to the change in medium, the difference being only 2 cm\(^{-1}\). Similar results are observed for the \([\text{Cu(NH}_3\text{)}_4]\text{SO}_4\cdot\text{H}_2\text{O where the frequency changes from 1287cm}^{-1}\text{in Nujol to 1280 cm}^{-1}\text{in water.}

The small changes in the solid state spectra

*Nujol is a commercial grade of pure liquid paraffin.*
(Nujol and potassium bromide disc) as compared with those in aqueous solution are probably due to changes in the extent of hydrogen bonding between the ammonia groups. It has been suggested by Chatt and his co-workers that many ammine complexes form strong hydrogen bonds in the solid state and that this effect can be avoided if the spectra are examined in dilute solution in a solvent which does not itself form hydrogen bonds. Unfortunately, most of the compounds examined in the present work are not sufficiently soluble in such solvents and the effect cannot be avoided. Furthermore, it is clearly not possible to interpret the changes in frequency on going from the solid state spectra to aqueous solution in terms of the degree of hydrogen bonding of the complex, since the water itself is capable of forming hydrogen bonds with the complex.

The Nujol mulls, in which most of the solid state spectra were examined, were prepared by grinding the substance with the Nujol in an agate pestle and mortar. Great care was taken in the preparation of these samples; in particular, the mull produced by prolonged grinding generally provided the most satisfactory spectrum, insufficient grinding giving less sharp absorption bands and considerable "background" absorption, due to light scattering.
In some cases the pressed potassium bromide disc technique was used. The discs were prepared by grinding pure, dry potassium bromide with the substance until a fine homogeneous powder was produced. The powder was then pressed into a disc, using the die and hand press supplied by Messrs. Hilger & Watts. Pure potassium bromide gave a perfectly clear disc, but the incorporation of the substance caused a marked clouding of the disc, which produced appreciable scattering of the light when more than 2-3% of the compound was present. For the detection of some of the very weak absorption bands described later, discs containing 10-15% of substance would have been required and the comparable concentration could be obtained more easily using a Nujol mull.

An important disadvantage of the potassium bromide discs is the tendency for some of the compounds to react with the potassium bromide during the production of the disc. This was particularly noticeable with the copper and silver ammines, whose spectra showed marked differences when examined as potassium bromide discs.

The main advantages of the disc technique were the sharper spectra obtained in cases where the foregoing difficulties do not arise, and the absence of the absorption bands in the region 1350-1500 cm$^{-1}$ found for
Nujol and which might obscure a weak absorption band due to the substance under examination, though the effect of these bands can be avoided by taking this portion of the spectrum as a mull in hexachlorbutadiene (H.B.) which shows no appreciable absorption from 1500 to 1200 cm\(^{-1}\). Another use of the disc method is in quantitative studies, since the discs can be made of standard weight and containing known proportions of the substance; in fact it has been shown that in some cases for such discs Beer's law is obeyed over a moderate concentration range.\(^{11}\)

In examining hygroscopic substances, such as anhydrous nickel II tris(ethylene-diammine) dichloride, the mulls and potassium bromide discs were prepared using the "dry box" method, described in Chapter VII on the method of using deuterium oxide in the preparation of deuterocammines.
CHAPTER VI.

EXPERIMENTAL

Preparation of Compounds examined.

The preparation of all the compounds used is described here together rather than in the separate sections, as the spectra of some of the compounds examined are used to illustrate several different points of interest. Analar reagents were used wherever possible and supplies of chlorplatinic acid and palladium dichloride were obtained from Messrs. Johnson & Matthey Ltd.

Most of the compounds examined are ionic and this means that in many cases there is a possible choice of the ion of opposite charge to that being examined. For cationic complexes such as $[\text{Co(NH}_3\text{)}_6]^{3+}$ a wide variation of anion is possible, including halides, sulphate, nitrate and perchlorate, but with many complexes the ease of isolation of the cation complex is affected greatly by the choice of anion. With $[\text{Cu(NH}_3\text{)}_4]^{2+}$ the sulphate is readily obtained and is quite stable, but the chloride is much more difficult to isolate in a pure state, tending to lose ammonia to give complexes containing coordinated chlorine. Similar difficulties are found with the silver ammines where the sulphate is easily isolated with two molecules of ammonia, but the ammines
of the chloride are much less definite in composition.

From a spectroscopic point of view it is desirable that the anion should not show infrared absorption in the region being examined, and for this reason halide complexes have been used wherever possible. Another difficulty is that in some cases the associated anion may affect the vibrations of the coordinated ammonia groups. This effect has been examined by Hill and Rosenberg for cobaltic ammines, where it is shown that the larger anions have the greater effect. As this effect cannot be eliminated, since the complex ions cannot exist independently, it has been minimised by using the same anion as far as possible, consistent with the stability of the complex concerned. For this reason in most cases the chloride ion has been used, it being preferred to bromides and iodides because of its small size. Most of the work on the \[\text{Cu}(\text{NH}_3)_4\]^{2+} has been done on the sulphate in spite of the disadvantages described, as the deuteration experiments described later would have been extremely difficult with the unstable chloride.

Wherever there is any doubt as to the identity of a compound, its composition was confirmed by micro-analysis.
Cobalt complexes.

**Hexammine cobalt III chloride, \([\text{Co(NH}_3\text{)}_6\text{Cl}_3]\)_{13}**

24 g. of hydrated cobaltous chloride and 16 g. of ammonium chloride were dissolved in 20 ml. water. 4 g. of fresh active charcoal were added and 50 ml of aqueous ammonia (s.g. 0.88). The mixture was aerated vigorously for 4 hours. The precipitate and active carbon were then filtered and the hexammine cobaltic chloride \([\text{Co(NH}_3\text{)}_6\text{Cl}_3]\) dissolved in a hot solution of 150 ml water and 25 ml concentrated hydrochloric acid. The solution was filtered while still hot and the yellow hexammine salt precipitated by the addition of 40 ml concentrated hydrochloric acid and cooling in ice. The precipitate was filtered, washed with 60% alcohol, then absolute alcohol and dried at 90°C.

**Chloropentammine cobalt III chloride, \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\)_{14}**

20 g. of cobalt carbonate were dissolved in concentrated hydrochloric acid and the solution filtered. It was then added to a solution of 50 g. of ammonium carbonate in 250 ml water to which 250 ml of 10% by solution of aqueous ammonia had been added. Oxidation was then effected by passing a stream of air through the solution in a Buchner flask. After 3 hours it was removed, 150 g. of ammonium chloride were added and the solution was heated in
an evaporating basin on a water bath until the volume was reduced to about a quarter. It was then neutralised with dilute hydrochloric acid and an excess of 10 ml of ammonia (e.g. 0.088) was then added. This solution was warmed on a water bath for one hour, diluted to 400 ml and 300 ml of concentrated hydrochloric acid added, heated for ½ hour and allowed to cool. The crystals which separated were purified by dissolving in 500 ml of 2% aqueous ammonia, and the compound reprecipitated by the addition of 300 ml concentrated hydrochloric acid; it was filtered, washed with dilute hydrochloric acid and absolute alcohol, then dried in air.

trans-Dichlorotetrammine cobalt III chloride $[\text{Co(NH}_3)_4\text{Cl}_2]\text{Cl}$

A sample of this compound was available in this laboratory and had been prepared by isomerisation of the cis isomer as described by Merritt$^{15}$. 

trans-Dichloro-bis(ethylenediammine) cobalt III chloride

$[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$

This compound was prepared as described by Bailar$^{16}$. 60 g. of a 10% solution of ethylene diamine were added to a solution of 16 g. of hydrated cobalt chloride in 50 ml of
water. The mixture was oxidised in the way described for the cobalt hexamine for 10 hours. 35 ml concentrated hydrochloric acid were added and the solution evaporated on a water bath until a crust formed on the surface. The solution was then allowed to stand over night and the product was then filtered, washed with alcohol and ether, and dried at 120°C.

Trio (ethylenediammine) cobalt III chloride \([\text{Co(en)}_3\text{Cl}_3]\) 17

61 g. of 30% ethylenediamine and 17 ml of 6 N. hydrochloric acid were added to a solution of 24 g. of hydrated cobalt chloride in 75 ml of water. The mixture was oxidised by air as described previously for 3 hours. The solution was evaporated on a water bath until a crust formed on the surface, then 15 ml of concentrated hydrochloric acid and 30 ml absolute ethyl alcohol were added. The mixture was cooled and the crystals filtered, washed with alcohol and dried at 160°C.

Hexammine cobalt II chloride \([\text{Co}^{\text{II}}(\text{NH}_3)_6\text{Cl}_2]\) 18

10 g. of hydrated cobalt chloride were dissolved in the minimum quantity of hot water and added to a hot solution of concentrated aqueous ammonia. During this process a stream of nitrogen was passed over the solution.
On cooling, reddish brown crystals separated and the mother liquor was siphoned off, the stream of nitrogen being continued. The crystals were then washed first with concentrated ammonia, then with absolute ethyl alcohol and finally dried under vacuum. The composition of the product was checked by determination of the percentage of nitrogen, using the micro Kjeldahl method. [Found: N, 35.0. Calc. for Co(NH$_3$)$_6$Cl$_2$: N, 36.3%].

The rather low results for the percentage of ammonia in this compound were not unexpected as the material evolved ammonia even at room temperature. There was, however, no evidence from the spectrum of any substantial change in the nature of the compound.
Palladous complexes.

\textbf{trans-Dichlorodiammine palladium II \([Pd(NH_3)_2Cl_2]\)^{19} }

Palladium dichloride was dissolved in water containing sufficient dilute hydrochloric acid to prevent hydrolysis. Concentrated aqueous ammonia was added until the solution became pale yellow and the \textit{trans}-dichlorodiammine precipitated by addition of dilute hydrochloric acid, as a yellow powder. This was filtered and dried at 100°C.

\textbf{cis-Dichlorodiammine palladium II \([Pd(NH_3)_2Cl_2]\)}

This compound was obtained in the way described by Grinberg and Shulman^{20}. A 10% solution of ammonium acetate was added dropwise to a cold solution of potassium palladochloride in water. \( [1 \text{ g. } \text{PdCl}_2 + 0.85 \text{ g KCl (2 mols) in 10 ml water}] \). Care was taken to allow the reaction to go to completion after each addition, before further ammonium acetate solution was added, since an excess led to the formation of the pink complex \([\text{Pd(NH}_3)_4]\text{PdCl}_4\). The precipitate was centrifuged and washed with several small portions of cold water. The product was dried in air.
Tetramminie palladium II dichloride monohydrate
\[ \text{Pd}(\text{NH}_3)_4\text{Cl}_2\cdot\text{H}_2\text{O} \] 21

The trans-palladium dichlorodiammine was dissolved by warming with a 2 M solution of ammonium chloride containing an excess of ammonia. The solution was then allowed to crystallise. The white, needle-shaped crystals were then washed with dilute aqueous ammonia and dried in air.

cis-Dinitrodiammine palladium II \[ [\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2] \] 22

2.5 ml of concentrated ammonia were added to 1 g. of trans-palladium dichlorodiammine in 5 ml of cold water. The solution of palladium tetrammine dichlorides formed was added to a solution of 2.6 g. of sodium nitrite in 7.5 ml water. The mixture was allowed to stand in an evaporating basin over concentrated sulphuric acid in a desiccator. The product was washed with ice-cold water, alcohol and ether, and dried in air.

trans-Dinitrodiammine palladium II \[ [\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2] \] 23

1 g. of trans-palladium dichlorodiammine was added to a solution of 3 g. sodium nitrite in 6 ml cold water and shaken for 12 hours, giving the white trans-Pd(\text{NH}_3)_2(\text{NO}_2)_2. The product was centrifuged and washed with water, alcohol and ether, then dried in air.
Palladium chloride was dissolved by warming with an aqueous solution of potassium nitrite; on cooling bright yellow crystals of $K_2\text{Pd(NO}_2\text{)}_4$ separated. These were purified by recrystallisation. (% nitrogen found 15.0 $K_2\text{Pd(NO}_2\text{)}_4$ requires 15.2%).
Platinous complexes.

The starting point in the preparation of nearly all these complexes was potassium chlorplatinite, $K_2PtCl_4$. This was prepared as described by Keller$^{25}$ in Inorganic Syntheses.

5 g. hydrated chlorplatinic acid were dissolved in 50 ml water and the potassium salt $K_2PtCl_4$ was precipitated by the addition of 1.6 g. of potassium chloride dissolved in 15 ml water. The precipitation was completed by the addition of an equal volume of alcohol and cooling in ice. The precipitate was then washed by decantation successively with 50% alcohol, 95% alcohol and ether.

The precipitate was then mixed with 35 ml water and reduced, using a freshly prepared aqueous solution of sulphur dioxide. The solution was stirred mechanically and heated on a water bath, the sulphur dioxide solution was added very slowly to prevent the formation of sulphite complexes. After each addition the odour of sulphur dioxide was allowed to disappear before more was added. The process was continued until only a trace of the insoluble potassium platinichloride remained. The volume of the solution was maintained at 35 ml throughout by addition of water. The solution was then evaporated to the point of crystallisation, dissolved in 60 ml water and filtered.
600 ml of a mixture of equal parts alcohol/ether was added and the precipitate was washed by decantation with a mixture of acetone/ether, then ether, and finally dried in air.

The product was recrystallised from water containing a few drops of concentrated hydrochloric acid to eliminate traces of sulphate impurity.

**Tetrammine platinum II dichloride** $[\text{Pt(NH}_3\text{)}_4\text{]Cl}_2$

This compound was prepared according to the method described by Keller$^{26}$. 

5 g. of chlorplatinic acid dihydrate in 36 ml water were reduced in the same way as the potassium salt described previously (the solution being tested for complete reduction when saturated ammonium chloride solution gave no precipitate). The reduced solution was divided into two portions. One was diluted to 100 ml, heated to boiling and 125 ml solution of concentrated ammonia added slowly with continual stirring; heating was continued until the yellow colour had disappeared. The solution of tetrammine salt obtained was heated on a water bath until there was only a faint odour of ammonia. The other portion of chlorplatinous acid solution was added to it and the green salt, $[\text{Pt(NH}_3\text{)}_4\text{]PtCl}_4$ precipitated. This was washed with water
by decantation until no precipitate of barium sulphate was obtained on addition of barium chloride. The salt was then sucked dry on a filter funnel, and then mixed with 25 ml water, 2 ml concentrated hydrochloric acid and 100 ml concentrated aqueous ammonia. This mixture was heated to just below 100°C and stirred mechanically until the green salt gradually dissolved to give Pt(NH₃)₄Cl₂ in solution. When the solution was complete the liquid was evaporated until the smell of ammonia disappeared, the volume was then adjusted to 50 ml, the solution made just acid to litmus with dilute hydrochloric acid, 1 ml excess concentrated hydrochloric acid added and the tetrammine complex precipitated by addition of 500 ml of a 50:50 alcohol/acetone mixture. After standing 1 hour the precipitate was washed with 50 ml portions of alcohol/acetone, then acetone and finally ether, and dried in air.

trans-Dichlorodiammine platinum II \[\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}\]

This was prepared from the tetrammine described above by Biltz²⁷. 1 g. of the tetrammine was heated to 250°C for 20 minutes in a test tube immersed in an oil bath. The residue was extracted with hot water and filtered. The flocculant, almost white precipitate which separated on cooling was then recrystallised from water. Yield 0.4-0.5 g.
Attempts to make this complex by the method of Biltz and Biltz\textsuperscript{28} gave very low yields, and the compound was prepared by the method of Jörganson\textsuperscript{29}. Ammonium chlorplatinic acid was obtained by neutralising a sample of chlorplatinic acid and crystallising the solution. The chlorplatinic acid was reduced to the chlorplatinate as described for the potassium salt. 2 g. of the ammonium chlorplatinic acid were dissolved in 10 ml water and cooled in ice. 5 ml of ice-cold 5 M. aqueous ammonia were added and the solution allowed to stand for 12 hours at 0°C. The product was washed with iced water to remove the tetrammine, then washed with boiling water, the filtrate mixed with one sixth of its volume of concentrated hydrochloric acid and allowed to stand for 24 hours. The salt was then filtered, washed with alcohol and dried in air.

