

SUBSTITUTION OF PYRIDINE
INTO COBALT (III) COMPLEXES

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ABSTRACT

An investigation has been carried out of the reactions of some cobalt (III) complexes with organic ligands, with emphasis on the rates and mechanisms of reaction.

A literature review is given of the development of the theory and practical study of reaction rates and mechanisms, leading on to a discussion of reaction rates and mechanisms in solution, and the reactions of transition metal complexes in particular.

Nucleophilic substitutions are discussed, first at carbon atoms and then at transition metals. It is seen that very little work has previously been done on the rates and mechanisms of substitution at transition metals by uncharged nucleophiles, other than solvation studies.

Solvation studies are limited in scope by the fixed concentration and great excess of one reactant, the solvent, and so it seems desirable to investigate substitutions by uncharged nucleophiles other than the solvent.

The substitution of pyridine into trans dichlorobis(ethylene-diamine) cobalt is investigated spectrophotometrically in methanol solution. Before this is done, a spectrophotometric investigation

of some cobalt (III) complexes is made, and the results discussed in relation to the investigations of other workers on similar compounds. A number of new assignments are made for infrared, visible, and ultraviolet spectra.

The substitution of pyridine into the cobalt complex is shown to be methoxide catalysed, either directly or via a cobalt (II) species. Unbuffered pyridine produces enough methoxide from the solvent to enable reaction to take place, but the addition of acid suppresses this. Reactions other than substitution take place, including the reduction of some cobalt (III) to cobalt (II).

The reduction of cobalt (III) to cobalt (II) by pyridine is investigated and shown not to be photochemical.

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PART I

DEVELOPMENT OF THE THEORY AND PRACTICAL STUDY
OF REACTION KINETICS

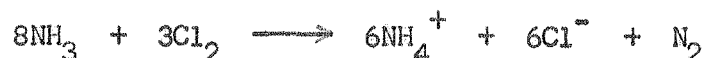
1. Relevance and Importance of the Study of
Reaction Kinetics

The study of thermodynamics, including chemical equilibria, is concerned only with the initial and final states of the system. It indicates the stable state of the system, but does not give any indication of the rate of approach to that stable state. A reaction may be thermodynamically feasible, but never observed to occur because the rate of approach to equilibrium is immeasurably small. Two cases of this are the lack of reaction between hydrogen and oxygen at room temperature and the inertness of the hexammine cobalt (III) ion to attack by boiling dilute acids. In each of these reactions, as shown below, equilibrium lies almost entirely to the right. The logarithms of the equilibrium constants for the reactions are respectively 93.1 (1) and 22 (2), but no reaction has been observed.



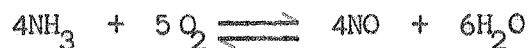
The large majority of reactions are not simple one step reactions where the step is expressed by the stoichiometric equation

for the reaction. For example, the reaction of aqueous ammonia and chlorine takes place by a number of simple steps, not by an eleven body collision as might be thought from the overall equation:



In the study of kinetics, interest centres on the intermediate steps in the reaction, rather than just on the initial and final states.

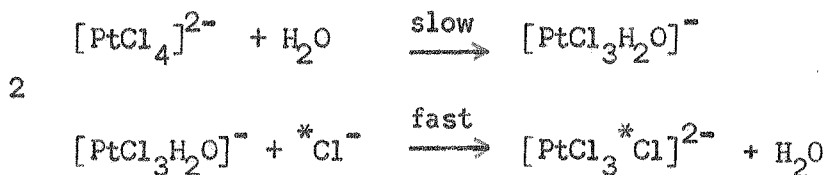
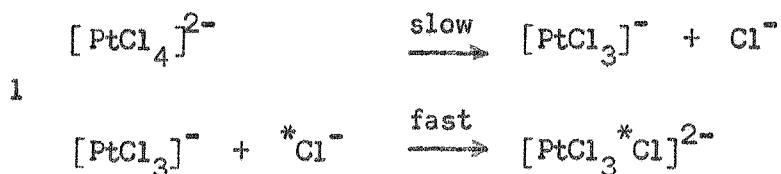
Sometimes alternative reactions are possible for given reactants. The products which would be obtained, were the system allowed to come to equilibrium, are determined by the thermodynamics of the reaction. However, the reaction system may not be in equilibrium, and the products are determined by the relative rates of the various reactions. An example, of industrial importance, is that of the oxidation of ammonia. Two possible reactions are shown below.



The logarithms of the equilibrium constants are given by Cotton and Wilkinson (3) as 228 and 168 respectively. Thus for an equilibrium system, nitrogen and water would be almost the sole products. However, the latter reaction is selectively catalysed

by platinum at elevated temperatures and nitric oxide is formed as the system is not allowed to reach equilibrium.

Studies of reaction kinetics enable the formulation of reasonable mechanisms for given reactions and can sometimes completely rule out certain mechanisms. However, Daniels and Alberts (4) point out: "The deduction of reaction mechanisms from various types of kinetic data cannot be completely certain because it is impossible to rule out the possibility that there is another mechanism which could also account for the experimental data." An example of this which will be discussed later (see page 53) is the impossibility of distinguishing between the two following mechanisms for the isotopic exchange of chlorine in tetrachloroplatinate (II) ion in water:



2. Experimental Techniques of Study of Reaction Kinetics

Before discussing the manner in which experimental data are used, an account of methods of obtaining these data will be given.

Chemical reactions may be followed by the change in any property (usually chemical or physical, but occasionally biological) as the reaction proceeds. A large number of properties have been used for measurement, and some of them will be considered later. Either discrete samples may be taken for determination of concentrations of materials at particular times, or continuous methods of obtaining observations may be employed. The former method is not suitable for the study of fast reactions, and only a limited number of points are available per run. However, the equipment may be excessively complex for continuous studies, and also the method of measurement may affect the reaction rates. For example, continuous exposure of materials to light (e.g. in polarimeter tubes) may accelerate the reaction. This acceleration does not appear in the inversion of sucrose



which was first studied by L. Wilhelmy (5) in 1850.

However, Brown and Ingold (6) found that the loss of optical

activity in the reaction,



was accelerated by light of the wavelength of the sodium D lines.

It is often important to measure independent properties and to note if the rates of reaction calculated from each method are the same. Were only the total pressure measured during the decomposition of ethane, and the rate of reaction calculated from this, erroneous results would be obtained as other reactions also take place.



and other products also form.

a) Methods not suitable for continuous monitoring of reactions.

(i) Gravimetric Analysis

This is a simple technique, but is not used as much as the more convenient volumetric analysis. However, gravimetric determination of the reactant complex ion concentration (as the insoluble hexacyanocobaltate (III)) was used by Kilpatrick (7) to study the aquation of hexakis (urea) chromium (III) in water:



(ii) Volumetric Analysis

This method is often employed. Determination of halides or pseudohalides with silver ion is frequent, but results tend to be too high. This is due to the rapid aquation of many halide-containing complex ions resulting in halide release (8, 9), and also to a specific attack by silver ion upon the complexes (10).