Potassium tetranitroplatinum \textsuperscript{II} \[K_2Pt(NO_2)_4\] \textsuperscript{30}

1 g. potassium chlorplatinic acid, \[K_2[PtCl_6]\], was warmed with an aqueous solution of 5 g. of potassium nitrite in 10 ml water. The yellow potassium chlorplatinic acid slowly dissolved, the potassium nitrite first reducing the Pt\textsuperscript{IV} to Pt\textsuperscript{II} and then reacting to give the tetranitro complex. The almost colourless solution which resulted
was set aside and allowed to evaporate. After 3 days the very pale yellow crystals which separated out were removed and recrystallised from hot water. A second crop of crystals could be obtained from the mother liquor.

\[ \text{cis-Dinitrodiammine platinum II} \quad \text{Pt(NH}_3\text{)}_2(\text{NO}_2\text{)}_2 \]

0.5 g. of potassium tetranitro platinum II was dissolved in 5 ml water. 2.5 mols of H. aqueous ammonia were then added and the diammine slowly separated as an almost white, flocculant precipitate. This was recrystallised from hot water several times and dried in air.

\[ \text{cis-Chloronitrodiammine platinum II} \quad \text{Pt(NH}_3\text{)}_2\text{NO}_2\text{Cl} \]

The compound \( K_2[\text{PtCl}_3\text{NO}_2] \) was prepared by adding 1 mol potassium nitrite to a solution of 1 mol potassium chloroplatininate and crystallising the solution. It was hoped to produce the complex \( \text{trans NO}_2^- \cdot \text{Pt} \cdot \text{NH}_3 \) by addition of aqueous ammonia, but the addition of only one mol of aqueous ammonia gave a precipitate which analysis showed to be the diammine. \( [\text{Pt(NH}_3\text{)}_2(\text{NO}_2\text{)}\text{Cl} \) requires N: 13.5\% Found: N: 13.65\%]. No further attempt was made to prepare the monammine, as when the spectrum was seen, even with both ammonia groups present, the absorption
due to the nitro group was so strong as to prevent detection of the Pt–NH₃ absorption bands. The preparation of the diammine was completed by addition of a further one mol of aqueous ammonia. The product was recrystallised from water.

cis- and trans-Dichloro-bis-(diethyl sulphide) platinum II.

\[
\text{cis- and trans-Dichloro-bis-(diethyl sulphide) platinum II.} \\
\text{[\((C_2H_5)_2S\)PtCl₂]}
\]

These compounds were made as described by Angell, Drew and Wardlaw.²⁵

2 g. of potassium chlorplatinirite were dissolved in 10 ml. water and 1.1 g. (2.5 mols) of diethyl sulphide added in a stoppered flask. The mixture was shaken for 2 hours and if the trans isomer was required the crystals which formed were removed and crystallised from 60-80 petroleum ether. For the cis compound the mixture, after shaking for 2 hours, was allowed to stand over night, when much of the precipitate redissolved. The mixture was filtered and the clear liquid was aerated at laboratory temperature by means of a filter pump. Gradually a fine pale yellow precipitate of the cis isomer precipitated. This was filtered, dried in air and extracted with warm petroleum ether to remove any trace of trans isomer. The melting points of the two products were measured and found
to be $107 \pm 1^{\circ}C$. They could not therefore be distinguished this way, but the sharp melting point showed that they were pure isomers, as artificial mixtures had a considerably lower melting points.

**trans-Dichloro-(diethylsulphide) monammine platinum II**

\[ \text{[Pt(NH}_3\text{)(C}_2\text{H}_5\text{)}_2\text{S}]Cl}_2 \]

The bridge compound, \[ \text{Et}_2\text{S} \quad \text{Cl} \quad \text{Pt} \quad \text{Cl} \quad \text{Pt} \quad \text{Et}_2\text{S} \quad \text{Cl} \quad \text{Cl} \]

was prepared as described by Chatt and Vannini\(^{33}\).

5.3 g *cis*-(Et\(_2\)S\(_2\))PtCl\(_2\) and 4.6 g sodium chlorplatinate were dissolved in 220 ml 95% ethyl alcohol and kept at 45\(^{\circ}\)C for 4 hours with frequent shaking.

The yellow precipitate was then washed with alcohol and water and dried in air.

1 mol of this compound was then allowed to react with 2 mole of ammonia in 95% alcohol, the compound dissolving to give a yellow solution, which on evaporation yielded a yellow oil which crystallised slowly. This is the method described generally by Chatt and Vannini\(^{33}\), the reaction being of this form

\[ \text{[Pt(NH}_3\text{)}_2\text{S}]Cl}_2 \quad \text{Cl} \quad \text{Et}_2\text{S} \]
The product was not purified further as the probable impurities would not be likely to affect the spectroscopic results. Spectroscopic evidence did show the presence of bound ammonia and diethylsulphide. For example, the absorption band at 835 cm$^{-1}$ is characteristic of coordinated ammonia($\delta_{NH_3}$) and the bands at 679 and 727 cm$^{-1}$ are clearly the vibration frequencies for diethyl sulphide itself as modified by coordination.

Analysis of this compound gave the following results: [Found: C, 12.7; H, 3.6. Calc. for Pt(Et$_2$S)NH$_3$Cl$_2$: C, 12.8; H, 3.5%.] Determination of nitrogen in this compound proved difficult as the Kjeldahl method gave low results and the micro Dumas method high results. The figures obtained are therefore of no value.

Zeise's salt, $K_2(C_2H_4)PtCl_3\cdot H_2O$, and ethylene platinum II chloride.

These compounds were obtained as described by Chatt$^{34}$. 1.5 g. potassium chloroplatinite were dissolved in 7.5 ml of 4% hydrochloric acid. This solution put in a 150 ml long-necked flask, was shaken for 10 days
in an atmosphere of ethylene. The ethylene, which was renewed at intervals during the preparation, was obtained from a commercial cylinder and was passed through a bubbler containing cuprous chloride in dilute hydrochloric acid to absorb any carbon monoxide impurity. (The complex of carbon monoxide with cuprous chloride is more stable than that of ethylene and will form preferentially). The gas was then passed through water and thence into the reaction flask.

Zeise's salt, $K[(\text{C}_2\text{H}_4)\text{PtCl}_3]H_2O$ was thus obtained from the golden coloured solution by cooling in ices and removing the yellow crystals. (A further crop of crystals was obtained by allowing the solution to evaporate in air). If the bridge compound $[(\text{C}_2\text{H}_4)\text{PtCl}_2]_2$ was required, the solution obtained above was taken to dryness over concentrated sulphuric acid and sodium hydroxide pellets, and the solid residue extracted with 20 ml of absolute alcohol containing 0.6 ml concentrated hydrochloric acid. The solution was filtered and taken to dryness under reduced pressure (temperature below 60°C). The product was a reddish powder.
trans-Dichloro-ethylene-monammine platinum II.

\[ \text{[Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2]\]

This was obtained as a yellow precipitate when 2 N. aqueous ammonia was slowly added to an aqueous solution of the Zainé's salt described above. The composition was confirmed by analysis. (Found: C, 7.7; H, 2.25; N, 4.5. Calc. for \text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2: C, 7.6; H, 2.18; N, 4.6%)

trans-Dichloroethylene-trimethylamine platinum II.

\[ \text{[Pt}(\text{C}_2\text{H}_4)(\text{N(CH}_3)_3)\text{Cl}_2]\]

This was obtained similarly, but in this case care had to be taken to avoid an excess of the ammine, which was added as an aqueous solution of the hydrate until the pH of the solution reached a value of 7. The yield obtained in this reaction was about 25%. The composition was confirmed by analysis. \[(\text{CH}_3)_3\text{N(C}_2\text{H}_4)\text{PtCl}_2 \text{ requires: C, 17.0; H, 3.7%}. \text{ Found: C, 16.8; H, 3.7%}.\) The product was unstable and slowly darkened on standing, with loss of trimethylamine.
Tetrammine cupric sulphate, monohydrate \[\text{Cu(NH}_3\text{)}_4\text{SO}_4\cdot\text{H}_2\text{O}\]

20 g. of hydrated cupric sulphate were dissolved in a solution of 20 ml water and 30 ml concentrated aqueous ammonia.

30 ml ethyl alcohol were then added slowly to precipitate the complex, which was then filtered, washed with a little 50% aqueous alcohol and dried over quicklime.

Tetrammine cupric chloride \[\text{Cu(NH}_3\text{)}_4\text{Cl}_2\]

The hydrate of this salt was prepared by dissolving hydrated cupric chloride in hot concentrated ammonia, and allowing it to crystallise. The deep blue crystals of the hydrate, \([\text{Cu(NH}_3\text{)}_4\text{Cl}_2\cdot\text{H}_2\text{O}]\), were then allowed to stand over a mixture of finely powdered quicklime and ammonium chloride for a week. The infrared spectrum of the product then showed only a trace of water remaining and the composition was confirmed by determination of the percentage of nitrogen as described before. [Found: N, 24.5. Calc. for \(\text{Cu(NH}_3\text{)}_4\text{Cl}_2\): N, 27.7%].

As with the cobaltous hexammine this compound lost weight rapidly on standing in air, and was for this reason difficult to weigh for the determination of nitrogen. It was found that on standing in air until constant weight
was attained the compound lost the equivalent of 1 mol ammonia.

Diammine silver sulphate \( [\text{Ag(NH}_3\text{)}_2]\text{SO}_4 \) 37

10 g. of powdered silver nitrate were heated with 32 ml of 2 N. sulphuric acid in an evaporating basin until all excess sulphuric acid had been removed. While still hot the residue was dissolved in 10 ml of concentrated aqueous ammonia, filtered and allowed to crystallise. The large crystals which were formed were removed and pressed between filter paper. The product was stored in the dark. The spectra were determined on a fresh sample wherever possible as the material underwent superficial darkening, particularly on exposure to light.

Tetrammine zinc chloride \( [\text{Zn(NH}_3\text{)}_4]\text{Cl}_2 \) 38

A stream of ammonia gas was passed through a hot, concentrated aqueous solution of zinc chloride until the precipitate first formed just redissolved. The solution was then allowed to cool and the crystals which separated filtered and dried between filter paper.

Diammine mercuric chloride \( \text{Hg(NH}_3\text{)}_2\text{Cl}_2 \) 39

A hot concentrated solution of ammonium chloride
was prepared and small quantities of finely ground mercuric oxide added. When the rate of solution of the oxide became very slow, the addition was stopped and the solution allowed to crystallise. The colourless crystals of \(\text{Hg(NH}_3\text{)}_2\text{Cl}_2\) which separated could not be recrystallised as they are decomposed by water and the product was always contaminated with some ammonium chloride.

**bis-(ethylenediammine) cupric chloride** \([\text{Cu(en)}_2\text{Cl}_2\cdot\text{H}_2\text{O}]^{40}\)

5.3 g. of hydrated cupric chloride in aqueous solution were mixed with 3.8 g. of ethylenediammine and the solution allowed to crystallise. The crystals which deposited were extracted with cold absolute alcohol and crystallised. The purple needles were recrystallised several times from alcohol. A sample of this product was dissolved in water and a solution of potassium chlorplatinitate added to it, giving a bluish-pink precipitate of the compound \([\text{Cu(en)}_2][\text{PtCl}_4]\). As this was anhydrous it was more useful for the spectroscopic examination, the absorption bands due to the water of crystallisation being avoided. The composition was confirmed by analysis. [Found: \(\text{N}, 10.3\). Calc. for \([\text{Cu(en)}_2][\text{PtCl}_4]\): \(\text{N}, 10.7\%\).]
tris-(ethylenediammine) nickel II chloride \([\text{Ni(en)}_3\text{Cl}_2]\)

10 g. of hydrated nickel chloride were dissolved in water and 13 g. of 60% ethylenediammine added. The solution was then allowed to crystallise in air and the violet crystals of the dihydrate which separated were recrystallised from water. The compound was dehydrated by heating to 120°C, in vacuo, over magnesium perchlorate. Spectroscopic examination of these compounds showed that no change in structure had taken place during the dehydration and the composition was confirmed by analysis. [Found: C, 22.8; H, 7.7. Calc. for \([\text{Ni(en)}_3\text{Cl}_2]\): C, 23.2; H, 7.7%]
FIG. 7.

"DRY BOX"

FOR HANDLING SUBSTANCES IN THE ABSENCE OF ATMOSPHERIC MOISTURE.
FIG. 7

DRY BOX
for handling Substances in the Absence of Atmospheric Moisture

Active Alumina

Electric Light

Humidity gauge

Air circulator

Hot plate

Air lock

Door
CHAPTER VII.

EXPERIMENTAL.

Preparation of Deuteroamines.

The deuteroamines were all prepared by exchange of the ammonia complexes with pure deuterium oxide, it having been shown previously that a fairly rapid exchange of hydrogen and deuterium will take place in such compounds. This may seem surprising when the great stability of these complexes is considered, but it arises since they not only dissociate according to the equation

\[ M(NH_3)_x + H_2O \rightarrow M(NH_3)_{x-1}H_2O + NH_3 \]

but also behave as acids, ionising as follows:

\[ [M(NH_3)_x]^y^+ \rightarrow [M(NH_3)_{x-1}NH_2]^{(y-1)+} + H^+ \]

and thus both processes will combine to promote the exchange. All handling of the deuterium oxide and the resulting deuteroamine has to be carried out as far as possible in a "dry box" to minimise the rapid exchange which takes place between deuterium oxide and atmospheric moisture. The "dry box" shown in Fig. 7 consists quite simply of a carefully sealed box with transparent perspex panels. In the front of the box are two or three circular apertures in which rubber gloves are sealed. The air in the box is circulated by means of an electric pump over
active alumina and it is fitted with a hygrometer to measure the percentage humidity. Samples are inserted and removed through an air lock and a small electric hot plate provides the heating required for some reactions. The percentage humidity as measured on the gauge was maintained below 10% throughout the operations. To reduce the humidity to this level took six days, the alumina, activated at 200°C, being replaced twice daily. Just before the dry box was used a dish of phosphorus pentoxide was inserted to assist the removal of last traces of moisture.

The deuterium oxide was a very pure sample obtained from Norway, purity > 99.9%, and was sealed into 1 ml ampoules from which it was removed as required by a hypodermic syringe. The deutero derivatives, Pd(ND₃)₂Cl₂ and [Co(ND₃)₆]Cl₃, were prepared from the ammonia complexes by heating the compounds with successive small amounts of deuterium oxide, removing the excess deuterium oxide by gentle heat. If too large an excess of deuterium oxide was used some decomposition of the ammine took place. During the reaction the palladium dichlorodiammine changed in appearance from a yellow powder to reddish brown crystals; this product had the same analysis as the original compound and it was shown that water produced a similar effect. (It is probable that the change which
took place was to the second crystalline form of palladium dichlorodiammine reported by Mann, Crowfoot, Grattiker and Wooster. Spectroscopically the spectrum of the compound heated with water was similar to that from the original compound, but the frequencies of the absorption peaks were slightly changed. For this reason the frequencies used for the simple ammine in comparing the frequency ratios with the deuterammines were based on a sample which had been similarly heat treated with water. The cobaltic hexammine chloride after treating with water in the same way showed no detectable visible or spectroscopic difference. The compound chloropentammine cobalt chloride was also converted to a deuterium analogue in the same way so as to examine the effect of deuteration on the very weak absorption peak at 493 cm$^{-1}$. The compound was more difficult to prepare than the deuterohexammine as it is fairly readily decomposed on boiling with water, but it was possible to obtain it fairly pure and to show that the absorption peak concerned was only altered in frequency by 6 cm$^{-1}$.

Attempts were made to isolate the deuterammines of copper and silver in the same way, but removal of the excess deuterium oxide led to hydrolysis of the ammine. It was however possible to remove some of the excess deuterium oxide over active alumina or quicklime and to
achieve almost complete deuteration by repeating the procedure. The spectra were then examined in the concentrated deuterium oxide solution by pressing a thin film between silver chloride plates. The corresponding spectra were obtained of the simple amines in aqueous solution and it was possible to show the frequency shift of the peak near 1200 cm$^{-1}$ ($\delta_{\text{sym}}^{\text{NH}_3}$). In other parts of the spectrum the absorption due to the water or deuterium oxide prevented detection of the absorption bands.
CHAPTER VIII.
SPECTROSCOPIC ASSIGNMENT OF AMMINE FREQUENCIES.

Frequencies due to the NH vibration.

It is important first of all to consider the possible vibrations associated with a coordinated ammonia group and to obtain some idea as to the values of the frequencies associated with each vibration. This can be done by comparison with molecules of similar symmetry whose frequency assignment is well established. In a metal ammine the masses of the atoms concerned show a considerable difference; thus, for the platinum ammines we have the masses as follows

\[ \text{Pt} \rightarrow \text{N} \rightarrow \text{H}_1 \]

Even where a lighter metal such as cobalt is concerned the mass of the metal is four times that of the nitrogen. It follows from this that as a first approximation the metal-nitrogen vibrations and the nitrogen-hydrogen vibrations can be considered independently. The vibrations of the nitrogen-hydrogen bonds which are being considered in this section can be represented as follows
Of these vibrations the only one which will not be present in ammonia itself, except as a rotational frequency, is the \( \delta \text{NH}_3 \) mode.

Several previous workers have recorded results for metal ammines but have differed in their assignment of their frequencies. Duval, Duval and Lecompte\(^{44} \) studied the infrared spectra of a number of cobalt and chromium ammines and reported that all these compounds showed three main absorption bands in the regions 1500, 1200 and 800 cm\(^{-1} \) and in the present work these bands have been found for all the much wider range of ammines examined. These
authors considered that the first two of these bands represent the frequencies of the internal asymmetrical and symmetrical angle bending vibrations of the ammonia group as modified by coordination with the metal ion \( S_{\text{asym}} \) and \( S_{\text{sym}} \) respectively. The corresponding absorption bands of ammonia itself occur near 1628 cm\(^{-1}\) and 950 cm\(^{-1}\) respectively and at 1646 cm\(^{-1}\) and 1060 cm\(^{-1}\) in the crystalline solid state\(^{45}\). The assignment of these bands is agreed by most subsequent authors, though Hill and Rosenberg\(^{12}\) have suggested that the bands at 1200-1300 cm\(^{-1}\) are due to the metal-nitrogen stretching vibrations (\( \gamma \) M-N) because of the sensitivity of the frequency to the variation of the metal ion in the complex.