Mathieu (8, 9) used cold methanol as a solvent to reduce the errors when determining the concentration of ionic chloride in reaction mixtures of cobalt (III) complexes, while Brown and Ingold (6) further improved the method by using cold acetone/methanol mixtures in similar work. However, when Baldwin, Chan and Tobe (11) considered similar systems in their work on the aquation of dichloro and chloroaquabis(ethylenediamine) cobalt (III), they first passed the samples through a cooled cation exchange column and then determined the hydrochloric acid in the effluent.

(iii) Chromatographic Analysis

Much work has been done by a number of workers (18, 19, 20, 21, 22) on the separation of metal ions by chromatography on a number of media. Some of the few examples of reactions followed by this means are the aquation and base hydrolysis of hexammine and several pentammine and tetrammine chromium (III) complexes by Jørgensen and Bjerrum (22).

(iv) Other Methods

Other less frequently used methods include changes in freezing point and changes in coagulation value (12).

b) Methods Suitable for Continuous or Discrete Observation

(i) Polarimetry

This was the first method ever used for the study of homogeneous reactions, being employed by Wilhelmy (5) in 1850 (pp5, 14). By taking measurements of light rotation at several different wavelengths of light, a number of independent observations can be made, enabling one to characterise a mixture of several species (providing all are optically active and the optical activity of any one is not a linear function of the optical activities of the others).

(ii) Spectrophotometric and Colorimetric Analysis

Like polarimetry, a number of independent observations on each sample may be taken by simply changing the wavelength of the light employed. Treatment of such data will be discussed later in this thesis (see page 128). Unlike polarimetry, it is not restricted to optically active materials, but cannot be used to follow racemisation reactions. Examples of the use of this method are the study by Johnston and Yost (13) of the disappearance of the brown nitrogen dioxide in the reaction



and the study by Nyholm and Tobe (14) of base hydrolysis and aquation of halogeno and nitrate bis(ethylenediamine) cobalt (III) ions.

The use of infrared and ultraviolet radiation has extended the use of spectrophotometric methods. The solid state reaction,



was followed by Beattie and Satchell (15) by observation of the change in the absorption of infrared radiation of 9.5 millimicrons wavelength.

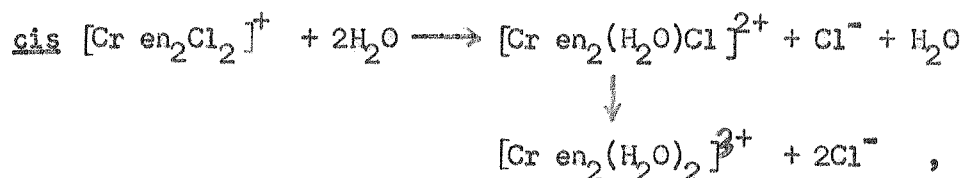
(iii) Measurement of Change in Pressure or Volume

This method has been extensively used for gas reactions. However, independent additional evidence is needed to enable the reaction scheme to be characterised (see page 6).

(iv) Potentiometry

The potential between two electrodes has often been used to follow the progress of reactions. The method is usually limited to reactions involving the following ions: H^+ , Cl^- , Br^- , I^- , NCS^- , as other reference electrodes are rarely reversible.

Selbin and Bailar (16) followed the reaction,

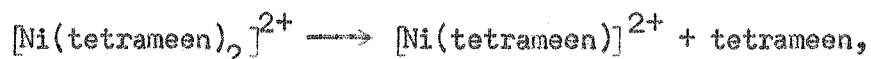


by the use of a silver/silver chloride electrode in the reaction

cell. The concentration (actually the activity) of silver ions was given by

$$\text{Potential} = \frac{RT}{F} \ln \frac{a_{\text{Cl}^- \text{ mixture}}}{a_{\text{Cl}^- \text{ standard}}} .$$

Usually the change in potential of a system is studied as a function of time, but Wilkins (17) followed the reaction,



which results in the release of the basic tetrameen (2, 3 dimethyl-2, 3 diaminobutane) by adding acid so as to keep the potential of the hydrogen electrode constant and measuring the volume of acid as a function of time.

(v) Conductance

Although every ion has its characteristic conductance, the conductance of equally charged ions of like nature is very similar, and so the use of conductance as a tool for determining the extent of reaction is best limited to cases where the charge of particles in solution changes. Early use of this method included that of Mathieu (8, 9) on the aquation of dichlorobis(ethylenediamine) cobalt (III) ions.

(vi) The Use of Isotopic Labelling

Some studies of reactions use isotopic tracers as a convenient manner of measuring the overall kinetics of a reacting system. The

concentration of the isotopic tracer in a material may be determined by radioactivity, spectrophotometry or by density measurement. The common isotopes available of hydrogen (^2H), nitrogen (^{15}N), and oxygen (^{18}O) are not radioactive, but hydrogen is available also as tritium (^3H) which is radioactive. Most other elements can be obtained as radio-isotopes.

The non-radioactive deuterium, nitrogen 15, and oxygen 18 can be detected by infrared spectrophotometry as the absorption bands of their compounds are at lower frequencies than those of the analogous protium, nitrogen 14, and oxygen 16 compounds. Deuterium can also be determined by density measurements.

The reaction rates of the heavier isotopes are generally lower than those of the lighter isotopes, and the magnitude of this effect can give fine details of the reaction mechanism. For example, Cahill and Taube (23) studied the reduction of hydrogen peroxide by a number of reducing agents, using oxygen 18. Calculations indicated that the isotope effect, the percentage difference in the rate constants, for the reduction of $\text{H}-^{18}\text{O}-^{16}\text{O}-\text{H}$ and $\text{H}-^{16}\text{O}-^{16}\text{O}-\text{H}$ would be 6.1% if the oxygen-oxygen bond was severed in the transition state. Observations showed the isotope effect to be 6% when the reducing agent was iron (II), tin (II), or copper (I), but only 0.5% when the reducing agent was titanium (III). This showed that the oxygen-oxygen bond was broken in the transition state in the former cases, but not when the reducing agent was

titanium (III).

The absolute labilities of compounds can also be determined by isotope exchange reactions (see page 56).

(vii) Other Methods

Changes in dielectric constant, refractive index, viscosity, and thermal expansion coefficient have also been used to study reaction kinetics (24, 12).

c) Special Methods for Fast Reactions

These are the subject of a discussion (25) and will be only briefly mentioned here.

(i) Flow Reactions

The reactant solutions are rapidly mixed in a specially designed mixing chamber. They may then be passed through an observation tube along which measurements are made (e.g. spectrophotometrically) as a function of distance rather than time. Alternatively they may be "instantaneously" quenched or stopped and analysed after a particular flow-time.

(ii) Nuclear Magnetic Resonance Studies

Electronic transitions are very rapid compared to the rate of vibrations of atoms (Franck-Condon Principle). However, the transition of a nucleus in a magnetic field is comparatively slow, taking of the order of 10^{-2} seconds. This time may be of a similar

order of magnitude to the half-life of a fast reaction. If a different peak is given by each of the reactants, then the resultant nuclear magnetic resonance spectrum is not a simple sum of these two peaks. It shows an averaging effect, and the magnitude of this averaging effect can be used to determine the reaction rate.

(iii) Relaxation Techniques

Unlike the flow reaction method, relaxation techniques are not limited by the rates of mixing of the materials.

Systems in equilibrium are taken, and the equilibrium is disturbed by a rapid variation of some physical parameter. The chemical reaction lags behind the variation by the "relaxation" time, and there is an observable displacement from equilibrium. The usual parameters varied are pressure, electric field intensity, and temperature.

3. Early Studies of Reaction Kinetics

The first quantitative investigation of any aspect of the rates of reaction antedates the first quantitative study of equilibria (26). In 1777 C.F. Wenzel experimented on the rate of dissolution of metals in acids, but it was not until 1799 that C.L. Berthollet observed the reversibility of reactions, which was to be written in his "Essai de Statique Chimique" two years later (27).

Wenzel found that if the temperature was kept constant and the same area of metal exposed each time, then the rate at which the metal dissolved was directly proportional to the concentration of the acid.

Reactions in heterogeneous systems such as those studied by Wenzel are complicated by diffusion effects, and so the studies of homogeneous systems are less liable to error. The first investigation of kinetics of reaction in a homogeneous system is that of Wilhelmy (5), who studied the inversion of sucrose (see pages 5, 8). Wilhelmy found that if the concentration of sucrose at time t was c , then

$$\frac{dc}{dt} = -k_1 c, \text{ where } k_1 \text{ is a constant now known as the rate constant.}$$

In 1862 Marcellin Berthelot and Pean de St. Gilles investigated the thermodynamics of the reversible hydrolysis of esters

such as ethyl acetate,



This was followed by the expression by Guldberg and Waage of the principle of dynamic equilibrium, whereby equilibrium is considered to be not the cessation of reaction but the condition in which the forward and the reverse reactions are of equal speed. Van't Hoff then stated the equilibrium constant was the ratio of the forward and reverse rate constants, i.e. for the reaction



$$K = \frac{k_f}{k_r} \quad (24, 27).$$

In succeeding years, A.V. Harcourt and W. Essen studied the reaction between potassium permanganate and oxalic acid, in which the rate is dependent on the concentration of both reactants, and also discussed consecutive reactions (24).

4. Treatment of Experimental Results

If for any reaction the rate of attack of a reactant, $\frac{-d c_r}{dt}$, is found to follow the relation

$$\frac{-d c_r}{dt} = k \prod_{i=1}^n c_i^{a_i},$$

where the concentration of reactant i is c_i , then the order of the reaction is defined to be $\sum_{i=1}^n a_i$. The order of the reaction is an empirical number, which is not necessarily integral. It is not necessarily the same as the molecularity of any step in the reaction, i.e. to the number of molecules of reactants which form the transition state (activated complex). A particular case of this is discussed later (see page 53).

The molecularity must be an integral number. It cannot be observed directly, and applies to the theoretical mechanism of the reaction rather than to the observed data.

Neither the molecularity nor the reaction order is necessarily the same as the number of molecules of reactants in the stoichiometric equation.

Most simple reactions are of first or second order kinetics, although a few are third order. Some examples of reaction schemes

are given below. Except in the simplest cases the mathematical forms are not worked out below. They are given in detail by Moore (24), who also mentions still more complex reaction schemes.

(a) First Order Reactions

These are characterised by the rate equation

$$\frac{dx}{dt} = -k_1 x, \text{ where } x \text{ is the concentration of the reactant at time } t.$$

Then

$$\int_a^x \frac{dc}{c} = -k_1 \int_0^t dT,$$

where the concentration at time $t = 0$ is a .

Thus, $\ln \frac{a}{x} = k_1 t$

If the concentration of a product, one mole of which is formed for each mole of the reactant destroyed, is y ,

then $x = a - y$

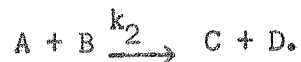
and $\ln \frac{a}{a - y} = k_1 t.$

$$\therefore \log_{10} \frac{a}{x} = \frac{k_1}{\ln 10} t$$

$$\approx \frac{k_1}{2.303} t.$$

$$\therefore \log_{10} x = \log_{10} a - \frac{k_1}{2.303} t$$

A graph of $\log_{10} x$ is drawn against t . If the reaction has first order kinetics, this graph is linear and is of slope $-\frac{k_1}{2.303}$.

(b) Second Order Reactions

Concentration of A at time $t = 0$ is a.

Concentration of B at time $t = 0$ is b.

Concentration of C and D at time $t = 0$ is 0.

Concentration of C and D at time t is y.

$$\text{Then } \frac{dy}{dt} = k_2(a-y)(b-y)$$

$$\therefore \int_0^y \frac{dc}{(a-c)(b-c)} = \int_0^t k_2 dT$$

$$\therefore \frac{1}{a-b} \ln \frac{b(a-y)}{a(b-y)} = k_2 t$$

This is the general equation for a second order reaction.

Two particular cases are of interest.

(i) $b \gg a$, so that $(b-y)$ can be considered constant.

The equation,

$$\frac{1}{a-b} \ln \frac{b(a-y)}{a(b-y)} = k_2 t ,$$

$$\text{reduces to } \frac{1}{-b} \ln \frac{b(a-y)}{ab} = k_2 t$$

$$\text{i.e. } \ln \frac{a}{a-y} = k_2 b t .$$

This is similar to the first order equation,

$$\ln \frac{a}{a-y} = k_1 t, \text{ with the equality } k_2 b = k_1.$$

However, in the case of the second order reaction, the pseudo-first order rate constant would vary directly with the concentration b of B .

(ii) $a = b$. Put concentration at time t of A or $B = x$.

$$\text{Then } \frac{dx}{dt} = -k_2 x^2$$

$$\therefore \int_a^x \frac{dx}{x^2} = - \int_0^t k_2 dT$$

$$\therefore \frac{1}{x} = k_2 t + \frac{1}{a}$$

Thus for a second order reaction with the concentrations of both reactants equal, a graph of the reciprocal of the concentration against time would be linear. A particular example of this is when A and B are the same compound: for example, in the decomposition of gaseous hydrogen iodide (see page 21).

(c) Third Order Reactions

There are very few of these, and all are of the form



They include the combination of nitric oxide with chlorine, bromine or oxygen, designated X_2 in the reaction below.



and also recombination reactions in the gas phase, such as



In the latter case the presence of the third atom serves to carry off some of the excess energy which otherwise would cause redissociation.

(d) Consecutive Reactions

The product of one reaction may be the reactant for another. An example of two successive first order reactions is the aquation of cis $[Cr en_2Cl_2]^+$, studied by Selbin and Bailar (16).



If one reaction is much slower than the others in a reaction sequence, the kinetics approximate to a simple first order rate law, with the rate constant equal to the constant for the slowest step.

(e) Opposing Reactions

All reactions are, in principle, reversible. However, in many reactions, the position of the equilibrium is so far on the product side that only the forward reactions need be considered in kinetic studies.