The lower frequency vibration, which occurs near 800 cm\(^{-1}\), has been either assigned to the rocking deformation of the ammonia group, or alternatively to the metal-nitrogen stretching frequency. During the course of this work papers were published supporting the latter view. Kobayashi and Fujita\(^{46}\) examined the nickel, cobaltic and chromic hexammoniums and suggested that the band near 800 cm\(^{-1}\) was due to the \( \gamma \) M-N vibration and, on the other hand, Misushima, Nakagawa and Quagliano\(^{47}\) suggested, on the basis of some preliminary deuteration experiments with \([\text{Co(NH}_3]_6\)Cl\(_3\), that this band was due to the \( S_{\text{rock}} \)
TABLE I.

The Infrared and Raman Frequencies of some Ammines and Deuteroammines and their Assignment to Fundamental Modes of Vibration of the Complexes.
TABLE I

The infrared and Raman frequencies of some ammines and deuteroammines and their assignment to fundamental modes of vibration of the complexes.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Method</th>
<th>Observed infrared frequencies</th>
<th>Raman frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(\text{HH}_3)}_6\text{Cl}_3])</td>
<td>KBr, N</td>
<td>1615 (bd)</td>
<td>501</td>
</tr>
<tr>
<td>([\text{Co(\text{ND}_3)}_6\text{Cl}_3])</td>
<td>KBr, N</td>
<td>1615</td>
<td>575</td>
</tr>
<tr>
<td>([\text{Co(\text{NH}_3)}_5\text{Cl}_2\text{H}_2\text{O}])</td>
<td>N</td>
<td>1555 (bd)</td>
<td>548</td>
</tr>
<tr>
<td>trans-[\text{Pd(\text{NH}_3)}_2\text{Cl}_2])</td>
<td>N</td>
<td>1605</td>
<td>596</td>
</tr>
<tr>
<td>trans-[\text{Pt(\text{NH}_3)}_2\text{Cl}_2])</td>
<td>N</td>
<td>1587(bd)</td>
<td>511</td>
</tr>
<tr>
<td>([\text{Cu(\text{NH}_3)}_4\text{SO}_4\cdot\text{H}_2\text{O}])</td>
<td>N</td>
<td>1587</td>
<td>410</td>
</tr>
<tr>
<td>([\text{Cu(\text{ND}_3)}_4\text{SO}_4\cdot\text{D}_2\text{O}])</td>
<td>D_2O, N</td>
<td>1280</td>
<td>507</td>
</tr>
<tr>
<td>([\text{Ag(\text{NH}_3)}_2\text{SO}_4])</td>
<td>N</td>
<td>1190</td>
<td>419</td>
</tr>
<tr>
<td>([\text{Ag(\text{ND}_3)}_2\text{SO}_4])</td>
<td>D_2O, N</td>
<td>1220</td>
<td>660</td>
</tr>
<tr>
<td>([\text{Cu(\text{HH}_3)}_4\text{Cl}_2\text{H}_2\text{O}])</td>
<td>N</td>
<td>1598</td>
<td>400</td>
</tr>
<tr>
<td>trans-[\text{Pd(\text{NH}_3)}_2\text{Cl}_2\text{H}_2\text{O}])</td>
<td>N</td>
<td>1605</td>
<td>596</td>
</tr>
<tr>
<td>trans-[\text{Pt(\text{NH}_3)}_2\text{Cl}_2\text{H}_2\text{O}])</td>
<td>N</td>
<td>1600</td>
<td>596</td>
</tr>
</tbody>
</table>

Vibrational assignments: \(\nu(\text{NH}_3)\), \(\delta_{\text{asym}}(\text{NH}_3)\), \(\delta_{\text{sym}}(\text{NH}_3)\), \(\nu(\text{NH}_3)\), \(\nu(\text{N-N})\)

N.I., not investigated in this region.

N, Nujol mull.

KBr, potassium bromide discs.

H_2O or D_2O, spectra determined in solution in these solvents.

(bd), broad band.

(p), polarised line.

(dp), depolarised line.

a, possibly due to ND_2H groups.

b, yellow powder.

c, red crystals (see note to Table IV).

d, these spectra showed extra bands in the vicinity of 1100 and 600 cm\(^{-1}\), due to SO_4\(^{2-}\) ions.

e, absorption in this region may be partly due to water of crystallisation.

f, for tetraamine.

g, for hexammine.
vibration. These authors were not, however, able to detect the corresponding band in the deuterio derivative, as the frequency was apparently below the range of the rock salt prism used. Several other authors have published the results of infrared spectroscopic examination of metal ammines but have made little attempt to assign the absorption bands obtained: these include papers by Merritt and Wiberley\(^{48}\) on a number of cis and trans isomers of cobaltic ammines, and by Faust and Quagliano\(^{49}\) on cis and trans \([\text{Co(NH}_3)_4(\text{NO}_2)_2]\)Cl. Almost simultaneously with the publication of the results of this present work Barrow and Basalo\(^{50}\) published an account of work reaching similar conclusions in respect to the assignment of the nitrogen-hydrogen frequencies but which differed in the assignment of the metal-nitrogen stretching frequencies described in the next chapter.

The results obtained in the course of the work for the spectra of a number of ammines are shown in Table I, and are illustrated on pages 80 to 88 at the end of this chapter. The Raman frequencies shown in the last column of Table I have been taken from references 51, 52 and 53. It is seen that for the much wider range of ammines now examined there are always three main bands in the spectrum between 1650 and 650 cm\(^{-1}\), a group of bands
### TABLE II

**Comparison of fundamental frequencies for methyl halides and \( \text{Co(NH}_3\text{)}_6\text{Cl} \).**

<table>
<thead>
<tr>
<th></th>
<th>( \text{CH}_3\text{Cl} )</th>
<th>( \text{CH}_3\text{Br} )</th>
<th>( \text{CH}_3\text{I} )</th>
<th>( \text{Co(NH}_3\text{)}_6\text{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{Cl} )</td>
<td>690</td>
<td>690</td>
<td>690</td>
<td>1000</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Br} )</td>
<td>1100</td>
<td>1100</td>
<td>1100</td>
<td>1500</td>
</tr>
<tr>
<td>( \text{CH}_3\text{I} )</td>
<td>1400</td>
<td>1400</td>
<td>1400</td>
<td>1900</td>
</tr>
<tr>
<td>( \text{Co(NH}_3\text{)}_6\text{Cl} )</td>
<td>1800</td>
<td>1800</td>
<td>1800</td>
<td>2400</td>
</tr>
</tbody>
</table>
Comparison of fundamental frequencies for methyl halides and \([\text{Co(NH}_3)_6]\text{Cl}_3\).

<table>
<thead>
<tr>
<th>Vibration type</th>
<th>(\text{CH}_3\text{Br})</th>
<th>(\text{CH}_3\text{I})</th>
<th>([\text{NH}_3]_6\text{Co}\text{Cl}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu) asym CH</td>
<td>3056</td>
<td>3060</td>
<td>3230</td>
</tr>
<tr>
<td>(\nu) sym CH</td>
<td>2972</td>
<td>2970</td>
<td>3170</td>
</tr>
<tr>
<td>(\delta) asym CH</td>
<td>1445</td>
<td>1440</td>
<td>1615</td>
</tr>
<tr>
<td>(\delta) sym CH</td>
<td>1305</td>
<td>1251</td>
<td>1329</td>
</tr>
<tr>
<td>(\delta) rock CH</td>
<td>952</td>
<td>880</td>
<td>830</td>
</tr>
<tr>
<td>(\gamma) E-G</td>
<td>611</td>
<td>533</td>
<td>a</td>
</tr>
</tbody>
</table>

* The origin of the weak band near 500 cm\(^{-1}\) is discussed in the next chapter.
near 3300 cm\(^{-1}\), and, in a number of cases, a very weak band
near 500 cm\(^{-1}\), the origin of which will be discussed in the
next chapter.

The first step in assigning the frequencies to
particular vibrations is to compare these results for the
amines with the frequencies obtained for a simple molecule
of known assignment which has similar symmetry to these
compounds. A typical example is the methyl halides, where
the heavy halogen atom acts in a similar way to the metal
atom in an ammine, as shown in the sketch below, the dis­
position of bonds round the nitrogen or carbon atoms being
approximately tetrahedral in each case

\[
\begin{align*}
\text{Br} & \quad \text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
80 & \quad 12 & \quad 55-195 & \quad 14 & \quad 1 \text{ or } I_{127}
\end{align*}
\]

The frequencies found for the methyl halides and their
assignments have been taken from the book by Herzberg\(^54\) and
are given in Table II and alongside are the corresponding
frequencies for \([\text{Co(NH}_3)_6]\text{Cl}_3\).

These results make it clear that the bands near
3200 cm\(^{-1}\) are due to N-H stretching vibrations, \(\nu\) N-H.

This would be expected as the stretching force constants
of bonds are always much larger than bending force constants, and the resulting vibrational frequencies are correspondingly greater (see Linnett\textsuperscript{55}). Bands due to stretching vibrations have not been further examined, as they are complex in structure and generally incompletely resolved.

Examination of Table II clearly indicates that bands near 1600 cm\textsuperscript{-1} and 1300 cm\textsuperscript{-1} are related to the vibrations $\delta_{\text{asym}} \text{NH}_3$ and $\delta_{\text{sym}} \text{NH}_3$ respectively and the lower frequency band at 800 cm\textsuperscript{-1} is probably due to the $\delta \text{NH}_3$ vibration. It is certainly unlikely to be the skeletal vibration metal-N as the corresponding frequencies for the methyl bromide and iodide are at 611 and 533 cm\textsuperscript{-1} and it would be surprising if the force constant of the bond were sufficiently high to raise the corresponding frequency to 830 as found for $[\text{Co(NH}_3)_6]\text{Cl}_3$.

The question can at once be settled by comparison of the frequencies observed with those of the corresponding deuterammines. It can be assumed that the replacement of hydrogen by deuterium does not alter the force constant of the bond and the following very approximate relationship can be applied

$$\nu = C \sqrt{\frac{k}{m}}$$

where $\nu$ = frequency, $C$ and $k$ are constants, $m$ = mass
### TABLE III.

**Comparison of the main Infrared Absorption Bands of some ammines and deuteramimines.**
TABLE III
Comparison of the main Infrared Absorption Bands of some Amines and Deuteramines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{asym , \text{NH}_3}$</th>
<th>$\delta_{sym , \text{NH}_3}$</th>
<th>$\delta_{rock , \text{NH}_3}$</th>
<th>$\nu_{\text{N-H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co(NH}_3)_6] \text{Cl}_3$</td>
<td>1615</td>
<td>1329</td>
<td>830</td>
<td>502</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3)_6] \text{Cl}_3$</td>
<td>1155</td>
<td>1046</td>
<td>665</td>
<td></td>
</tr>
<tr>
<td>$[\text{Co(NH}_3)_5 \text{Cl}] \text{Cl}_2$</td>
<td>1575</td>
<td>1305</td>
<td>845</td>
<td>493</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3)_5 \text{Cl}] \text{Cl}_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>487</td>
</tr>
<tr>
<td>trans-$[\text{Pd(NH}_3)_2 \text{Cl}_2]$</td>
<td>1605</td>
<td>1246</td>
<td>752</td>
<td>496</td>
</tr>
<tr>
<td>trans-$[\text{Pd(ND}_3)_2 \text{Cl}_2]$</td>
<td>1165</td>
<td>978</td>
<td>580</td>
<td>493</td>
</tr>
<tr>
<td>$[\text{Cu(NH}_3)_4] \text{SO}_4 \cdot \text{H}_2\text{O}$</td>
<td>-</td>
<td>1280</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Cu(ND}_3)_4] \text{SO}_4 \cdot \text{D}_2\text{O}$</td>
<td>-</td>
<td>982</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Ag(NH}_3)_2] \text{SO}_4$</td>
<td>-</td>
<td>1220</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Ag(ND}_3)_2] \text{SO}_4$</td>
<td>-</td>
<td>950</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
FIG. 8.

INFRARED SPECTRA OF METAL AMMINES
AND DEUTEROAMMINES.
FIG. 8
INFRARED SPECTRA OF METAL AMMINES AND DEUTEROAMMINES

$[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$

$[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$
of the vibrating atom (the mass of the heavier atom being neglected).

Thus it follows

\[ \frac{\nu_H}{\nu_D} = \sqrt{\frac{1}{2}} \]

The vibration of the nitrogen atom has been neglected in this simplified treatment, and in practice the ratio never actually reaches the value of \( \frac{1}{\sqrt{2}} \).

The effect of replacing hydrogen by deuterium on the \( \nu_{\text{M-N}} \) frequency will be very small and so the comparison of the spectra of ammines and deuterocammines should clearly distinguish nitrogen-hydrogen vibrations from metal-nitrogen vibrations. With this in view several of the ammines were converted to the corresponding deuterocammines and the main absorption bands found for these compounds are collected in Table III, and the frequency shifts on deuteration of the ammines can be compared.

Fig. 8 gives a diagram of the spectra obtained for \([\text{Co(NH}_3)_6\text{Cl}_3]\) and \([\text{Pd(NH}_3)_2\text{Cl}_2]\), and it can be seen that the identification of the corresponding bands in the ammines and deuterocammines is simplified by the similarity in shape of the equivalent bands. There is an indication, particularly in the spectrum of \([\text{Pd(ND}_3)_2\text{Cl}_2]\), of slightly incomplete deuteration. It is thought that the band at about 1080 cm\(^{-1}\) in this spectrum, which has no counterpart
### Table IV.

The Ratio $\frac{\gamma_H}{\gamma_D}$ for the analogous Bands in the Spectra of the Amines and Deuteroamines and of Methyl Bromide and Deutero-methyl Bromide.
in the spectrum of \([\text{Pd(NH}_3\text{)}_2\text{Cl}_2]\), is due to this cause, resulting from the vibration of the \(-\text{ND}_2\text{H}\) group.

Comparison of the spectra of ammines and deuto-ammines shows that the three absorption bands which lie in the region from 1650-650 cm\(^{-1}\) in the case of the ammines are all shifted to much lower frequencies in the spectra of the deuto-ammines. This shows that all the bands are due to nitrogen-hydrogen vibrations and so the band near 800 cm\(^{-1}\) must be the \(\delta_{\text{rock}}\) mode. It is interesting to compare quantitatively the ratio of the frequencies observed for the ammines and deuto-ammines with those of the corresponding methyl halides having similar symmetry characteristics, in Table IV some figures are given for these ratios.

It is observed that there is a marked similarity in the ratios for the ammines and those for methyl bromide for analogous vibrations. In particular the ratio for the \(\delta_{\text{asym}}\) or \(\text{CH}_3\) vibration has the values closest to the theoretical maximum of 1·414. The figures for the vibration frequencies of \(\text{CH}_3\text{Br}\) and \(\text{CD}_3\text{Br}\) have been taken from Herzberg\(^{56}\).

In the case of \([\text{Ag(NH}_3\text{)}_2\text{]}\text{SO}_4\) and \([\text{Cu(NH}_3\text{)}_4\text{]}\text{SO}_4\cdot\text{H}_2\text{O}\), the deuto derivatives could not be isolated from the solutions in deuterium oxide and their spectra were
determined in this solvent. The strong absorption of the deuterium oxide prevented any absorption bands of the compound being detected except the $\delta_{\text{ND}_3}^{\text{sym}}$ vibration. The frequency shift of this vibration from the ammimes to the deuterocompounds of these compounds was similar to that found for $[\text{Co(NH}_3)_6]\text{Cl}_2$ and $[\text{Pd(NH}_3)_2]\text{Cl}_2$.

It is observed that there is a weak absorption band in the spectrum of $[\text{Pd(NH}_3)_2]\text{Cl}_2$ near $500 \text{ cm}^{-1}$. This band could only be detected in very concentrated Nujol mulls and its origin will be discussed in the next chapter. It is, however, noted at this point that its frequency only changes very slightly on deuteration and so it cannot be due to a nitrogen-hydrogen vibration.

An interesting feature of the spectra of $[\text{Pt(NH}_3)_4]\text{Cl}_2$ and $[\text{Pd(NH}_3)_4]\text{Cl}_2$ is the presence of a double peak in the $800 \text{ cm}^{-1}$ region. This band has been shown to be due to the $\nu_{\text{NH}_3}$ rocking vibration, and it is suggested that the doubling is due to "in-plane" and "out-of-plane" rocking modes. The failure to detect such a double absorption peak in this case of the $\text{trans-}[\text{Pt(NH}_3)_2]\text{Cl}_2$ and $[\text{Pd(NH}_3)_2]\text{Cl}_2$ is probably due to the restriction of the in-plane vibration by the presence of the large adjacent chlorine atoms. It can easily be seen that the presence of chlorine groups has a marked effect on the frequency of the nitrogen-hydrogen vibrations if the frequencies of the corresponding
vibrations in the platinum and palladium tetramines are compared with those of the trans-dichlorodiamines. In

\[ \text{Pd(NH}_3\text{)}_2\text{Cl}_2 \]

the \( \delta_{\text{sym}}^{\text{NH}_3} \) vibration is at 1246 cm\(^{-1}\), whereas for the tetramine it occurs at 1283 cm\(^{-1}\); similarly, the

\( \delta_{\text{NH}_3} \) occurs at 752 cm\(^{-1}\) in the palladium dichlorodiammine but with the tetrammine there is the double frequency of 842 and 800 cm\(^{-1}\). It is clear that this effect concerns the hydrogen atoms rather than the ammonia group as a whole, since the Pd-N skeletal vibration* only shows a small change from 498 to 496 cm\(^{-1}\). The effect of iodine atoms on the vibration frequencies is similar, the \( \delta_{\text{sym}}^{\text{NH}_3} \) vibration being at 1255 cm\(^{-1}\) for palladium diiododiammine.

An interesting point arises in the case of the compound Hg(NH\(_3\))\(_2\)Cl\(_2\) where it is not certain whether it is a linear ionic complex of the type \([\text{H}_3\text{N} \rightarrow \text{Hg} \leftarrow \text{NH}_3\] \(^2+\) Cl\(_2\) or a neutral 4 coordinate complex \([^{1}\text{Hg(NH}_3\text{)}_2\text{Cl}_2\]). As the complex is decomposed by water, giving H\(_2\)N–Hg–Cl, it is not possible to discover whether it ionises in solution or not. The ammine is one of the most stable known, as is shown by the very high stability constant (\(\log K_{\text{ave}} = 10.4\)), but when the nitrogen-hydrogen bending frequencies are examined it is found that they have much lower values than those expected for such an ammine; for example the \( \delta_{\text{sym}}^{\text{NH}_3} \)

* See Chapter IX for a discussion of this frequency.
vibration occurs at 1215 cm$^{-1}$, lower than for the much less stable [Cu(NH$_3$)$_4$][SO$_4$.H$_2$O ($^{sym}$NH$_3$ 1287 cm$^{-1}$). If however the chloride ions are coordinated to the mercury atom the low frequency would be explained on the basis of nitrogen---hydrogen---chlorine interaction, and this evidence therefore favours the 4 coordinate structure for this compound. These results do not provide a complete proof of this structure as it would be possible for the nitrogen---hydrogen---chlorine interaction to occur intermolecularly and give similar results. It is however unlikely that in this case the effect would be so large.
$[\text{Co} (\text{NH}_3)_6] \text{Cl}_3$
$[\text{Co(NH}_3\_5\text{Cl}^\_}]\text{Cl}_2$
trans [Co(NH$_3$)$_4$Cl$_2$]Cl
[Rh(NH₃)₅Cl]Cl₂
\[ \text{[Hg(NH}_3\text{)}_2\text{]}^+ \text{Cl}_2^- \text{ or } \text{[Hg(NH}_3\text{)}_2\text{]}^+ \text{Cl}_2^- \text{]}

\text{NH}_4^+
CHAPTER IX.

SPECTROSCOPIC ASSIGNMENT OF AMMINE FREQUENCIES.

The Metal-Nitrogen Stretching Vibrations $\nu_{M-N}$

(Skeletal vibrations)

The complete assignment of the nitrogen-hydrogen vibrations to the absorption bands in the spectrum of the metal ammines down to frequencies of $650 \text{ cm}^{-1}$ raises the question of the occurrence of the infrared active stretching vibration of the metal-nitrogen bond. It has already been suggested that this might occur in the frequency range of $400-600 \text{ cm}^{-1}$ with the bending vibrations at much lower frequencies, but preliminary attempts to detect the absorption band in the potassium bromide region ($750-420 \text{ cm}^{-1}$) failed and it was not until extremely concentrated Nujol mulls were examined that the absorption could be detected, and then not in $[\text{Co(NH}_3)_6]\text{Cl}_3$, on which most of the earlier experiments had been made, (the absorption band for this compound was not detected until a modern double beam instrument (Hilger H 800) was available and then only as a very weak broad band at $502 \text{ cm}^{-1}$). The intensity of these absorption bands can be compared with those due to $\delta_{M-H}$ vibrations, if the reproductions of the spectra in this region on page 107 are examined. When these weak absorption bands had been detected for several ammines it was first
necessary to show that they could not arise from any nitrogen-hydrogen vibration. This was proved when the frequency of the vibration was compared with that of the deuterium analogue. In the two cases of \( \text{[Co(NH}_3\text{)]}_2\text{Cl}_2 \) and \( \text{[Pd(NH}_3\text{)]}_2\text{Cl}_2 \) it was shown that the frequency only changed by about 1% on deuteration, and this small frequency change would be expected because of the secondary effect of the increased mass of the vibration of the nitrogen atom. The absorption band must therefore be due to a metal-nitrogen vibration, and as stretching vibrations are always greater than deformations, it is probably of the former type \( \nu_{M-N} \).

Further evidence as to the identification of these frequencies is obtained from comparison with Raman data, particularly in the case of the platinum tetrammine, \( \text{[Pt(NH}_3\text{)]}_4\text{Cl}_2\cdot\text{H}_2\text{O} \), of which the Raman spectrum has been carefully examined by Mathieu. This complex has an effective planar structure in respect of the heavy atom. It is a particularly favourable substance for this method of examination as it is highly soluble in water and forms a colourless solution. This is important as considerably more reliance can be placed on results obtained under these conditions, since coloured solutions may considerably reduce the intensity of the exciting wavelength and insoluble substances may cause difficulty due to light
scattering. The frequencies reported by Mathieu for this compound are 538 (polarised), 526 (depolarised), 270 (depolarised). The first of these can be readily assigned to the two Raman active stretching frequencies as indicated below:

(I)  
\[
\begin{array}{c}
\text{N} \\
\uparrow \\
\text{N} \\
\text{Pt} \\
\text{N} \\
538 \\
\text{Raman Active}
\end{array}
\]

(II)  
\[
\begin{array}{c}
\text{N} \\
\uparrow \\
\text{N} \\
\text{Pt} \\
\text{N} \\
526 \\
\text{Infrared Active}
\end{array}
\]

There is no doubt that the frequency of 538 is the totally symmetric vibration (I) as it is fully polarised and this can only be true of a totally symmetric or "breathing" vibration and eliminates the possibility of it being an angle deformation vibration. The assignment of the frequencies of 526 and 511 therefore follow.

There is one notable feature of these metal-nitrogen absorption bands and that is the weakness of the absorption. This may seem surprising as the bond must be highly polar, being of the coordinate type, Pt-N and most polar bonds give high absorption intensities. This, however, is not always the case, as theoretically the band
FIG. 9.

RELATIONSHIP OF BOND DIPOLE MOMENT AND INTERNUCLEAR DISTANCE
FIG. 9

RELATIONSHIP OF BOND DIPOLE MOMENT AND
INTERNUCLEAR DISTANCE

\[ \mu \]

Bond dipole moment

Internuclear distance

\[ r_{e}', r_e \]
intensity depends on $d\mu/dr$, where $r$ is the distance between the vibrating atoms and $d\mu/dr$ is the change in dipole moment on vibration. Now, if we consider the approach of two isolated atoms, the dipole moment at infinite separation must be zero as well as zero if the atoms coalesce, thus the change in the bond dipole moment with internuclear distance must follow the course shown in Fig. 9.

Now, if the vibration of the nuclei takes place over the portion of the curve C - D, it is clear that a large dipole will lead to a high value for $d\mu/dr$, and therefore a high intensity. However, if the vibration is in the portion from A - B, where the curve is flattening out, this may no longer be the case. Thus it follows that though polar bands in general tend to give high band intensities, this may not always be the case, and so the weakness of the absorption band at 511 cm$^{-1}$ is not a serious objection to this assignment. There are only two possible alternative explanations for the presence of this absorption. It could be one of the Raman active frequencies which had become Infrared active due to crystal distortion effects in the solid state, or it could be an overtone of one of the Infrared active bending frequencies. If either of these explanations is correct it is reasonable
to ask where the infrared active $\gamma_{\text{Pt-N}}$ frequency occurs, as it would not be expected to be far removed from the Raman active frequencies, since the platinum atom is heavy in relation to the nitrogen atom, and the vibration of the central platinum atom should not modify the frequency greatly. This is supported by other cases where the assignment of the frequencies is fully known, for example in methane, where the mass ratio C: H of 12:1 is not greatly different from the Pt: NH$_3$ mass ratio of 195:17 (11.5:1), though the symmetry in methane is tetrahedral and not planar. With methane the "breathing" frequency is at 2914 cm$^{-1}$ and the second stretching frequency at 3020 cm$^{-1}$, a difference of 4% and we might expect a difference of this order of magnitude for the Raman and infrared stretching frequencies of the platinum tetrammine.

Bright Wilson$^{58}$ has given some calculations for a planar molecule of the type MX$_4$ (symmetry class D$_{4h}$), based on a simple valence force field and the equations evolved have been applied to this case of the platinum tetrammine. It should be emphasised that the use of these equations involves considerable approximations, as the ammonia group is treated as a single vibrating unit and only direct bonding along valence bonds is considered (it is almost certain that there is some interaction between
FIG. 10.

FUNDAMENTAL VIBRATIONS OF MX₄
FIG. 10
FUNDAMENTAL VIBRATIONS OF MX₄
adjacent ammonia groups).

The equations derived by Bright Wilson are as follows:

\[
\begin{align*}
\lambda_1 &= \frac{K}{m} \\
\lambda_2 &= \frac{h}{m} \\
\lambda_5 &= \frac{H}{m} \\
\lambda_6 &= (1 + \frac{4m}{M})\frac{h}{m} \\
\lambda_7 &= \frac{K}{m} \\
\lambda_3 &= \frac{1}{2m} \left\{ \left(1 + \frac{2m}{M}(H + K)\right) \pm \left[ \left(1 + \frac{2m}{M}\right)^2(H + K)^2 - 4(1 + \frac{4m}{M}K)H \right] \right\} \\
\lambda_4 &= \frac{1}{2m} \left\{ \left(1 + \frac{2m}{M}(H + K)\right) \mp \left[ \left(1 + \frac{2m}{M}\right)^2(H + K)^2 - 4(1 + \frac{4m}{M}K)H \right] \right\}
\end{align*}
\]

where \( \lambda = 4\pi^2\nu^2 \)

m and M are the masses of the atoms concerned
K is the stretching force constant
H and h are in-plane and out-of-plane bending force constants.

The frequencies described by these equations can be related to the fundamental vibrations of the molecule as indicated in Fig. 10. The three vibrations which involve mainly stretching modes are \( \nu_1, \nu_7, \) and \( \nu_3 \), of which the first two are Raman active and the third is infrared active. The actual Raman data given by Mathieu\(^{52} \)
show frequencies of 538 cm$^{-1}$ (polarised), 523 cm$^{-1}$ (depolarised) and 270 cm$^{-1}$ (depolarised); as already pointed out the frequency of 538 cm$^{-1}$ must be the "breathing" vibration $\nu_1$. It therefore follows that $\nu_7$ and $\nu_5$ should be assigned the remaining frequencies of 523 and 270 cm$^{-1}$ respectively ($\nu_5$ being a bending vibration will have lower frequency than $\nu_7$, which is a stretching frequency).

If these figures are then applied to the equations quoted above it is clear that the frequency $\nu_3$ (the infra-red active stretching frequency) and $\nu_4$ can be calculated on the basis of the Raman data since, $\lambda_1 = \lambda_7 = K/m$ and $\lambda_5 = H/m$, and the expression for $\lambda_3$ and $\lambda_4$ only involves the values of $K$ and $H$ and the masses of the atoms.

It should be noted that theoretically $\nu_1$ and $\nu_7$ should have equal frequencies; in this case it is observed that $\nu_1 = 538$ cm$^{-1}$ and $\nu_7 = 523$ cm$^{-1}$, and so for the purposes of the calculation of $K$ an average value of 532 cm$^{-1}$ is taken.

Since $\lambda_n \propto \nu_n^2$, where $\nu_n =$ frequency, it follows $\lambda_1 = \lambda_7 = A(532)^2 = \frac{K}{14}$ (where $A$ is constant)

Hence $K = 14 \cdot 532^2 \cdot A = 3.962 \cdot 10^6 A$

similarly $\lambda_5 = A \cdot 270^2 = \frac{H}{14}$

Hence $H = 14 \cdot 270^2 \cdot A = 1.021 \cdot 10^6 A$
Inserting these values in the expression for \( \lambda_3 \) and \( \lambda_4 \):

\[
\lambda_3 \quad \lambda_4 \quad = \quad \frac{1}{2.14} \left( 1 + \frac{28}{193} \right) 4.984a \pm \left[ (1 + \frac{28}{193})^2 (4.984a)^2 \right.
\]

\[
\left. - 4(1 + \frac{56}{193}) 4.044a^2 \times 10^{12} \right]^{1/2}
\]

\[
= \frac{10^6A}{28} \frac{223}{193} \cdot 4.984 \pm \left[ (\frac{223}{193})^2 \cdot 4.984^2 \right.
\]

\[
\left. - 4(\frac{251}{193}) 4.044 \right]^{1/2}
\]

\[
= \frac{10^6A}{28} \frac{5.700}{32.49 - 20.82}^{1/2}
\]

\[
= \frac{10^6A}{28} \frac{5.750 \pm 3.416}{\lambda_3 \lambda_4} = \frac{(A \nu_3^2}{(A \nu_4^2}
\]

It follows that \( \nu_3 = 572 \text{ cm}^{-1} \)

\( \nu_4 = 289 \text{ cm}^{-1} \)

In this calculation the mass of the light atom was taken as the mass of a nitrogen atom (atomic weight 14). If the value of 17 is taken for the mass of the whole ammonia molecule the calculated frequency is only very slightly altered (by about 5 cm\(^{-1}\)).
The value for the infrared active stretching frequency $\nu_3$ of 570 cm$^{-1}$ is not in very good agreement with the observed frequency of 511 cm$^{-1}$; nevertheless, these calculations involve a considerable degree of approximation and agreement within 10% is probably as good as could be expected. Certainly these figures do suggest that this vibration is not likely to occur at a frequency much lower than the Raman frequencies.

These results are interesting in the light of the suggestions by Barrow et al.\textsuperscript{50}, who, using a caesium bromide prism were able to extend the spectral range examined to 250 cm$^{-1}$. These authors found in many cases a strong band at much lower frequencies, which they assigned to the $\nu_{\text{N-N}}$ (stretching) vibration. There are, however, a number of inconsistencies in this paper: for [Pt(NH$_3$)$_4$]Cl$_2$.H$_2$O a band at 497 cm$^{-1}$ is assigned to the $\nu_{\text{Pt-N}}$ vibration, but for [Pt(NH$_3$)$_4$][PtCl$_4$] a band at ca. 300 cm$^{-1}$ is assigned to this vibration and there seems to be no reason for this marked difference in frequency, as the same ion is involved in each case. For cis and trans-Pt(NH$_3$)$_2$Cl$_2$ frequencies of 326 and 422 are reported and again it seems surprising that these frequencies are so different from those for the tetrammine. It seems very probable that the low frequency absorption near 300 cm$^{-1}$ is due to one of the bending
FIG. 11.

FUNDAMENTAL VIBRATIONS OF $\text{MX}_6$. 
FIG. II
FUNDAMENTAL VIBRATIONS OF MX
vibrational modes, and it is interesting to observe that the 
\( \gamma_4 \) vibration has a calculated frequency of 290 cm\(^{-1} \) and is 
in reasonable agreement with the lower frequencies reported 
by Barrow et al.\(^{50} \) of "near 300 cm\(^{-1} \)."

On the basis of the results reported in the present 
work it seems highly probable that the frequency observed 
for the platinum tetrammine of 511 cm\(^{-1} \) is correctly assigned 
to the \( \gamma_{\text{Pt-N}} \) stretching vibration and that the other authors 
have not used sufficiently concentrated samples of the 
ammines to detect the weak absorption bands found.

Similar calculations to those applied to the 
\([\text{Pt(NH}_3)_4]^{2+} \) ion can be applied to the more complicated case 
of an octahedral molecule of the type MX\(_6\). Calculations 
for molecules of this type are given by Heath and Linnett\(^{59} \), 
and the fundamental vibrations of this molecule are shown 
in Fig. 11.

The equations relating to the vibrational frequencies, 
given by Heath and Linnett are as follows:

\[
\lambda_1 = \frac{(k_1 + 3A)}{m_2}
\]
\[
\lambda_2 = \frac{(k_1 - \frac{8}{3} \frac{B}{R} + \frac{8}{3}A)}{m_2}
\]
\[
\lambda_3 + \lambda_4 = \frac{(k_1 - 2 \frac{B}{R} + 4A)\left(\frac{1}{m_2} + \frac{2}{m_4}\right) + (k + 3 \frac{B}{R} + 2A)}{m_4}
\]
\[
\left(\frac{4}{m_4} + \frac{1}{m_2}\right) - 4\sqrt{2}/m_4 (2\sqrt{2} A - \sqrt{2} \frac{B}{R})
\]
\[ \lambda_3 \lambda_4 = \frac{(k_1 - 2 \frac{B}{M} + 4A)(k + 3 \frac{B}{M} + 2A)}{- (2\sqrt{2} A - \sqrt{2} \frac{B}{M})^2 \left( \frac{1}{m_2^2} + \frac{6}{m_1m_2} \right)} \]

\[ \lambda_5 = \frac{(k + 2 \frac{B}{M} + 4A)}{m_2} \]

\[ \lambda_6 = \frac{(k + 2A)}{m_2} \]

In these equations \( \lambda_n = 4 \pi^2 \nu_n^2 \)

\( m_1 \) is the mass of the central atom (M) and \( m_2 \) is the mass of surrounding atoms (X).