If the free energy of the reaction is not very great, then the forward and the backward reactions are both of importance. An example is the hydrolysis of esters mentioned previously. (see page 14).

Opposing first order reactions have been studied extensively by Kistiakowsky and Smith (28), while the first studies on opposing bimolecular reactions was by Bodenstein and Meyer (29), who investigated the system



(f) Parallel Reactions

These may be alternative paths through which a reaction may proceed, and the amount of each product depends upon relative reaction rates, not upon the thermodynamic stability of each product (see page 3).

5. The Theory of Reaction Rates

a) Arrhenius's Theory

The temperature dependence of equilibrium constant for any reaction, K , is related to the change in internal energy of the system, ΔE , by the following equation, which is due to Van't Hoff (30).

$$\frac{d \ln K}{d T} = \frac{\Delta E}{RT^2}$$

Also the equilibrium constant, K , is related to the rate constants k_f and k_r for the forward and reverse reactions,

$$K = \frac{k_f}{k_r} \quad (\text{see page 15}).$$

Arrhenius (31) then substituted $\frac{k_f}{k_r}$ for K .

$$\therefore \frac{d \ln(k_f/k_r)}{d T} = \frac{\Delta E}{RT^2}$$

or, putting $\Delta E = E_f - E_r$,

$$\frac{d \ln k_f}{d T} - \frac{d \ln k_r}{d T} = \frac{E_f}{RT^2} - \frac{E_r}{RT^2}$$

Van't Hoff suggested this could be split to give

$$\frac{d \ln k_f}{d T} = \frac{E_f}{RT^2} + B$$

$$\frac{d \ln k_r}{d T} = \frac{E_r}{RT^2} + B$$

Experimentally it was found that the best value for B was zero. This result then showed

$$\frac{d \ln k_f}{d T} = \frac{E_f}{RT^2} \quad \text{and} \quad \frac{d \ln k_r}{d T} = \frac{E_r}{RT^2} ,$$

or more generally, $\frac{d \ln k}{d T} = \frac{E_a}{RT^2}$

$$\therefore \int d \ln k = \int \frac{E_a}{RT^2} d T$$

If E_a is not dependent on temperature,

$$\ln k = \frac{-E_a}{RT} + C \quad \text{where } C \text{ is a constant}$$

$$= \frac{-E_a}{RT} + \ln A \quad \text{where } \ln A = C$$

$$\text{or } \log_{10} k = \frac{-E_a}{2.303RT} + \log_{10} A .$$

A graph of $\log_{10} k$ against $\frac{1}{T}$ is approximately linear, with slope $\frac{-E_a}{2.303R}$ and intercept on the $\frac{1}{T} = 0$ line of $\log_{10} k = \log_{10} A$.

In exponential form,

$$k = A e^{\frac{-E_a}{RT}}$$

Arrhenius suggested that there existed an equilibrium between "normal" and "active" molecules, and that only the latter could take part in reaction. If the difference between a normal and an active molecule is that the latter has a greater heat content, then an equation of the above form would be expected. Arrhenius's interpretation was that molecules had to have an excess energy ("activation energy") of E_a to be capable of reacting, and that the exponential factor was the fraction of molecules having this excess energy. The great increase in speed of many reactions with increase in temperature is due to a larger fraction of molecules having the excess energy, not to an increased number of collisions. Our present interpretation of the activation energy is still much the same as that of Arrhenius, although the significance of the pre-exponential factor, A , is now clearer.

b) Collision Theory

The collision theory equates the rate of a reaction to the product of the number of collisions of molecules and the probability that each collision will result in reaction.

The simplest case to consider is that of a bimolecular homogeneous gas reaction between two different substances.

(i) Number of Collisions

Kinetic theory shows that the number of collisions per unit time per cubic centimetre of gas, Z_{12} , is

$$Z_{12} = 2^{3/2} d_{12}^2 \pi^{1/2} k^{1/2} T^{1/2} \mu^{-1/2} N_1 N_2 ,$$

where N_1 is the number of molecules of component 1 per cubic centimetre

N_2 is the number of molecules of component 2 per cubic centimetre

d_1 is the molecular diameter of component 1

d_2 is the molecular diameter of component 2

m_1 is the molecular mass of component 1

m_2 is the molecular mass of component 2

k is Boltzmann's Constant,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} , \quad d_{12} = \frac{d_1 + d_2}{2}$$

At room temperature Z is of the order of 10^{28} collisions per cubic centimetre per second.

(ii) Effectiveness of Collisions

As reaction occurs in general for only a small fraction of the collisions, we assume there is a function, $P(E)$, defined on the set of possible molecular energies, $\frac{E}{L}$, where L is Avagadro's Number, such that

$$Z_{12} P(E) = \frac{dN}{dt} = \text{number of molecules reacting per second per cubic centimetre.}$$

In the simplest case only consider the energies in two degrees of freedom, the components of translation of each molecule along the line of approach to each other. Also, assume that $P(E)$ is a step function, and that there exists a value, E_c , of E such that

$$P(E) = 0 \quad \text{for } E \leq E_c$$

$$\text{and } P(E) = 1 \quad \text{for } E > E_c.$$

That is, assume that if the energy of two colliding molecules is greater than a fixed value $\frac{E_c}{L}$ they will always react, but otherwise will never react. This assumption is very crude, and more refined approximations are often employed.

The fraction of molecules which have a relative head-on velocity greater than c , where c is the velocity corresponding to energy E_c (i.e. $E_c = \frac{1}{2}L\mu c^2$) is given by

$$P(E) = \int_{E_c}^{\infty} \frac{1}{RT} e^{\frac{(-E)}{(RT)}} dE = e^{\frac{(-E_c)}{(RT)}}$$

(iii) Predicted Value of Rate Constant

Thus the number of molecules reacting per cubic centimetre per second is

$$\frac{dN}{dt} = Z_{12} e^{\frac{(-E_c)}{RT}}$$

The number of gram moles reacting per litre per second is

$$\frac{dx}{dt} = \frac{10^3}{L} e^{\frac{(-E_c)}{RT}} Z_{12}, \text{ where } x \text{ is the concentration of a product in gram moles per litre.}$$

But $\frac{dx}{dt} = k_2 x_1 x_2$

$$= k_2 \left(\frac{10^3 N_1}{L} \right) \left(\frac{10^3 N_2}{L} \right)$$

$$\therefore k_2 = \frac{d_{12}^2}{10^3} \sqrt{\frac{8 \pi L R}{\mu}} T^{\frac{1}{2}} e^{\frac{-E_c}{RT}}$$

$$k_2 = \frac{A}{T^{\frac{1}{2}}} e^{\frac{-E_c}{RT}}$$

This is quite similar in form to the Arrhenius equation

$$k_2 = A e^{\frac{-E_a}{RT}}, \text{ except that the collision theory predicts}$$

a value for the pre-exponential factor, and inserts a term representing the temperature dependence of the latter.

$$\frac{d \ln k_2}{d T} = \frac{E_c + \frac{1}{2}RT}{RT^2} \quad (\text{Collision Theory})$$

$$\frac{d \ln k_2}{d T} = \frac{E_a}{RT^2} \quad (\text{Arrhenius})$$

Thus $E_a = E_c + \frac{1}{2}RT.$

The derivation above assumes that the activation energy is independent of temperature. This may not be so. The energy of the overall reaction, ΔE , is temperature dependent, and E_c may well be so too.