\( k_1, k \) and A are constants. The term \( B/R \) is introduced to allow for the repulsion between non-bonded atoms, and is determined by the equation \( B/R = \frac{2}{7}A \). In the present work the term \( B/R \) is omitted from the equations as the single atom X is replaced by a group (NH3) and it is not likely that the same conditions apply to the interaction of these groups as in the case of simple atoms. The simplified equations are as follows:

(1) \( \lambda_1 = \frac{(k_1 + 8A)}{m_2} \)

(2) \( \lambda_2 = \frac{(k_1 + 8/3 A)}{m_2} \)

(3) \( \lambda_3 + \lambda_4 = \frac{(k_1 + 4A)(1/m_2^2 + 2/m_1)}{(k + 2A)(4/m_1 + 1/m_2)} - 16A/m_1 \)
\begin{align}
(4) & \quad \lambda_3 \lambda_4 = \left[ (k_1 + 4A)(k + 2A) - 8A^2 \right] \left( \frac{1}{m_2^2} + \frac{6}{m_1 m_2} \right) \\
(5) & \quad \lambda_5 = \frac{(k + 4A)}{m_2} \\
(6) & \quad \lambda_6 = \frac{(k + 2A)}{m_2} \\
\end{align}

The only octahedral ammine for which all three Raman active frequencies have been observed is the rhodium hexammine \([\text{Rh(NH}_3)_6]\text{Cl}_3\); for \([\text{Co(NH}_3)_6]\text{Cl}_3\) only the two higher frequencies of 575 and 485 have been observed. The Raman frequencies observed for \([\text{Rh(NH}_3)_6]\text{Cl}_3\) are as follows:
500 cm\(^{-1}\) (polarised), 475 cm\(^{-1}\) and 270 cm\(^{-1}\). These can clearly be assigned to the frequencies \(\nu_1\), \(\nu_2\) and \(\nu_5\) respectively (as with \([\text{Pt(NH}_3)_4]\text{Cl}_2\) the polarised frequency is identified with the "breathing" frequency \(\nu_1\)).

If we now take \(\lambda_n = C\nu_n^2\) and the mass of the group \(m_2\) as 17 and the mass of the central atom, \(m_1\) is 103, we can calculate \(A\), \(k_1\), and \(k\). Substituting in the equations above
\[
A = \frac{3}{16} \left( \nu_1^2 - \nu_2^2 \right) m_2 C = 7.770 \times 10^4 C \\
k_1 = \frac{1}{2} \left( 3 \nu_2^2 - \nu_1^2 \right) m_2 C = 3.628 \times 10^6 C \\
k = \left[ \nu_5^2 - \frac{3}{4}(\nu_1^2 - \nu_2^2) \right] m_2 C = 9.285 \times 10^5 C
\]
If the values of these constants are substituted in equations (3) and (4), it follows
\[ \lambda_3 + \lambda_4 = 4.021 \times 10^5 \text{ cm}^{-1} \]
\[ \lambda_3 \lambda_4 = 2.907 \times 10^{10} \text{ cm}^{-2} \]

Solving these equations:

\[ \lambda_3 = 3.076 \times 10^5 \text{ cm}^{-1} \]
\[ \lambda_4 = 9.45 \times 10^4 \text{ cm}^{-1} \]

Since \( \lambda_n = c \gamma_n^2 \), it follows:

\[ \gamma_3 = 545 \text{ cm}^{-1} \]
\[ \gamma_4 = 310 \text{ cm}^{-1} \]

No rhodium hexamine salt was available but \([\text{Rh(NH}_3)_5\text{Cl}]\text{Cl}_2\) was examined and a weak doublet was detected at 483 and 473 cm\(^{-1}\). This is the only case where a doubling of this skeletal frequency has been observed, though in several cases a broad band was obtained, notably in \([\text{Co(NH}_3)_6]\text{Cl}_3\). The probable reason for this effect is the crystal interactions of the molecules which often cause frequency splitting of this type. The infrared spectrum of \([\text{Rh(NH}_3)_5\text{Cl}]\text{Cl}_2\) is otherwise very similar to that of \([\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2\) and if it is assumed that as \([\text{Co(NH}_3)_6]\text{Cl}_3\) has a frequency \(\gamma_{\text{Co-N}}\) larger than \([\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2\), the same difference

* Two extremely weak but sharp absorption bands were also detected at 903 and 516 cm\(^{-1}\), but the origin of these is not apparent and may be due to an impurity.
would apply to rhodium hexammine, we would expect a frequency of about 490 cm$^{-1}$ for the vibration $\gamma_{\text{Rh-N}}$

This figure is considerably smaller than the calculated value of 545 cm$^{-1}$, but considering the approximations involved in the calculation the agreement is not unreasonable. The calculation certainly makes it clear that the infrared active stretching vibration is not likely to occur at much lower frequencies as this would increase the discrepancy between the calculated and observed values. It is interesting to note that the percentage difference between the calculated and observed values is very similar to that noted for the platinum tetrammine (about 10% in each case).

The simplified equations have also been applied to TeF$_6$, which is one of the molecules for which the original equations were proposed, so as to test the validity of the simplifications used in the equations. The values of the Raman frequencies observed are as follows; $\gamma_1 = 701$ cm$^{-1}$, $\gamma_2 = 674$ cm$^{-1}$ and $\gamma_5 = 313$ cm$^{-1}$ and the application of these simplified equations to this case gives $\gamma_3 = 770$ cm$^{-1}$ and $\gamma_4 = 330$ cm$^{-1}$, the experimental values being 752 cm$^{-1}$ for $\gamma_3$ and an estimated value of from 340 to 380 cm$^{-1}$ for $\gamma_4$, which was not observed directly. The reasonable agreement of calculated and experimental values in this case justifies the use of the simplified equations chosen.
Frequencies near 500 cm$^{-1}$ which can similarly be ascribed to skeletal vibrations of this type have now been detected for a number of ammines, and most of these have been recorded in Table I. These include cis and trans [Pt(NH$_3$)$_2$Cl$_2$], [Pd(NH$_3$)$_4$]Cl$_2$, cis and trans [Pd(NH$_3$)$_2$Cl$_2$], [Co(NH$_3$)$_5$Cl]Cl$_2$, [Rh(NH$_3$)$_5$Cl]Cl$_2$ and [Co(NH$_3$)$_6$]Cl$_3$. With the latter compound the band proved extremely difficult to detect as it was extremely weak and broad. Most of the other ammines examined in this work were much less stable and their skeletal frequencies appeared to be too low for detection with potassium bromide optics. An indication of a band near 400 cm$^{-1}$ was obtained for [Cu(NH$_3$)$_4$]Cl$_2$, but it was not possible to identify the frequency exactly; however, this is the spectral region where an infrared active band might be expected by comparison with the observed Raman frequencies.
SPECTRA OF CONCENTRATED NUJOL MULLS
900 to 400 cm\(^{-1}\)

\[ [\text{Rh} (\text{NH}_3)_5 \text{Cl}] \text{Cl}_2 \]

\[ \nu_{\text{Rh-N}} \]

\[ [\text{Pd} (\text{NH}_3)_2 \text{Cl}_2] \]

\[ \nu_{\text{Pd-N}} \]
CHAPTER X.

STABILITY OF COMPLEXES AND THE INFRARED SPECTRA
OF METAL AMMINES.

One of the most widely investigated quantitative properties of complexes is their stability, and numerous methods have been used in its determination. No stability constants have been determined in the course of this work and the values used have been taken from the literature, notably the table of collected data published by Bjerrum. These values were mostly determined in dilute aqueous solution, in the presence of neutral salts to preserve constant ionic strength, and at normal laboratory temperature.

It is appreciated that there is only an indirect relationship between the stability constants and the bond strength, related in turn to the vibration frequencies of the complexes; nevertheless the two properties are generally expected to follow similar trends, i.e. strong bonding of a group should lead to a high value for the stability constant.

Let us first consider the factors involved in each case, taking first the stability constant, as usually defined by the equation

\[ k = \frac{[MA_x]}{[M][A]^x} \]

as from the equation \( M + xA \rightleftharpoons MA_x \).
However, this does not allow for the hydration of the metal ion $M$, and a modified constant is more accurately used, based on the equation

$$M(H_2O)_x + xA \rightleftharpoons MA_x + xH_2O$$

$$k' = \frac{[MA_x][H_2O]^x}{[M][A]^x}$$

For the addition of one group $A$, the two constants are related as follows: $\log k' = \log k + \log 55$ (55 being molar concentration of water).

For the comparisons used here $\log k'$ average is used, being the average value of the constant for the addition of groups up to the normal maximum coordination numbers.

If the equilibrium constant for the reactions is known, it can be used as a measure of the free energy of formation of the complex, since $\Delta G = -RT \log k$, and since the temperature range of stability determination is small and can usually be ignored, $\Delta G \propto \log k'$. Actually a better measure of the bond strengths would be obtained by use of $\Delta H$, the heat of formation, rather than $\Delta G$, the change in free energy. These are related by the expression $\Delta G = \Delta H - T \Delta S$ and $\Delta H$ can be found if stability constants at different temperatures are available. These have been
examined only rarely in the past, and usually it is only possible to use $\Delta G$ and assume that $\Delta S$ is small, or at least does not vary much from case to case. This is probably justified where

(a) one unidentate group replaces another,

(b) the replaced group has the same charge (See Burkina$^{60a}$).

These conditions are satisfied in the formation of ammines from the hydrated ions which are being considered in this work.

When the vibration characteristics of a molecule are considered, the stretching vibrations will give the most accurate measure of the strength of the bond as indicated by the stretching force constant. If we consider a typical molecule such as $[\text{Pt(NH}_3\text{)}_4]^2+\text{Cl}_2^-$, the stretching frequencies of the Pt–N bond can be reproduced as shown below:

```
$\text{Pt} \quad \text{Pt} \quad \text{Pt} \quad \text{Pt}$
```

Raman active  Infrared active

It is clear that the Raman active vibrations do not involve movement of the platinum atom itself, thus variation in the mass of the central atom will not affect the vibration frequencies and the measured frequencies can be directly
as a measure of the force constant of the bond; on the
other hand, the infrared active frequency will be affected
by the mass of the central metal, particularly with the
lighter metals. Thus the most accurate measure of the
bond strength should result from using the totally sym-
metric, or "breathing" Raman active frequency. Similar
considerations will apply to other symmetries, such as
tetrahedral and octahedral. This is easily identified as
it is fully polarised in each case and often has the
highest frequency.

The nitrogen-hydrogen vibrations should also
give an indirect measure of the bond strength. The
change in the nitrogen-hydrogen vibrational frequency as
an ammonia group is coordinated to a metal ion is probably
associated with the change in bond type. This effect can
be observed if the corresponding frequencies of ammonia
and the ammonium ion are compared, where the stretching
force constant for the N-H bond changes from $6.5 \times 10^{-5}$
dynes/cm$^2$ to $5.4 \times 10^{-5}$ dynes/cm$^2$. The indirect nature
of these frequencies reduces their value as a measure of
bond strength; in addition, hydrogen bonding may be of
significance in solid state spectroscopy, and in some
cases it has been suggested that direct bonding of the
hydrogen atom to the platinum takes place due to an
FIG. 14

\[ \gamma_{M-N} \]

- ○ Infrared frequency
- X Raman frequency

- \( \text{Cu}^{2+} \)
- \( \text{Co}^{3+} \)
- \( \text{Zn}^{2+} \)
- \( \text{Al}^{3+} \)
- \( \text{Hg}^{2+} \)
overlap of a platinum "d" orbital with the hydrogen orbital. They are, however, less affected by variation of the mass of the central metal ion and by the symmetry of the particular ammine.

In the graphs opposite, the values of log \( k_{\text{average}} \) + log 55 are plotted against values of the following frequencies, (a) \( S_{\text{sym}} \) \( \text{NH}_3 \) (Fig. 12), (b) \( S_{\text{rock}} \) \( \text{NH}_3 \) (Fig. 13), (c) \( \nu_{\text{M-N}} \) (Raman active) and \( \nu_{\text{M-N}} \) (infrared active) (Fig. 14).

It is observed that there is a fairly close general relationship between the properties compared, and the use of infrared data should enable an approximate estimate to be made of the value of the stability constant for a simple anion. This may be of particular value where the stability constant is difficult to obtain directly, as in cases where the hydrated metal ion is unstable. An example of this is the platinous ion. Taking the known values of the vibration frequencies as indicated on Table I, we can estimate the stability constant (log \( k \) + log 55). Using the curves in Fig. 12 we obtain the value of 7.8, and using Fig. 14, 7.5. The constant cannot be determined directly as the ion \([\text{Pt(H}_2\text{O)}_4]^2^+\) is unstable in solution.
CHAPTER XI.

THE TRANS-EFFECT IN PLATINOUS COMPLEXES.

The power of certain ligands to promote substitution at a trans position in planar complexes has been known for a considerable time, one of the first examples being the production of cis or trans platinoous dichlorodiammine depending on whether coordinated chlorine is displaced by ammonia or vice versa.

(a) \([\text{Pt}(\text{NH}_3)_4]^{2+} + 2\text{Cl} \rightarrow \text{trans-Pt(NH}_3)_2\text{Cl}_2\]

or

(b) \([\text{PtCl}_4]^{2-} + 2\text{NH}_3 \rightarrow \text{cis-Pt(NH}_3)_2\text{Cl}_2\]

In these reactions, chlorine is the trans directing group and so diagrammatically it can be seen how reactions (a) and (b) arise, since in (a), after one ammonia has been replaced we have the compound shown in I, where the ammonia at (4), being trans to chlorine is the next to be replaced

\[
\begin{align*}
(1) \text{NH}_3 & \quad \text{Cl} & \quad (2) \quad \text{NH}_3 & \quad \text{Cl} \\
(4) \text{NH}_3 & \quad \text{NH}_3 & \quad (3) & \quad \text{Cl} & \quad \text{Cl} \\
\text{Pt} & & & & \text{Pt}
\end{align*}
\]

I

whereas in (b) the compound produced after one chlorine is replaced is as shown in II, where it is clear that the next chlorine to be replaced will be either (2) or (4), leading
in either case to the formation of the cis isomer.

It is possible on the basis of the substitution reaction to arrange ligands in a series of increasing trans directive effect, although the exact order is sometimes doubtful. Russian workers quoted by Chatt, Duncanson and Venanzi\textsuperscript{61} give the following ligands in order of increasing trans-directive power:

\[ \text{H}_2\text{O} < \text{OH} < \text{NH}_3 < \text{R NH}_2 < \text{pyridine} < \text{Cl} < \text{Br} < \text{CN} < \text{I} < \text{NO}_2 \]

\[ \text{SO}_3\text{H} < \text{PR}_3 < \text{R}_2\text{S} < \text{SO(NH}_2)_2 < \text{NO} < \text{CO} < \text{C}_2\text{H}_4 < \text{CH} \]

The cause of the trans effect was until recently generally assumed to be the weakening of the metal-ligand bond trans to the directive group, and thus favouring dissociation of the complex, so that a rapid attachment of the substituting group can take place. This will give effectively an \( S_{\text{N}}^1 \) type of mechanism

\[
\begin{align*}
\text{X} & \quad \text{L} \quad \text{M} \quad \text{X} \\
\text{L} \quad \text{M} \quad \text{X} & \quad \text{L} \quad \text{M} \quad \text{X} \\
\text{weakened} & \quad \text{rate determining} \\
\text{X} & \quad \text{X}
\end{align*}
\]

\[ \text{L} \quad \text{M} \quad \text{Y} \]

\[ \text{L} \quad \text{M} \quad \text{Y} \]

\[ \text{L} \quad \text{M} \quad \text{Y} \]

Guagliano and Schubert\textsuperscript{62} have reviewed many examples of the trans effect and have discussed the cause
of it in terms of such a dissociative mechanism. More recently Chatt, Duncanson and Venanzi have suggested that the cause of the trans effect was not the weakening of the bond of the trans ligand but that the trans-directive groups are able to withdraw electrons from "d" orbitals of the metal, thus causing an electron deficiency, mainly trans to the directive group. This would promote attack by another ligand at this position through an $S_N^2$ type mechanism.

\[
\begin{array}{ccc}
X & \rightarrow & X \\
\downarrow & & \downarrow \\
L & \rightarrow & L \\
M & \rightarrow & M \\
X & +X & +Y \\
\end{array}
\]

The withdrawal of electrons from the metal orbitals can take place in the platinum complexes by the formation of a $\pi$ bond in addition to the normal $\sigma$ bond, using a 5d6p hybrid orbital of the platinum combined with an orbital of the ligand having the correct symmetry characteristics. The evidence for this form of back coordination comes mainly from dipole measurements, where for example the bond dipole moment of the ethylene-platinum bond is much lower than expected for a measured simple coordinate bond.

Ligands which cannot readily form a double bond of this type, such as water, ammonia and amines, are only weakly trans directive, whereas groups such as trialkyl
phosphine, dialkyl sulphides or olefines, which have available orbitals of the required type are strongly trans-directive.

The limited kinetic evidence available supports the view of Chatt and his co-workers\textsuperscript{10,61} on the nature of the substitution process and, for example, in studies of the rate of exchange using radioactive isotopes in the reaction:

$$K_2^3\text{Pt}X_4 + \text{NH}_4^\text{X}^+ \rightarrow K_2^3\text{Pt}X_3^+ + \text{NH}_4\text{X}$$

$$(X = \text{Cl, Br, I or CNS})$$

where it is found that the exchange is more rapid with the more stable complexes; this could not be explained on the basis of a dissociative type mechanism\textsuperscript{63}.

It would clearly be of value to obtain some evidence as to change of strength in the metal-ligand bond with trans ligands of varying trans directive strength in order to see if there is any appreciable bond weakening which might facilitate dissociation. Chatt, Duncanson and Venanzi\textsuperscript{10} have attempted to obtain information on the strength of the metal-nitrogen bond when organic amines are coordinated trans to ligands of varying trans directive power. Their results are based on the variation of the frequencies and intensities of the absorption bands due to the nitrogen-hydrogen stretching frequencies in various
The amines used included piperidine, p-toluidine and ligands of widely varying types. These authors were able to show that the nitrogen-hydrogen stretching frequencies did not follow the order of the trans directive strengths of the ligands and thus concluded that weakening of the metal-nitrogen bond was not an important factor in determining the trans directive power of a ligand.

The study of nitrogen-hydrogen vibrations can only give indirect evidence of the nature of the metal-nitrogen bond and although it may be possible on this basis to obtain a fairly reliable comparison of bond strengths in a series of closely related compounds, no estimate can be made of the numerical value of bond strength differences. These are essential if the possible contribution of bond weakening to the trans effect is to be considered.

The identification of the metal-nitrogen skeletal stretching frequencies for a number of different metal ammines (see Chap. IX) affords a means of obtaining a much more direct comparison of the bond strength when the ammonia group in a complex is trans to various ligands. Ammonia is a particularly useful group with which to examine the
directive effect of other groups as it shows no significant trans directive effect and it is not likely to form a \( \pi \) bond with the electrons of the metal ion as it has no suitable orbital available.

In an initial series of experiments cis and trans isomers of the type \( \text{Pt} (\text{NH}_3)_2^\text{X}_2 \) were compared, as in the cis isomer both groups are trans to \( X \), whereas in the trans isomer they are trans to each other.

\[
\begin{array}{ccc}
\text{NH}_3 & X & \text{NH}_3 \\
X & \text{NH}_3 & X
\end{array}
\]

The main difficulty in comparing compounds of this type is that in the trans compound there is only one infrared active metal-nitrogen stretching vibration, whereas in the cis compound there are two and it is therefore difficult to decide on the correct vibrations to compare (the most reasonable method would be to compare average frequencies of the two vibrations of the cis compound with that of the trans). In practice, although both absorption frequencies were detected for cis palladium dichlorodiammines, only one was detected with the corresponding compounds involving the heavier platinum atoms.

A more satisfactory group of compounds is that of
### TABLE V.

<table>
<thead>
<tr>
<th>Main Infrared Absorption Frequencies of Palladium&lt;sup&gt;II&lt;/sup&gt; and Platinum&lt;sup&gt;II&lt;/sup&gt; Complexes (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Palladium Complexes</td>
</tr>
<tr>
<td>(b) Platinum Complexes</td>
</tr>
</tbody>
</table>
### TABLE V.
Main Infrared Absorption Frequencies of Palladium$\text{II}$ and Platinum$\text{II}$ Complexes (cm$^{-1}$)

(a) Palladium Complexes

<table>
<thead>
<tr>
<th>trans</th>
<th>cis</th>
<th>trans</th>
<th>cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(NH$_3$)$_2$Cl$_2$</td>
<td>Pd(NH$_3$)$_2$Cl$_2$</td>
<td>Pd(NO$_2$)$_2$(NH$_3$)$_2$</td>
<td>Pd(NO$_2$)$_2$(NH$_3$)$_2$</td>
</tr>
<tr>
<td>496*</td>
<td>497*</td>
<td>496*</td>
<td>463*</td>
</tr>
<tr>
<td>752</td>
<td>477*</td>
<td>477*</td>
<td></td>
</tr>
<tr>
<td>1246</td>
<td>1605</td>
<td>3230</td>
<td>3320</td>
</tr>
<tr>
<td>3230</td>
<td>3320</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The 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.

* Due to $\gamma$ Pd-N vibration.

See Table VI for higher frequencies.

"NO$_2$" absorption below 650 cm$^{-1}$ omitted.
TABLE V.

(b) Platinum Complexes
### Table V.

**Main Infrared Absorption Frequencies of Palladium and Platinum Complexes (cm⁻¹)**

(b) Platinum Complexes

<table>
<thead>
<tr>
<th>trans</th>
<th>cis</th>
<th>cis</th>
<th>cis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pt(NH₃)₂Cl₂</strong></td>
<td><strong>Pt(NH₃)₂Cl₂</strong></td>
<td><strong>Pt(NH₃)₂(NO₂)Cl</strong></td>
<td><strong>Pt(NH₃)₂(NO₂)₂</strong></td>
</tr>
<tr>
<td><strong>trans</strong></td>
<td><strong>cis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>507 ν</td>
<td>508 ν</td>
<td>ca. 510 ν</td>
<td>-</td>
</tr>
<tr>
<td>828 m</td>
<td>805 m</td>
<td>533 s</td>
<td>No Pt–N frequency detected</td>
</tr>
<tr>
<td>1288 s (1305)</td>
<td>1300 s</td>
<td>545 s</td>
<td>due to very strong NO₂ absorption</td>
</tr>
<tr>
<td>1538 w.</td>
<td>1536 w.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1638 w.</td>
<td>1630 w.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3170 cm.</td>
<td>3270 cm. (3200)</td>
<td>Not examined in rock salt region.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>trans</th>
<th>cis</th>
<th>cis</th>
<th>cis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(Et₂S)₂PtCl₂</strong></td>
<td><strong>(Et₂S)₂PtCl₂</strong></td>
<td><strong>(Et₂S)₂PtCl₂</strong></td>
<td><strong>K[Pt(C₂H₄)₂]</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>(NH₃)₂PtCl₂</strong></td>
</tr>
<tr>
<td><strong>trans</strong></td>
<td><strong>cis</strong></td>
<td><strong>trans(Et₂S)₂</strong>(NH₃)₂PtCl₂</td>
<td><strong>K[Pt(C₂H₄)₂]</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>(NH₃)₂PtCl₂</strong></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>677</td>
<td>677 m</td>
<td>500 ν ν s</td>
<td>481 ν w.</td>
</tr>
<tr>
<td>679 m</td>
<td>620 ν</td>
<td>550 broad (H₂O)</td>
<td></td>
</tr>
<tr>
<td>726 w.</td>
<td>625 w.</td>
<td>617 w.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>717 m</td>
<td>735 m.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>820 w.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1011 m</td>
<td>1010 m (1023)</td>
</tr>
<tr>
<td>Not examined in rock-salt region</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1037 w.</td>
<td>1023 s.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1045 w.</td>
<td>1240 w.</td>
<td>1255 s.</td>
<td>-</td>
</tr>
<tr>
<td>1245 w.</td>
<td>-</td>
<td>1267 s.</td>
<td>-</td>
</tr>
<tr>
<td>1284 s.</td>
<td>1425 s.</td>
<td>1422 m.</td>
<td>-</td>
</tr>
<tr>
<td>1317 w.</td>
<td>1612 s.</td>
<td>1610 m.</td>
<td>-</td>
</tr>
<tr>
<td>1631 m.</td>
<td>3480 m.</td>
<td>3300 m.</td>
<td>-</td>
</tr>
<tr>
<td>3170 w.</td>
<td>3540 m.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3260 w.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* 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.

* These frequencies have been recorded previously.

* Due to v Pt–N vibration.
where only a single frequency would be expected for the $\gamma_{Pt-N}$ vibration. In this work a series of compounds of this type, of which trans-$[Pt(NH_3)_2Cl_2]$ is the first member, has been examined.

The compounds examined and the frequencies observed are contained in Table V. In addition to the spectra in the potassium bromide region, spectra in the rock salt region have also been determined in some cases where they show features of special interest, or to confirm the purity of particular isomers. Wherever possible, spectra of related compounds, but not containing an ammonia group, have been included to confirm the identification of the $M-N$ frequency.

The similarity of the $\gamma_{M-N}$ frequencies observed for cis and trans $[Pt(NH_3)_2Cl_2]$ indicates that chlorine has no appreciable bond weakening effect on the Pt-N bond. In the corresponding compounds for palladium the presence of the chlorine atoms does appear to give some bond weakening, as the double frequencies observed for the cis compound (497 and 477) have an average value of 487 cm$^{-1}$, appreciably
less than the single frequency of 496 cm$^{-1}$ found for the trans isomer.

The results for cis and trans nitroammines are much less conclusive as the detection of the weak $\nu_{\text{Pt-NH}_3}$ frequency is difficult because of the very strong absorption band due to the nitro group vibration in the same region. In the case of cis and trans-Pd(NH$_3$)$_2$(NO$_2$)$_2$, the average of the two frequencies observed for the cis compound (496 and 463 cm$^{-1}$) is 480 cm$^{-1}$, which is considerably lower than the frequencies observed for other palladium ammines (e.g. [Pd(NH$_3$)$_4$]Cl$_2$ = 498 cm$^{-1}$) but it was not possible to detect the $\nu_{\text{Pd-N}}$ absorption in the corresponding trans dinitrodi-ammine. Similar difficulty was found with the platinum nitro compounds, where no absorption band due to $\nu_{\text{Pt-NH}_3}$ could be definitely detected in cis Pt(NH$_3$)$_2$(NO$_2$)$_2$, though a very weak band at ca. 510 cm$^{-1}$ seemed to indicate that the nitro group exerts little weakening on the Pt–NH$_3$ bond. The band is too weak, however, for a definite conclusion to be reached.

It is apparent that though both chlorine and the nitro group cause some weakening in the trans M–NH$_3$ bond in the palladium compounds, no such bond weakening is observed with the platinum compounds. However, when the series of compounds of the type trans [LPTCl$_2$·NH$_3$] is examined, the
frequency of the $\nu_{\text{Pt-NH}_3}$ vibration shows a marked change as shown by the $\nu_{\text{Pt-N}}$ frequencies observed.

\[
\begin{align*}
L &= \text{NH}_3 & = 508 \text{ cm}^{-1} \\
L &= \text{Et}_2\text{S} & = 493 \text{ cm}^{-1} \\
L &= \text{C}_2\text{H}_4 & = 481 \text{ cm}^{-1}
\end{align*}
\]

In view of the large mass of the platinum atom it is probable that the stretching frequency of the Pt-N bond does not interact with other vibrations in the remainder of the molecule. It can therefore be assumed that the $\nu_{\text{Pt-N}}$ vibration of the Pt-NH$_3$ system can be treated as that of an effectively diatomic molecule. In such a case the frequency $\nu$ is related to the force constant $k$ by the relation

\[
\nu = \sqrt{\frac{k}{\frac{1}{m_1} + \frac{1}{m_2}}} \frac{2\pi}{L}
\]

where $m_1$ and $m_2$ are the masses of the atoms concerned.

It follows that if $\nu_1$ and $\nu_2$ are vibration frequencies of the same group in two different complexes

\[
\frac{k_1}{k_2} = \left(\frac{\nu_1}{\nu_2}\right)^2
\]

Inserting the values quoted above for the $\nu_{\text{Pt-N}}$ frequency in trans-Pt(NH)$_2$Cl$_2$ and trans-Pt(NH$_3$)(C$_2$H$_4$)Cl$_2$ we find the force constant in the latter is 10% smaller than the former.
The order of the bond weakening for these groups is the same as that reported by Chatt, Duncanson and Venanzi\textsuperscript{10}, based on the nitrogen-hydrogen stretching frequencies, but the extent of the weakening is greater than might have been expected on these results. For the effect of various trans groups on the nitrogen-hydrogen stretching frequencies of the compounds trans-[Pt L, piperidine, Cl\textsubscript{2}] in dilute carbon tetrachloride solution Chatt gives the following values: \( L = \text{piperidine} \) 3222 cm\textsuperscript{-1}; \( L = \text{Et}_2\text{S} \), 3223 cm\textsuperscript{-1}; \( L = \text{C}_2\text{H}_4 \) 3230 cm\textsuperscript{-1}, the change in the case of \( \text{C}_2\text{H}_4 \) being about 0.27\%. The band intensities suggest a rather greater difference in bond strengths, and for the same complexes the values of 10\textsuperscript{7} B are given as 1.68, 1.66 and 1.59 respectively.

Several factors may account for the lack of exact correlation between these different methods of assessing bond strengths, the most obvious being that the first ligand of the series in the work described here is ammonia, whereas Chatt and his co-workers 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 vibration frequency due to \( \gamma_{\text{M-N}} \) but it is probable that the changes in frequency due to this effect are very small. The effect
was minimised by Chatt and his co-workers by the use of dilute carbon tetrachloride solutions. It has also been suggested 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 $\gamma_{N-H}$ vibration. This factor will still be present even in dilute solution.

It would be useful to obtain some quantitative measure of the effect in terms of stability constants of the ammines as this would indicate the magnitude of the effect on the tendency of an ammonia group to dissociate. The greatest change in the value of the $\gamma_{Pt-N}$ is from 508 cm$^{-1}$ to 481 cm$^{-1}$ when ammonia is replaced by ethylene and reference to the graph in Fig. 14, Chap. X, relating stability constants and vibration frequencies indicates that the difference of 27 cm$^{-1}$ should correspond to a change in log $k$ of about 0.7.

These considerations show that in platinous complexes, although chlorine, and probably the nitro group, does not exert any bond weakening effect on a trans ammonia group, other groups, notably ethylene and to a lesser extent diethyl sulphide, do have an appreciable bond weakening effect. With the latter groups the extent of bond weakening is sufficient to have a significant effect on the tendency of the ammonia group to dissociate and in the
consideration of substitution reaction it is clear that the increased tendency to dissociation must have some influence on the course of the reaction, though there is no evidence that it is the sole or controlling factor in the trans directing properties of ligands. Indeed the fact that some ligands, such as chlorine, have an appreciable trans directive power without causing any bond weakening in a trans group shows that dissociation is not essential to the trans effect.

In the case of palladous complexes, less compounds have been examined, but it does appear that bond weakening of the trans group is much more common than with platinum, though the position is complicated by the two frequencies which appear for the oie isomers. If the average of these two frequencies is taken as comparable with the single frequency of the trans isomer, there is a distinct bond weakening effect, even with chlorine and the nitro group, which appear to produce no weakening in the case of platinous complexes.
CHAPTER XII.

VIBRATIONAL FREQUENCIES OF LIGANDS OTHER THAN AMMONIA.

Incidental to the study of the ammine complexes several features have been noted concerning other coordinated groups. These have not generally been examined in great detail, but some of the features of interest in them are discussed in this chapter.

Part I. The nitro group - NO₂

Spectra of several compounds containing this group have been examined, mainly with a view to the examination of the properties of this group in relation to the trans effect (Chap. XI). One of the most characteristic frequencies observed in these compounds is a strong absorption band near the range 500-600 cm⁻¹ and the interesting feature of this band is its marked sensitivity to the presence of other substituents in the complex. For example, in the series of palladium II nitro ammines this band occurs at the following frequencies:

\[
\begin{align*}
\text{cis-Pd(NH₃)₂(NO₂)₂} & \quad 509 \text{ cm}^{-1} \\
\text{trans-Pd(NH₃)₂(NO₂)₂} & \quad 490 \text{ cm}^{-1}
\end{align*}
\]

This is in marked contrast to the platinous ammines where the \(\nu_{\text{Pt-N}}\) frequency only changes from 511 to 508 cm⁻¹.
**TABLE VI.**

Main Absorption Bands of Nitro Complexes of Palladium II, Platinum II and Cobalt III.
### TABLE VI.

Main absorption Bands of Nitro Complexes of Palladium II, Platinum II and Cobalt III.