(iv) Test of Theory

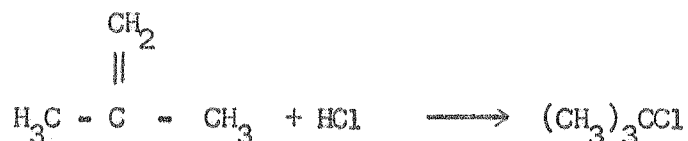
It is found that the insertion of a probability or steric factor, p , is necessary. Originally p was meant to represent the probability that the reactants, in addition to being of the right energy, were spatially arranged in a suitable manner for reaction. However, calculation of values of p from such considerations have been unsuccessful, and p is now only a measure of the agreement between theory and experimental results.

For the reaction



p is 0.33, and the collision theory agrees fairly well with experiment.

The agreement is very poor in many cases of addition reactions, such as

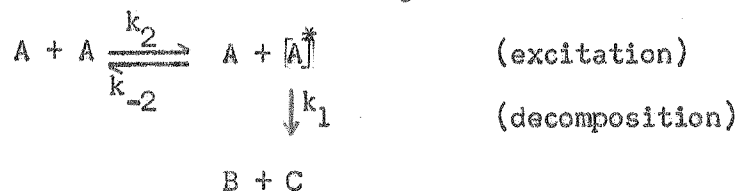


The value of p , taken as before from a table by Moore (32), is 3×10^{-6} .

(v) Collision Theory of First Order Reactions

After much discussion as to the mechanism of first order reactions, in which activation by radiation was suggested, Lindemann (33) in 1922 showed how a collisional mechanism could lead to first order kinetics. He suggested that a time lag occurred between collisional activation and decomposition, during which the energy of the molecule was rearranged among the various modes of excitation.

The reaction scheme envisaged is:



The approximation is made that $\frac{d[\text{A}^*]}{dt} = 0$

Then $\frac{d[\text{B}]}{dt} = k_1 [\text{A}^*]$

$$= \frac{k_1 k_2 [\text{A}]^2}{k_{-2} [\text{A}] + k_1}$$

If $k_1 \gg k_{-2} [A]$,

$$\begin{aligned}\frac{d[B]}{dt} &\approx \frac{k_1 k_2 [A]^2}{k_1} \\ &= k_2 [A]^2\end{aligned}$$

If $k_{-2} [A] \gg k_1$,

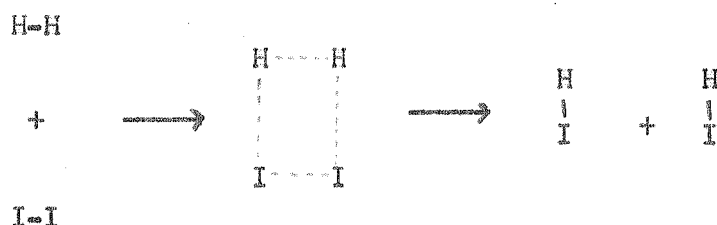
$$\begin{aligned}\frac{d[B]}{dt} &\approx \frac{k_1 k_2 [A]^2}{k_{-2} A} \\ &= k_1 \frac{k_2}{k_{-2}} [A] \\ &= k_1' [A]\end{aligned}$$

The first and second order kinetics are just special cases of a more general kinetic law.

c) Transition State Theory

Collision theory assumes hard body collisions, but this is a very rough approximation. There is no sharp line between interaction and non-interaction between molecules. For example, when a molecule of hydrogen approaches one of iodine, the hydrogen atoms begin to interact with the iodine atoms, while at the same time the hydrogen-hydrogen and iodine-iodine bonds begin to loosen. In

most cases the repulsion is such that the hydrogen and iodine molecules separate, but sometimes the hydrogen-iodine bonds continue to strengthen, while the hydrogen-hydrogen and iodine-iodine bonds loosen. The reaction is thus a smooth and continuous transition between reactants and products,



and details of reaction mechanisms may be investigated.

The transition state theory of reaction rates is largely due to Eyring and co-workers, and is, together with the theory of other "rate processes", the subject of a book by Glasstone, Laidler and Eyring (34).

The energy of the system can sometimes be expressed as "contour maps" showing the relationship of energy and bond distances. For example, the energies of the system $\text{H} \cdots \cdots \text{H} \cdots \cdots \text{H}$ are shown by the graph below from Glasstone, Laidler and Eyring (35).

The axes are drawn at a particular angle such that an object sliding smoothly on a solid model would have the same distribution of translational and vibrational energies as a system of atoms at the corresponding point in phase space. This makes such diagrams very useful for calculating translational and vibrational energies of molecules in reactions.

The position of maximum energy at the top of the barrier is known as the "activated complex" or "transition state".

FIGURE 1.

r_1 r_2
 ENERGY OF H.....H.....H SYSTEM AS
 FUNCTION OF r_1 AND r_2 .

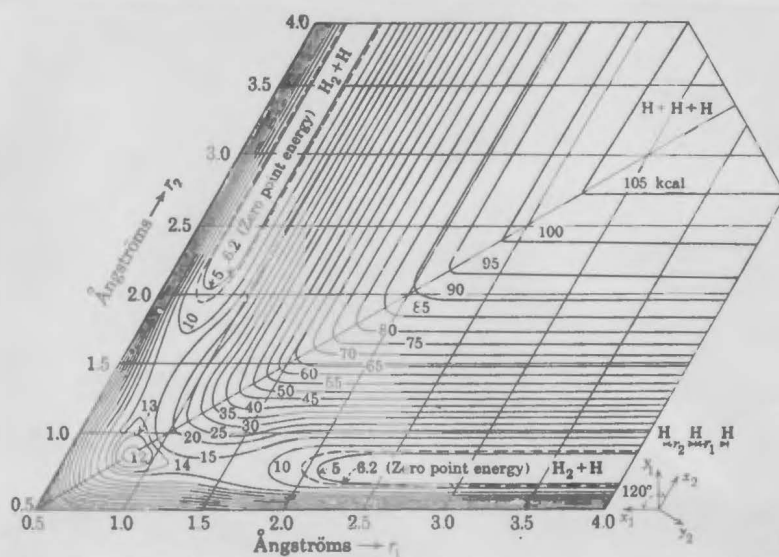


FIG. 27.—Potential-energy surface for the system of three hydrogen atoms based on 14 per cent coulombic energy. (Eyring, Gershinowitz and Sun.)

The rate of a reaction,



where $[AB]^*$ is the activated complex, is equal to the concentration of activated complexes, multiplied by the average velocity with which they pass over the energy barrier.

The rate of passage over the barrier is the frequency ν with which the activated complexes disintegrate into products.

$$\nu = \frac{\epsilon}{h} \quad \text{where } \epsilon \text{ is the average energy of the vibration leading to separation.}$$

The vibration is completely excited, and so

$$\epsilon = kt.$$

Thus the frequency at which the activated complex disintegrates is $\frac{kT}{h}$.

The concentration of activated complex is usually calculated by assuming that it is in equilibrium with the reactants. This assumption is not really justified, and calculations have been done without assuming equilibrium. Present (36) has shown that for reactions with high activation energies, the assumption does not introduce measurable errors. For the very low activation energy of $E_c = 5RT \approx 3 \text{ kcal mole}^{-1}$ at room temperature, the rate constant calculated on the basis of equilibrium is 9% higher than the true value. The error is thus only significant for reactions with very

low activation energies, such as



$$[\text{AB}^*] = K^* [\text{A}][\text{B}]$$

$$\text{Thus } \frac{-d[\text{A}]}{dt} = K^* [\text{A}][\text{B}] \frac{kT}{h}$$

$$\text{Also } \frac{-d[\text{A}]}{dt} = k_2 [\text{A}][\text{B}]$$

$$\therefore k_2 = K^* \frac{kT}{h}$$

Thermodynamic theory shows

$$\Delta G^{o*} = -RT \ln K^*$$

$$\therefore K^* = e^{\frac{-\Delta G^{o*}}{RT}}$$

where ΔG^{o*} is the standard free energy change.

$$\begin{aligned} \therefore k_2 &= \frac{kT}{h} e^{\frac{-\Delta G^{o*}}{RT}} \\ &= \frac{kT}{h} e^{\frac{\Delta S^{o*}}{R}} e^{\frac{-\Delta H^{o*}}{RT}}, \end{aligned}$$

where ΔS^{o*} is the entropy of activation

ΔH^{o*} is the enthalpy of activation.

It is necessary to insert another factor, κ , the transmission coefficient, which is the probability that the activated complex will disintegrate to products rather than to the original reactants.

$$\begin{aligned} \text{Thus } k_2 &= \frac{\kappa kT}{h} e^{\frac{\Delta S^{o*}}{R}} e^{\frac{-\Delta H^{o*}}{RT}} \\ &= \frac{kT}{h} e^{\frac{\Delta S^{o*}/}{R}} e^{\frac{-\Delta H^{o*}}{RT}}, \end{aligned}$$

where $\Delta S^{o*}/ = \Delta S^{o*} + R \ln \kappa$.

The transmission coefficient cannot be determined directly. It is usually included with the entropy of activation, and $\Delta S^{o*}/$ is quoted rather than ΔS^{o*} . This does not introduce a great error as κ is usually between 0.5 and 1.

For reactions in the solid and liquid phases (where the change in volume of the system during reaction is small),

$$\frac{d \ln k_2}{dT} = \frac{\Delta H^{o*} + RT}{RT^2}$$

c.f. Arrhenius

$$\frac{d \ln k_2}{dT} = \frac{E_a}{RT^2}$$

$$\therefore \Delta H^{o*} = E_a - RT$$

Calculation of Results

$$k_2 = \frac{kT}{h} e^{\frac{\Delta S^{o*}}{R}} e^{\frac{-\Delta H^{o*}}{RT}}$$

$$\therefore \frac{k_2}{T} = \frac{k}{h} e^{\frac{\Delta S^{o*}}{R}} e^{\frac{-\Delta H^{o*}}{RT}}$$

$$\therefore \ln \left(\frac{k_2}{T} \right) = \ln \left(\frac{k}{h} \right) + \frac{\Delta S^{o*}}{R} - \frac{\Delta H^{o*}}{R} \left(\frac{1}{T} \right)$$

$$\therefore \log_{10} \left(\frac{k_2}{T} \right) = \log_{10} \frac{k}{h} + \frac{\Delta S^{o*}}{2.303R} - \frac{\Delta H^{o*}}{2.303R} \left(\frac{1}{T} \right)$$

Thus a graph of $\log_{10} \left(\frac{k_2}{T} \right)$ against $\frac{1}{T}$ is linear, of slope $\frac{-\Delta H^{o*}}{2.303R}$, and intercept on $\frac{1}{T} = 0$ of $\log_{10} \frac{k}{h} + \frac{\Delta S^{o*}}{R}$.

The constants R , k and h are well known, and so

ΔH^{o*} and ΔS^{o*} can be calculated.

Entropy of Activation

If the entropy of activation is negative, this shows that the complex is more ordered than the reactants, while a loosely bound transition state is indicated by a positive entropy of activation.

According to the collision theory many combination reactions, $A + B \longrightarrow AB$ are abnormal because of their low steric factors. (see page 29). These low steric factors are the results of increases in order, and therefore decreases of entropy, in forming the transition state.



For example, the entropy of activation for the Menschutkin Reaction



is between - 35 and - 50 kcal mole⁻¹.

Reactions in Solution

Reactions in the gas phase are understood much better than those in solution. In part this may be due to the lack of an adequate model of a liquid.

Many first order gas reactions, such as the isomerisation of pinene and the decomposition of dinitrogen pentoxide, dichlorine monoxide and di-iodomethane, occur at about the same rate in solution as in the gas phase. This appears to indicate that collisions with

solvent molecules have the same effect in activating the molecules as collisions with other molecules of the reactant. In addition some second order reactions have rate constants of about the same magnitude as those for gas phase reactions. The number of encounters between molecules of reactants is fewer in solution, but reacting molecules in solution are trapped by a solvent cage and collide repeatedly. There are also reactions in which the observed liquid phase rate constant is as low as 10^{-9} or as high as 10^9 times the calculated gas kinetic constant.

North (37) considers reactions in solution as composed of two processes: the formation of "encounter pairs", pairs of reactant molecules sufficiently close to interact, and reactions in the encounter pairs.

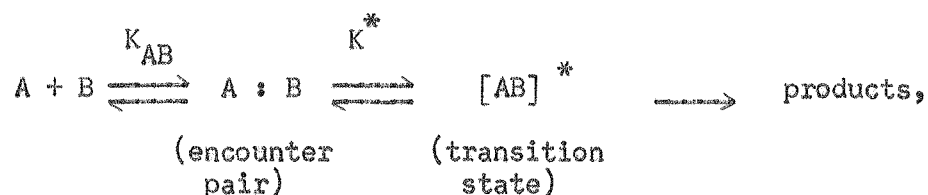
The formation of encounter pairs is a diffusive process and is governed by the law relating diffusion coefficients, D , to temperature,

$$D = a T^{\frac{1}{6}} e^{\frac{-b}{RT} + \frac{c}{T^2} + \frac{d}{T^3} + \dots}$$

$$= A e^{\frac{-B}{RT}},$$

as the $T^{\frac{1}{6}}$ in the pre-exponential term roughly balances out the contributions to the exponential term by powers of T lower than -1 .