<table>
<thead>
<tr>
<th>(K_2\text{Pd(NO}_2\text{)}_4)</th>
<th>(\text{trans-Pd(NH}_3\text{)}_2\text{(NO}_2\text{)}_2)</th>
<th>(\text{cis-Pd(NH}_3\text{)}_2\text{(NO}_2\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1436 s.</td>
<td>1650 m. (broad) (NH(_3))</td>
<td>1630 m. (NH(_3))</td>
</tr>
<tr>
<td>1387 s.</td>
<td>1390 s.</td>
<td>1395 s.</td>
</tr>
<tr>
<td>1335 s.</td>
<td>1330 s.</td>
<td>1334 s.</td>
</tr>
<tr>
<td>1258 s. (NH(_3))</td>
<td>1255 s. (NH(_3))</td>
<td></td>
</tr>
<tr>
<td>817 s.</td>
<td>816 s.</td>
<td>834 m.</td>
</tr>
<tr>
<td>785 m. (NH(_3))</td>
<td>(809) 804 s. ? (NH(_3))</td>
<td>754 m.</td>
</tr>
<tr>
<td>574 s.</td>
<td>586 s.</td>
<td>509 s.</td>
</tr>
<tr>
<td>554 s.</td>
<td>490 s.</td>
<td>457 s.</td>
</tr>
<tr>
<td>546 s.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(K_2\text{Pt(NO}_2\text{)}_4)</th>
<th>(\text{cis-Pt(NH}_3\text{)}_2\text{Cl(NO}_2\text{)})</th>
<th>(\text{cis-Pt(NH}_3\text{)}_2\text{(NO}_2\text{)}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1442 s.</td>
<td></td>
<td>1339 m. (NH(_3))</td>
</tr>
<tr>
<td>1416 s.</td>
<td></td>
<td>1555 m. (NH(_3))</td>
</tr>
<tr>
<td>1395 s.</td>
<td></td>
<td>1417 s.</td>
</tr>
<tr>
<td>1350 s.</td>
<td></td>
<td>1384 s.</td>
</tr>
<tr>
<td>(836) 828 s.</td>
<td></td>
<td>1350 m.</td>
</tr>
<tr>
<td></td>
<td>Not examined in Sodium Chloride region</td>
<td>1303 s. (NH(_3))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(837) 830 s. ? (NH(_3))</td>
</tr>
<tr>
<td>631 s.</td>
<td>800 m.</td>
<td>798 m</td>
</tr>
<tr>
<td>593 s.</td>
<td>589 m</td>
<td></td>
</tr>
<tr>
<td>577 s.</td>
<td>574 s.</td>
<td></td>
</tr>
<tr>
<td>Element</td>
<td>Value 1</td>
<td>Value 2</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Al</td>
<td>1.23</td>
<td>4.56</td>
</tr>
<tr>
<td>B</td>
<td>2.34</td>
<td>5.67</td>
</tr>
</tbody>
</table>

**TABLE VI. (cont'd)**

**Cobalt**

<table>
<thead>
<tr>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.23</td>
<td>4.56</td>
<td>7.89</td>
</tr>
<tr>
<td>2.34</td>
<td>5.67</td>
<td>8.90</td>
</tr>
</tbody>
</table>
### TABLE VI. (cont'd)

**Cobalt**

<table>
<thead>
<tr>
<th>( \text{Na}_3\text{Co(NO}_2\text{)}_6 )</th>
<th>trans-[\text{Co(NH}_3\text{)}_4\text{(NO}_2\text{)}_2\text{]}\text{Cl}</th>
<th>( \text{Co(NH}_3\text{)}_3\text{(NO}_2\text{)}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1430 s.</td>
<td>1612 m. (NH(_3))</td>
<td>1629 m. (NH(_3))</td>
</tr>
<tr>
<td>1418 s.</td>
<td>1523 w. (NH(_3))</td>
<td>1423 s.</td>
</tr>
<tr>
<td>1328 s.</td>
<td>1427 m.</td>
<td>1361 m.</td>
</tr>
<tr>
<td>1318 s.</td>
<td>1297 u. (NH(_3)) and (NO(_2))?</td>
<td>1320 s.</td>
</tr>
<tr>
<td>838 s.</td>
<td>(842) 830 w.</td>
<td>1287 s. (NH(_3))</td>
</tr>
<tr>
<td>638 m.</td>
<td>809 m.</td>
<td>1248 s. (NH(_3))</td>
</tr>
<tr>
<td>613 m.</td>
<td>500 m.</td>
<td>(815) (798) m. (NH(_3))</td>
</tr>
<tr>
<td>521 w.</td>
<td>474 w. (NH(_3))</td>
<td></td>
</tr>
<tr>
<td>443 w.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
when going from the tetrammine to the dichlorodiammine.

In order to examine this question further some other metal nitro complexes were examined, and the frequencies obtained are given in Table VI, and illustrated on pages 138 to 140 at the end of this section.

The spectrum of \( \text{Na}_3[\text{Co(NO}_2)_2] \) has been examined previously in the rock salt region\(^6^4\) and, in addition to the bands recorded in Table VI, a number of weak bands at frequencies > 1500 cm\(^{-1}\) have been recorded and appear to be due to overtones and combination frequencies of fundamental bands.

It is more difficult to assign the frequencies with the nitro complexes than with the amines, as the mass of the nitrogen and oxygen of the group are often comparable in mass to the metal atom concerned, and interaction between the fundamental vibrations is more likely. This is particularly so when cobalt, having an atomic weight of only 59, is concerned. For this reason the assignment of frequencies is likely to be easier in the cases of platinum (atomic weight 195) and palladium (atomic weight 101). Some idea of the assignment of the frequencies observed can be obtained by comparison with the spectrum of nitryl chloride on which a complete assignment of frequencies has been made\(^6^5\), and details of which are summarised in Table VII.
When chlorine is replaced by a heavier metal atom and assuming there is no marked change in the bond type, these frequencies are expected to be modified as follows: - \( \nu_1 \), \( \nu_2 \) and \( \nu_4 \) should be only affected relatively slightly, due to the restriction of the vibration of the nitrogen atom; \( \nu_3 \), \( \nu_5 \) and \( \nu_6 \) would all have their frequency reduced. In view of these considerations in a metal nitro compound the frequencies for \( \nu_5 \) and \( \nu_6 \) will lie below the limit of the potassium bromide prism used (400 cm\(^{-1}\)).

When Table VI is examined it can be seen that

**TABLE VII**
Vibrational Assignments of Infrared Absorption Bonds in Nitryl Chloride.

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>( \nu \text{ sym } N-O )</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>( \delta N-O \text{ in-plane} )</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>( \nu \text{ Cl-N} )</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>( \nu \text{ asym } N-O )</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>( \delta \text{ Cl-N in-plane} )</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>( \delta \text{ bend out-of-plane} )</td>
</tr>
</tbody>
</table>
there are in each compound four main absorption frequencies or pairs of frequencies. In the platinum tetranitro complex there is a pair of frequencies at 1442 and 1416 cm\(^{-1}\) and a pair at 1395 and 1350 cm\(^{-1}\), and these can be clearly assigned, by comparison with Table VII, as \(\nu_4\) and \(\nu_1\) respectively, the symmetrical and asymmetrical nitrogen-oxygen stretching vibrations. These are much closer in frequency than in nitryl chloride, where the separation is 392 cm\(^{-1}\), but this effect would be expected when the chlorine atom is replaced by a heavier metal atom. The doubling of the frequencies is probably due to the steric interaction of the adjoining nitro groups. A model of this compound, as far as possible to scale, showed that considerable interaction of the nitro groups would in fact take place.

The assignment of the lower frequencies is much less certain. For example, with K\(_2\)Pt(NO\(_2\))\(_4\), the frequency assigned to \(\nu_{\text{Pt-N}}\) could be either 828 cm\(^{-1}\) or the double peak at 634 and 605 cm\(^{-1}\), though the former seems larger than would be expected in comparison with the values for the frequency found for the ammine complexes. It would be possible for a reversal of the expected order of these two frequencies to take place if the nitrogen atom is bonded to the metal by a double bond, which could arise by "back coordination" of "d" electrons of the metal to the nitrogen; this has already been suggested to account for
the trans directive effect of some ligands. The two extreme types of bonding can be represented as follows:

\[
\begin{align*}
\text{(a)} & \quad \text{M} - \text{N} - \text{O} \\
\text{(b)} & \quad \text{M} - \text{N} - \text{O}
\end{align*}
\]

It follows that in the transition form (a) to (b) the strengthening of the M—N bond will be matched by a corresponding weakening of the M—O bond. If the bonding in NO₂Cl is of the type (a) where the frequency \( \nu_2 > \nu_3 \), it would be possible for this order to be reversed, in spite of the mass affect, if the bonding changed appreciably to type (b).

There seems no certain way of distinguishing these frequencies, though it seems likely that the higher frequency (near 800 cm⁻¹) is the \( \nu_3 \), as the comparatively high frequency of this bond would imply considerable double bonding of the type shown in (b); this would cause a considerable weakening of the M—O bonds and account for the lowering in frequency \( \nu_2 \) from 794 cm⁻¹ in nitryl chloride to the frequency in the region 600–650 cm⁻¹ (often doublet) found for the metal nitro compounds. This assignment of frequencies \( \nu_2 \) and \( \nu_3 \) is supported by the changes in value of the lower frequencies in the series of palladium nitroanamines shown in Table VII. If the lower two
frequencies are considered, it is seen that the average value of these decreases in the order

\[
\text{cis-Pd(NH}_3\text{)}\text{2(NO}_2\text{)}\text{2, trans-Pd(NH}_3\text{)}\text{2(NO}_2\text{)}\text{2, [Pd(NO}_2\text{)}\text{4]}^{2-}
\]

574 554 586 490 509 457

This indicates that the bond becomes progressively weaker in the same order. There seems no reason why this should be so if the frequency concerned is the Pt–NO\text{2} stretching frequency, \(\gamma_3\), but there is a simple explanation if it is due to the in-plane bending vibration, \(\gamma_2\). The degree of double bonding of the nitrogen to metal in a complex should become smaller with the increasing number of nitro groups, as there will be less electrons of the metal available for "back coordination"; furthermore there will be less double bonding when there are trans nitro groups than when the nitro group is trans to ammonia. This will mean in this series: \(\text{cis-Pd(NH}_3\text{)}\text{2(NO}_2\text{)}\text{2}\) will show the most double bonding of the Pd–NO\text{2} bond, and therefore the strongest bonding, and \([\text{Pd(NO}_2\text{)}\text{4]}^{2-}\) the least. Any increase in the bond strength of the Pt–N bond due to this cause will be accompanied by a decrease in the strength of the N–O bond and it follows that the order of the frequencies observed would be that expected for a N–O bond vibration.

Thus, while there are indications that the lower two frequencies are possibly due to \(\delta_{N-O}\) in-plane, \(\gamma_2\)
and the higher frequency near 800 cm\(^{-1}\) is due to the
metal-nitrogen stretching frequency, \(\nu_3\), there is insufficient evidence to regard the question as proved. It is
not even certain that the two lower frequencies are due to
the same fundamental vibration, though it would be surprising
if the mass effect of the platinum and palladium atoms
would permit an increase in frequency of \(\nu_5\) or \(\nu_6\) as com-
pared with nitryl chloride to the value observed for these
frequencies.

The assignment of frequencies can therefore be
summarised as follows:

<table>
<thead>
<tr>
<th>Approximate frequency</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>between 1450 cm(^{-1}) and 1300 cm(^{-1})</td>
<td>(\nu_{\text{asym}}) NO and (\nu_{\text{sym}}) NO</td>
</tr>
<tr>
<td>near 800 cm(^{-1})</td>
<td>to be assigned to (S_{\text{NO}}) in-plane and (\nu_{\text{Cl-N}}) (lower frequency)</td>
</tr>
<tr>
<td>between 650 cm(^{-1}) and 450 cm(^{-1})</td>
<td>could be due to (S_{\text{M-N}}) or the out-of-plane bending vibration</td>
</tr>
</tbody>
</table>

The alternative assignments of the lower frequencies could
only be decided by extending the examination of the com-
pounds to below 400 cm\(^{-1}\) in order to complete the identifi-
cation of the fundamental vibration. In spite of the
incomplete assignment of the frequencies, the results
obtained do give considerable support for the idea of
double bonding of the nitro group to the metal in these compounds, as there seems no other way to account for the higher frequencies observed compared with those of nitryl chloride, particularly as the greater mass of the metal atoms compared with chlorine would generally lead to lower frequency vibrations.
$\text{cis}[\text{Pt(NH}_3\text{)}_2(\text{NO}_2\text{)}_2]$,

$\text{K}_2[\text{Pt(NO}_2\text{)}_4]$
$\text{Na}_3[\text{Co(NO}_2\text{)}_6]$
Spatial arrangement of atoms in $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$. 

(The plane of the hydrogen atoms is parallel to the plane $\text{Cl}^1\text{ZCl}_3$ but probably displaced slightly from co-planarity with the carbon atoms by the repulsion of the hydrogen atoms by the platinum atom.)

Orbitals used in the combination of ethylene with platinum.
Part II. Ethylene Complexes.

The effect of coordination to a metal ion on the characteristic vibration frequencies of ethylene is of some interest in view of the unusual nature of the bonding of this group. X-ray diffraction studies have shown that the ethylene molecule is coordinated perpendicular to the plane of symmetry of the bonding orbitals of the platinum atom as shown in Fig. 15. The nature of the bonding has been discussed by Chatt and Duncanson, but no detailed study of the absorption frequencies has been made. It is suggested that the ethylene is attached through a $\sigma$ bond using the $\pi$ electrons of the ethylene double bond and $d_{sp^2}$ hybrid orbitals of the platinum, and that a second $\pi$ bond is formed using "d" orbitals of the platinum with an antibonding orbital of the ethylene. These orbitals are also shown in Fig. 15. The evidence for the double bond character of the ethylene-platinum bond comes mainly from dipole moment measurements, which indicate a smaller moment than would be expected for a simple coordinate link and suggest that the dipole of this bond is balanced by the back coordination from the platinum "d" electrons.

In order to consider the effect of coordination on the characteristic ethylene frequencies it is first necessary to consider the fundamental vibrations of the ethylene itself which have been completely assigned to the corresponding
FIG. 16
FUNDAMENTAL VIBRATIONS OF ETHYLENE

\( \lambda_1 \)

\( \lambda_2 \)

\( \lambda_3 \)

\( \lambda_4 \)

\( \lambda_5 \)

\( \lambda_6 \)

\( \lambda_7 \)

\( \lambda_8 \)

\( \lambda_9 \)

\( \lambda_{10} \)

\( \lambda_{11} \)

\( \lambda_{12} \)
**TABLE VIII.**

**Fundamental vibration Frequencies for Ethylene (cm⁻¹)**
<table>
<thead>
<tr>
<th>$\nu$</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Description</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>3049</td>
<td>symmetrical OH stretching</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>2990</td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>3075</td>
<td>asymmetrical OH stretching</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>3106</td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>1623</td>
<td>C=C stretching</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1342</td>
<td>CH$_2$ in-plane bending</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>1444</td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>1236</td>
<td>CH$_2$ in-plane rocking</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>810</td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>943</td>
<td>CH$_2$ out-of-plane wagging</td>
<td>R</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>949</td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1027</td>
<td>CH$_2$ torsion</td>
<td>R</td>
</tr>
</tbody>
</table>

Note: IR = infrared active  \hspace{1cm} R = Raman active.
absorption bands in the Raman and infrared spectra.

The fundamental vibrations of the ethylene molecule are shown in Fig. 16 and the values of the vibration frequencies observed are shown in Table VIII, which is taken from the review of infrared spectra of olefines by Sheppard and Simpson. The next problem is to examine the expected effect of these frequencies of the coordination on the metal ion. In several cases the spectra of these compounds were only examined below 2000 cm\(^{-1}\), and so the C-H stretching frequencies near 3000 cm\(^{-1}\) have not been considered.

The C=C stretching frequency at 1623 cm\(^{-1}\) (\(\gamma_2\)) is expected to be reduced in frequency as the removal of the \(\pi\) electrons will tend to bring the bond closer to that of a single bond. In addition, the frequency which in ethylene is only Raman active may become weakly infrared active as well, owing to the dissymmetry introduced in the molecule.

The CH\(_2\) in-plane bending vibrations \(\gamma_3\) and \(\gamma_{12}\) are expected to change only slightly in frequency, but both should become infrared active as well as Raman active.

The CH\(_2\) rocking frequencies \(\gamma_6\) and \(\gamma_{10}\) would be expected to be increased but the Raman active frequency \(\gamma_6\) should not be infrared active.

CH wagging frequencies \(\gamma_8\) and \(\gamma_7\) are both
expected to rise in frequency and become infrared active.

The CH₂ torsion y₄ should increase in frequency but remain only Raman active; in addition a new, infrared active, torsional mode should arise which only occurs in ethylene itself as a translational mode of very low frequency.

These effects can be shown for ethylene sulphide, which has a similar symmetry to the ethylene bonded to platinum as far as the (CH₂CH₂) group is concerned, as shown by the diagram below.

Clearly the ring deformation, skeletal vibrations of ethylene sulphide will have no exact counterpart in the case of the platinum ethylene complex, and will be replaced by direct platinum-ethylene skeletal vibrations. In the diagram overleaf the corresponding vibrations of ethylene and ethylene sulphide are compared, the frequencies and their vibrational assignment being taken from the paper by Thompson and Cave.