This may be applied to collision theory or to transition state theory. The reaction can be envisaged as



The concentration of the encounter pairs is calculated by assuming them to be in equilibrium with the reactants, while the activated complex is assumed to be in equilibrium with the encounter pairs. Similar calculations to those done in the simple transition-state theory (see page 33) lead to the following equation:

$$k_{\text{observed}} = \frac{kT}{h} e^{\frac{(\Delta S^* + \Delta S_{AB})}{R}} e^{\frac{-(\Delta H^* + \Delta H_{AB})}{RT}}$$

where ΔH_{AB} is the enthalpy of forming the encounter pair A:B

ΔS_{AB} is the entropy of forming the encounter pair A:B

ΔH^* is the enthalpy of forming the activated complex
 $[AB]^*$ from the encounter pair A:B

ΔS^* is the entropy of forming the activated complex
 $[AB]^*$ from the encounter pair A:B

North (38) states: "While terms ΔS_{AB} and ΔH_{AB} may often be small compared with ΔS^* and ΔH^* , this is not reason for assuming them to be negligible, nor constant for a series of reactions."

He later considers the meaning of the observed enthalpy and entropy of reactions, ΔH and ΔS in terms of fundamental energies and quantities, such as the energy transmitted during an encounter, the energy needed for diffusion to permit an encounter to take place, and the frequency of vibrations of atoms in the "cage" of molecules surrounding them. The resultant ΔH_{AB} may be up to three kilocalories per gram mole.

In spite of these considerations, he concludes that a completely satisfactory theory of reactions in liquids has yet to be formulated.

6. Studies of the Reactions of Transition Metal Complexes

Transition metal complexes have been known for many years. The first one made was probably Prussian blue, used by artists since the beginning of the 18th century. The first compound to be recognised as different from ordinary salts was hexammine cobalt (III) chloride, $\text{CoCl}_3 \cdot 6\text{NH}_3$, first discovered by Tassaert in 1798. It was not understood how stable compounds of saturated valence, cobaltic chloride and ammonia, could form another stable substance. During the succeeding decades other such complex compounds were made. Many of these were labile and gave the reactions of their constituent simple molecules, but a few gave strange reactions.

For example, a range of amines of cobalt (III) chloride was prepared. It was found that each gave a different number of ions. A. Werner (10) was the first to explain this satisfactorily. He postulated that an atom has two kinds of valence (in modern terminology, oxidation number and coordination number). He formulated $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$, $\text{CoCl}_3 \cdot 4\text{NH}_3$, and $\text{CoCl}_3 \cdot 3\text{NH}_3$ respectively as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, and $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, in agreement with the observation that they dissociated into, respectively, four, three, two, and zero ions.

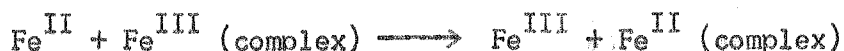
Werner, S.M. Jørgensen, and others concentrated on making many different complexes, and it is only recently that detailed studies of the thermodynamics and kinetics of reactions of transition metal complexes have been made. The thermodynamics of such reactions are the subject of a chapter by Rossotti (39), while Stranks (40) and Basolo and Pearson (41) have written about kinetics and mechanisms.

7. Interpretation of the Data of Kinetics of Reactions

Details of reactions can sometimes be gained by consideration of the dependence of reaction rates on various parameters of the reacting system. The determination by the use of isotopic labelling of whether bonds are broken or not was mentioned earlier (see page 11).

a) Temperature

The effect of temperature on the rate is determined by the enthalpy of activation, but both the enthalpy and the entropy of activation determine the reaction rate, and it is important to consider both. For example, electron exchange reactions of the type



usually have second order rate constants of between one and ten $\text{mole}^{-1} \text{second}^{-1}$ at 0°C .

If the iron (III) complex is $[\text{FeN}_3]^{2+}$ or $[\text{FeOH}]^{2+}$, then the rate constants are 1.8×10^3 and $1.0 \times 10^3 \text{ mole}^{-1} \text{second}^{-1}$ respectively at 0°C . A similar mechanism might be postulated for these two cases if the comparison was only made at 0°C . However, the respective enthalpies and entropies of activation are $13.7 \text{ kcal mole}^{-1}$ and $6 \text{ kcal mole}^{-1} \text{degree}^{-1}$, and $7.4 \text{ kcal mole}^{-1}$ and $-18 \text{ kcal mole}^{-1} \text{degree}^{-1}$, clearly indicating that the mechanisms are not very similar.

The entropies of activation depend on the entropy change in partially replacing one ligand by another, and on the variation in the amount of order of the adjacent solvent molecules due to the variation of the charge of the complex in the transition state.

b) Ionic Strength

For reactions between ions of charges z_A and z_B , the theory of Debye and Hückel predicts that the rate constant, k , at ionic strength μ is related to the rate constant, k_0 , at zero ionic strength by the relation

$$\log_{10} k = \log_{10} k_0 + 2Az_A z_B \mu^{\frac{1}{2}}$$

A is a parameter dependent on the dielectric constant of the solvent,

$$A \propto (\text{D.E.C.})^{3/2}$$

and for water at room temperature, $A = 0.5$.

For example, if the rate determining steps of the attacks by silver ion, water, and hydroxide ion on chloropentammine cobalt (III) ion are as shown below, the rates should increase, not alter, and decrease respectively with increasing ionic strength.



In some cases it may be possible to differentiate between solvation and attack by other nucleophiles by observing the rates of reaction as a function of ionic strength.

For ionic strengths above about 0.01 (and sometimes even below this), the Debye-Hückel theory fails as ion pairs and triplets form. It was once thought that perchlorates did not form ion pairs and so they were used for ionic strength variation. Perchlorate ion pairs and even perchlorate complexes are now known, the first being detected by Sutton (42). The buffers used to keep solutions at constant pH may interfere by substituting into complexes or at least forming ion pairs.

c) External Pressure

For a reaction in which the molar volume of the reactants increases by ΔV^* in the transition state, the rate constant, k_1 , at external pressure P_1 is related to the rate constant, k_2 , at external pressure P_2 by

$$\ln \frac{(k_2)}{(k_1)} = - \frac{(P_2 - P_1) \Delta V^*}{RT}$$

providing the pressure is sufficiently small for ΔV^* to be regarded as constant.

The change in volume, ΔV^* , is the sum of the change in volume of the reactants and the change in volume of the surrounding

solvent. There is a close relationship between the change in volume of the solvent and its change in order, and so there is often a correlation between the molar volume change of activation, ΔV^* , and the entropy of activation, ΔS^* , (see page 44). The sign and magnitude of ΔV^* can give information about the transition state. In particular they may sometimes be used to distinguish between an S_N1 and an S_N2 mechanism for aquation, the former having ΔV^* positive and the latter having ΔV^* negative.