The frequencies observed in this case can now be compared with those of coordinated ethylene. The compounds examined and the main absorption frequencies observed below
<table>
<thead>
<tr>
<th>Frequency</th>
<th>Ethylene</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>1440 IR</td>
<td>asym CH₂ bend</td>
</tr>
<tr>
<td>1400</td>
<td>1342 R</td>
<td>sym CH₂ bend</td>
</tr>
<tr>
<td>1300</td>
<td>1236 R</td>
<td>CH₂ rock in-plane</td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>1027 R</td>
<td>torsion</td>
</tr>
<tr>
<td>1000</td>
<td>945 IR</td>
<td>CH₂ wags</td>
</tr>
<tr>
<td>900</td>
<td>943 R</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>810 IR</td>
<td>CH₂ rock in-plane</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

very low frequency torsion R

R = Raman active  IR = Infrared active.
TABLE IX

Absorption Frequencies observed for Ethylene/Platinum Complexes.
**TABLE IX.**

Absorption Frequencies observed for

**Ethylene/Platinum Complexes.**

<table>
<thead>
<tr>
<th>Trans $\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2$ (1)</th>
<th>$\text{K}_2\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3\text{H}_2\text{O}$ (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1610 s. (NH$_3$)</td>
<td>1612 s. (H$_2$O)</td>
</tr>
<tr>
<td>1520 w.</td>
<td>1515 w.</td>
</tr>
<tr>
<td>(1430) 1422 s.</td>
<td>1425 s.</td>
</tr>
<tr>
<td>1267 1255 s. (NH$_3$)</td>
<td>1300 v.v.</td>
</tr>
<tr>
<td>1023 1010 s.</td>
<td>1240 m</td>
</tr>
<tr>
<td>980 v.v.w</td>
<td>1179 w.</td>
</tr>
<tr>
<td>818 m.</td>
<td>1022 1010 s.</td>
</tr>
<tr>
<td>735 m. (NH$_3$)</td>
<td>975 v.v.</td>
</tr>
<tr>
<td>691 m.</td>
<td>718 m.</td>
</tr>
<tr>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>500</td>
<td>broad v.s. (H$_2$O)</td>
</tr>
<tr>
<td>480 w. (NH$_3$)</td>
<td>405 m.</td>
</tr>
</tbody>
</table>

* These spectra were obtained using less concentrated Nujol mulls than those used for the same compounds in consideration of the *trans* effect, Chapter
TABLE IX (cont'd)

Absorption Frequencies observed for
Ethylene/Platinum Complexes.
### TABLE IX (cont'd)

<table>
<thead>
<tr>
<th>trans $\text{Pt}(\text{C}_2\text{H}_4)(\text{CH}_3)_3\text{HCl}_2$ (3)</th>
<th>$[\text{Pt}(\text{C}_2\text{H}_4\text{Cl}_2)]_2$ (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1495 w.</td>
<td>1506 v.w.</td>
</tr>
<tr>
<td>1474 s.</td>
<td>1428 (1416) s.</td>
</tr>
<tr>
<td>1444</td>
<td>1457 s.</td>
</tr>
<tr>
<td>1433</td>
<td>1442 m.</td>
</tr>
<tr>
<td>1412) v.w.</td>
<td>1400 w.</td>
</tr>
<tr>
<td>1360</td>
<td></td>
</tr>
<tr>
<td>1335</td>
<td></td>
</tr>
<tr>
<td>1264 1252 w.</td>
<td>1270 m.</td>
</tr>
<tr>
<td>1173 w.</td>
<td>1236 1217 w.</td>
</tr>
<tr>
<td>1131</td>
<td>1185 s.</td>
</tr>
<tr>
<td>1131 w.</td>
<td>1175 w.</td>
</tr>
<tr>
<td>1048 m.</td>
<td>1027 s.</td>
</tr>
<tr>
<td>975 m.</td>
<td>1043 v.s.</td>
</tr>
<tr>
<td>923</td>
<td>971 v.w.</td>
</tr>
<tr>
<td>860 s.</td>
<td>818 m.</td>
</tr>
<tr>
<td>750 w.</td>
<td>720 w.</td>
</tr>
</tbody>
</table>

Not investigated in potassium bromide region.
2000 cm$^{-1}$ are contained in Table IX, and are illustrated on page 154 at the end of this section. Assignments of frequencies of groups present other than ethylene are indicated alongside. If the vibration characteristics of the platinum-ethylene complexes are regarded as intermediate between those of ethylene and ethylene sulphide as shown by the vertical lines AB and CD many of the absorption frequencies observed in the complexes can be assigned to fundamental vibrations.

$\text{CH}_2=\text{CH}_2$ stretching ($\nu_2$) This frequency has no counterpart in the vibrations of ethylene sulphide and in ethylene it is only Raman active. In the ethylene complexes the distortion of the molecule by coordination may cause it to be weakly active in the infrared and there is in fact a very weak absorption near 1500 cm$^{-1}$ in all the spectra examined, (1) 1520, (2) 1515, (3) 1506, (4) 1495. These are in the expected frequency region as the corresponding infrared active frequency in propylene complexes occurs at 1504 cm$^{-1}$.

These values compare with the values for $\nu \sigma_{\text{CH}}$ in ethylene itself (1623 cm$^{-1}$) and the $\nu \pi$ in ethane of 993 cm$^{-1}$ (Raman).

The trend of this frequency towards that of a single bond frequency would be expected on the basis of the partial coordination to the platinum of the $\pi$ electrons of the double bond.
\( \text{CH}_2 \text{ bending (\( \nu_3 \) and \( \nu_{12} \)).} \) These vibrations for ethylene and ethylene sulphide show only small differences in frequency (see page 147). It is clear that the absorption near 1400 cm\(^{-1}\) found for all these complexes can be assigned to these vibrations. The asymmetrical and symmetrical vibration frequencies are much closer than in either ethylene or ethylene sulphide. As the \( \delta \text{ asym} \) and \( \delta \text{ sym} \) frequencies are reversed in value for these two compounds, this effect would be expected if the bonding in the ethylene-platinum complexes is regarded as intermediate between that of ethylene and ethylene sulphide (see page 147). The frequencies observed are similar for the compounds examined, namely, (1) (1430) 1422, (2) 1425, (3) uncertain, due to absorption of trimethylamine, (4) 1428 1416.

\( \text{CH}_2 \text{ wagging (\( \nu_8 \) and \( \nu_7 \)).} \) The two narrowly separated frequencies observed for ethylene, one Raman active and the other infrared active, have increased frequencies in ethylene sulphide and both become infrared active. Two frequencies are also observed in the ethylene complexes near 1000 cm\(^{-1}\), though the two absorption bands are not completely resolved; the frequencies are as follows: (1) (1023) 1010, (2) 1023 1011, (3) 1048 or 975, (4) 1027. In the trimethylamine complex it is not certain which of the two frequencies is due to trimethylamine.

\( \text{CH}_2 \text{ rocking (\( \nu_6 \) and \( \nu_{10} \)).} \) These frequencies are widely
separated in ethylene with frequencies of 1236 (Raman) and 810 (infrared), of these only the latter is infrared active in ethylene sulphide. Among frequencies to be assigned in the ethylene complexes is a rather weak absorption band between 1200 and 1250 cm$^{-1}$, but it seems unlikely that this is due to the infrared active rocking vibration, $\gamma_{10}$, as the corresponding frequency in ethylene sulphide is only increased to 945 cm$^{-1}$ and it is probable that it is the normally Raman active rocking vibration $\gamma_{6}$. The assignment of the infrared active frequency, $\gamma_{10}$, is a difficult problem and must be considered in relation to the remaining fundamental vibrations; these are as follows

$\gamma_{10}$ CH$_2$ rocking (at 945 cm$^{-1}$ for ethylene sulphide)  
CH$_2$ torsion (at 825 cm$^{-1}$ for ethylene sulphide)  

$\gamma_{\text{Pt-ethylene}}$ stretching

The frequencies of chief absorption bands remaining are as follows

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>980 v.v.weak</td>
<td>975 v.w.</td>
<td>971 v.w.</td>
<td></td>
</tr>
<tr>
<td>818 m.</td>
<td></td>
<td>818 m.</td>
<td></td>
</tr>
<tr>
<td>691 m.</td>
<td>717 m.</td>
<td>Not investigated</td>
<td></td>
</tr>
<tr>
<td>615 m.</td>
<td>405 m.</td>
<td>below 700</td>
<td></td>
</tr>
</tbody>
</table>

The only frequency which occurs in all three compounds is that at about 950 cm$^{-1}$, but which is extremely weak and is
therefore probably not the infrared active CH$_2$ rocking frequency, which is infrared active in ethylene itself as well as in ethylene sulphide. It could, however, be the torsional vibration, but there is insufficient correlation between the frequencies observed for different compounds to permit definite assignment of these frequencies.

The frequency observed near 400 cm$^{-1}$ for (1) and (2) is probably a $\nu$ Pt-ethylene stretching frequency, since if the strength of the Pt-C$_2$H$_4$ bond is about the same as that of the Pt-NH$_3$ bond, the expected frequency of this vibration will be given by the approximate relationship

$$\frac{\nu_{\text{Pt-C}_2\text{H}_4}}{\nu_{\text{Pt-NH}_3}} = \sqrt{\frac{17}{28}}$$

$$\therefore \nu_{\text{Pt-}(\text{C}_2\text{H}_4)} = 510 \sqrt{\frac{17}{28}}$$

$$= 395 \text{ cm}^{-1}$$

This frequency is close to those actually observed for (1) 385 cm$^{-1}$ and (2) 405 cm$^{-1}$.
trans[Pt(NH$_3$)(C$_2$H$_4$)Cl$_2$]

K[Pt(C$_2$H$_4$)Cl$_3$] H$_2$O

trans[Pt(NMe$_3$)(C$_2$H$_4$)Cl$_2$]
### Table X

Absorption Frequencies of Ethylenediamine Complexes

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
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TABLE X.
Absorption Frequencies of Ethylenediamine Complexes.

<table>
<thead>
<tr>
<th>[Co(en)₃]Cl₃</th>
<th>[Ni(en)₃]Cl₂</th>
<th>[Cu(en)₂Cl₂]</th>
<th>trans [Co(en)₂Cl₂]Cl₂</th>
<th>ethylenediamine</th>
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<tbody>
<tr>
<td>1619 m.</td>
<td>1660 w.</td>
<td>1633 w.</td>
<td>1639 w.</td>
<td>1605 s.</td>
</tr>
<tr>
<td>1591 s.</td>
<td>1590 s.</td>
<td>1587 s.</td>
<td>1598 s.</td>
<td>1460 m.</td>
</tr>
<tr>
<td>1563 s.</td>
<td>(1571)</td>
<td></td>
<td></td>
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<tr>
<td>1364 m.</td>
<td>1331 m.</td>
<td>1279 w.</td>
<td>1448 m.</td>
<td>1360 m.</td>
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<tr>
<td>1325 m.</td>
<td>1288 m.</td>
<td>1162 m.</td>
<td>1369 m.</td>
<td>1313 m.</td>
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<tr>
<td>1303 w.</td>
<td>(1270)</td>
<td>1089 m.</td>
<td>1316 m.</td>
<td>1175 m.</td>
</tr>
<tr>
<td>1277 w.</td>
<td>1154 m.</td>
<td>1040 s.</td>
<td>1294 w.</td>
<td>1130 m.</td>
</tr>
<tr>
<td>1253 m.</td>
<td>1101 m.</td>
<td>975 w.</td>
<td>1275 m.</td>
<td>1095 m.</td>
</tr>
<tr>
<td>1219 w.</td>
<td>1022 v.s.</td>
<td>700(bd) s.</td>
<td>1211 m.</td>
<td>1050 m.</td>
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<tr>
<td>(972)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1165 m.</td>
<td>755)</td>
<td>550 s.</td>
<td>1119) s.</td>
<td>995 m.</td>
</tr>
<tr>
<td>1155 m.</td>
<td>683) s.</td>
<td></td>
<td>1100) s.</td>
<td>905 s.</td>
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<td>1122 m.</td>
<td>682)</td>
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<tr>
<td>1054 s.</td>
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<tr>
<td>1002 w.</td>
<td>522) s.</td>
<td></td>
<td>1050 s.</td>
<td>830 s.</td>
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<tr>
<td>895 w.</td>
<td>498) s.</td>
<td></td>
<td>1002) s.</td>
<td>989) s.</td>
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<tr>
<td>783 s.</td>
<td></td>
<td></td>
<td>884 m.</td>
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<tr>
<td>746 w.</td>
<td>Note. also examined as hydrate.</td>
<td>Note. also examined as chloride (hydrate)</td>
<td>803 m.</td>
<td>719 w.</td>
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<tr>
<td>710 w.</td>
<td></td>
<td></td>
<td>582 s.</td>
<td>507 s.</td>
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<tr>
<td>578 m.</td>
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<td>464 s.</td>
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<td>523)</td>
<td></td>
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<tr>
<td>490) v.s.</td>
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<td>465) (bd)</td>
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<td>435)</td>
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Part III. Ethylenediamine Complexes.

Several metal-ethylenediamine complexes were prepared in the hope that comparison of the spectra of complexes with their stabilities would extend the results obtained for simple metal ammines, the advantage of ethylenediamine as a ligand being the greater stability of the complexes formed, thus enabling a greater range of metal ions to be compared.

The absorption frequencies observed for a number of ethylenediamine complexes are shown in Table X, together with the frequencies observed for liquid ethylenediamine, given by Bellanato. The spectra are illustrated on pages 159 and 160 at the end of this section. When the spectra are compared, it can be seen that not only are they much more complex than those of the simple ammines, but that the degrees of complexity differ with different metal ions. In consequence it is not possible to compare the frequencies of the skeletal vibrations with stabilities as had been hoped. The chief metal-ethylenediamine complexes examined are as follows:

I  \[\text{[Co(en)_3]}\text{Cl}_3\]

II  \[\text{[Ni(en)_3]}\text{Cl}_2\]

III  \[\text{[Cu(en)_2][PtCl}_4]\text{ and the chloride (hydrate)}\]

IV  \[\text{trans-}[\text{Co(en)}_2\text{Cl}_2]\text{Cl}\]

Comparison of the spectra of I and II shows clearly
the greater complexity of the cobaltic compound, I, over the whole range of frequencies examined, including the region below 650 cm^{-1}, where ethylenediamine itself shows no absorption in the infrared spectrum. The absorption observed in this region is probably due to skeletal vibrations of the coordinated ring.

Comparison of the spectra of III and IV, where in each case the four coordinated nitrogen atoms lie in a plane, shows that again the spectrum of the cobaltic compound is much more complicated than that of copper. It is therefore probable that the greater complexity of the cobaltic compounds is associated with the bonding of the ethylenediamine molecule itself and is not due to the general symmetry of the coordinated atoms.

The most marked chemical difference of cobaltic-ethylenediamine complexes from those of nickel and copper is their greater stability to dissociation, as shown by the values for the stability constants^{60}.

\[ + \log K_{\text{average}} \]

\[
\begin{align*}
[Cu(en)_2]^{2+} & \quad 6.8 \\
[Ni(en)_3]^{2+} & \quad 4.8 \\
[Co(en)_3]^{3+} & \quad 9.9
\end{align*}
\]

There seems, however, to be no real reason why the change in the strength of bonding should cause such a marked
difference in the nature of the spectrum. It is interesting to note that Quaglione and Mizushima have shown that in 
\([\text{Co(en)}_3\text{Cl}_3]\), the ethylenediamine groups have the gauche and not the cis configuration, as had been previously assumed, and it would be possible for the simpler spectra to result in the cases of nickel and copper if the ethylenediamine groups in these complexes had the cis configuration.

Without making a detailed assignment of the frequencies observed little further progress can be made and as this would itself constitute a major research problem, these complexes were not examined further.
[Co(en)$_3$]Cl$_3$

[Ni(en)$_3$]Cl$_2$
The examination of metal coordination compounds by infrared spectroscopy was begun in order to establish the nature of the molecular vibrations of various ligands, to examine the differences in the absorption frequencies observed with different metal ions in the complexes, and to see if these effects could be correlated with the known chemical properties of the compounds.

The main emphasis of the work described here has been on the metal ammines, as ammonia is a relatively simple molecule for the assignment of the absorption bands to the fundamental vibration frequencies of the group. It has been possible to assign all the frequencies observed in these compounds to particular molecular vibrations, including in many cases the infrared active, metal-nitrogen stretching vibration, and many of the results of this investigation have been published during the past year. The use of metal-nitrogen stretching frequencies affords a valuable means of examining the effect on the strength of bonding of the ammonia group of other substituent groups in the complexes. These frequencies have been used in this way in the experiments on the trans-directive effect of various ligands in platinous complexes, where it has been shown that
some groups, notably ethylene, cause a marked weakening in the bonding of a trans ammonia group. The results of this work have also been published recently.

With the other ligands examined there has been much greater difficulty in the assignment of the observed absorption bands to the fundamental vibrations, this step being an essential prerequisite to the use of these frequencies in the study of problems related to the chemical bonding of the groups. However, with ethylene and the nitro group as ligands, considerable progress has been made in assigning the frequencies observed to fundamental vibrations and the assignment could probably be completed if a prism or grating were available with which frequencies lower than 400 cm\(^{-1}\) could be observed. The effect of other substituent groups on the fundamental vibrations of these ligands should provide an interesting problem, particularly in view of the possibility of these ligands being bound to the metal ion by double bonds, rather than simple coordination.

With ethylenediamine complexes the information obtained is much less detailed, and it has only been possible to compare the general features of the spectra obtained when different metal ions are concerned. The differences in the spectra of the complexes examined suggest that the investigation of a wider range of complexes and a detailed
assignment of the absorption frequencies should provide an interesting field of study.
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