8. Nucleophilic Substitutions

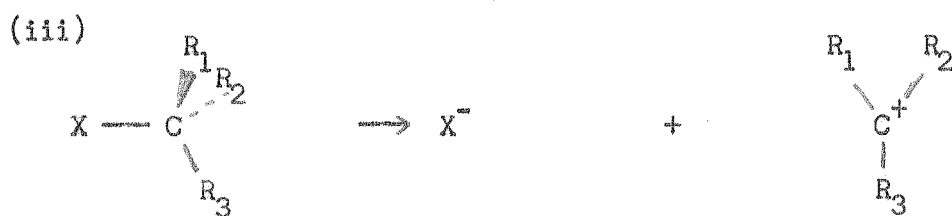
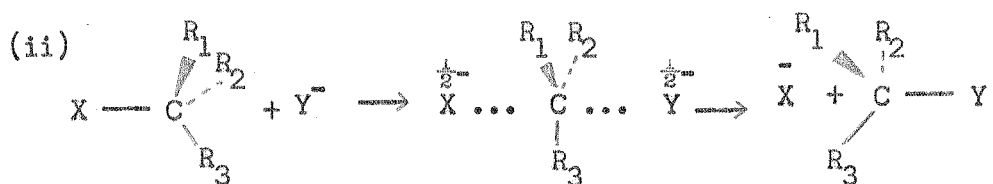
A nucleophilic reagent or nucleophile is an entity which is attracted to a particle with a deficiency of electrons, such as an atomic nucleus. Nucleophiles have at least local excesses of electrons. They may be negatively charged, neutral, or even positively charged, like 1-ammonium-2-amino-ethane ($\text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \overset{+}{\text{NH}}_3$), but some part of the molecule must have an excess of negative charge.

In nucleophilic substitutions, a free nucleophile replaces a nucleophile bound to another atom. Nucleophilic substitutions were first studied in detail at saturated carbon atoms by C.K. Ingold and co-workers, and a satisfactory theory of such substitutions was drawn up. The study of such reactions at transition metal atoms is more complicated because of the greater complexity of the stereochemistry and bonding properties possible in the latter case. As a result of this, theories of nucleophilic substitutions at transition metal atoms are tentative only. As the former are better understood nucleophilic substitutions at carbon atoms will be discussed, and then an account given of present theories and knowledge of substitution at transition metal atoms.

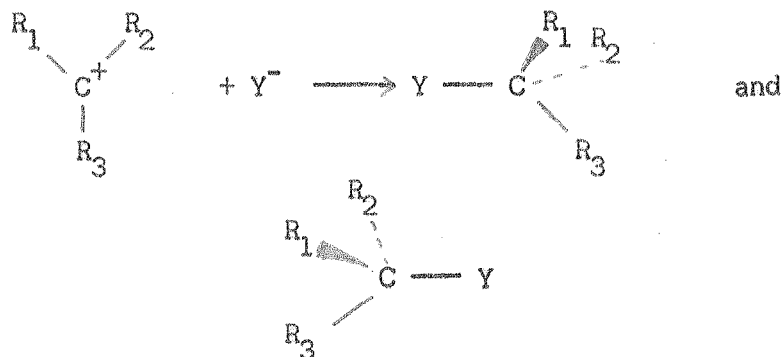
a) Nucleophilic Substitutions at Saturated Carbon Atoms

In a nucleophilic substitution, the nucleophile leaving the carbon atom may do so either after, during, or before the other nucleophile becomes attached to the carbon. These three possibilities were respectively suggested as the mechanism of substitution by Fischer (43) and Werner (44), by Le Bel (45), and by Lowry (46).

For the replacement of X in the general compound R_3CX by Y, the reaction schemes envisaged were respectively:



followed by



It became apparent that mechanism (i) was unlikely. Hughes and Ingold developed the theory of mechanisms (ii) and (iii), and the subject is dealt with by Ingold (47). Hughes and Ingold found that a nucleophilic substitution, S_N in the notation of Ingold, can take place by two different mechanisms.

One of these is a one step reaction, involving the simultaneous making and breaking of a bond (mechanism (ii) shown above).

The other is a two stage process. The former slow stage is the heterolytic breaking of a bond between the carbon atom and the attached nucleophile, X. The second step, which is fast, is the combination of the resultant positively charged species (carbonium ion) with another nucleophile, Y.

As these are respectively bimolecular and unimolecular reactions, they are designated S_N2 and S_N1 respectively. The subscripts apply to the molecularity of the slowest step of the reaction, not to its kinetic order.

If both reactants, R_3CX and Y^- , are present in small concentrations, the kinetic form of an S_N2 reaction is

$$\text{Rate} = k_2 [R_3CX][Y^-] \quad (S_N2 \text{ typical})$$

However, if Y^- is present in constant excess, then

$$k_2 [Y^-] = \text{constant} = k_1^*$$

$$\therefore \text{Rate} = k_1^* [R_3CX] \quad (S_N2 \text{ limiting})$$

* e.g. if Y^- is an important constituent of the solvent

Thus bimolecular substitution can give either second or first order kinetics (or a mixture of both).

Unimolecular substitution gives a carbonium ion CR_3^+ , the rate constant of whose formation is k_h , which may react with either X^- or Y^- and so form either the product R_3CY or regenerate the reactant R_3CX . If the specific rates for these two possibilities are in the ratio α , then

$$\text{Rate} = k_h [\text{R}_3\text{CX}] \frac{[\text{Y}^-]}{\alpha[\text{X}^-] + [\text{Y}^-]} \quad (\text{S}_\text{N}1 \text{ typical})$$

"This equation [using different nomenclature] expresses the typical kinetic form of reactions having the $\text{S}_\text{N}1$ mechanism: when it can be clearly distinguished from its simpler limiting forms, it is highly characteristic of the mechanism." (48)

When $\alpha[\text{X}^-] \ll [\text{Y}^-]$,

$$\text{Rate} = k_h [\text{R}_3\text{CX}] \quad (\text{S}_\text{N}1 \text{ limiting})$$

and first order kinetics are found.

When $\alpha[\text{X}^-] \gg [\text{Y}^-]$,

$$\begin{aligned} \text{Rate} &= k_h [\text{R}_3\text{CX}] \frac{[\text{Y}^-]}{\alpha[\text{X}^-]} \\ &= k' [\text{R}_3\text{CX}] \frac{[\text{Y}^-]}{[\text{X}^-]} \quad (\text{S}_\text{N}1 \text{ limiting}) \end{aligned}$$

If $[\text{X}^-]$ is constant,

$$\text{Rate} = k'' [\text{R}_3\text{CX}] [\text{Y}^-] \quad (\text{S}_\text{N}1 \text{ limiting})$$

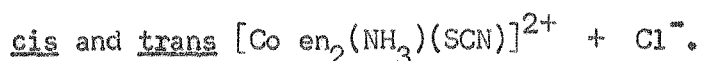
Thus either bimolecular or unimolecular nucleophilic substitutions can give first or second order kinetics, or more complex forms.

From the diagrams of the reactions (see page 48) it can be seen that the S_N2 mechanism implies inversion of configuration, while the S_N1 mechanism, which involves a planar intermediate, CR_3^+ , proceeds by an equal amount of inversion and retention of configuration (i.e. racemisation). This effect is used for studies of substitution using optically active reactants, $CR_1R_2R_3X$ and polarimetric observations.

The S_N2 mechanism implies that one nucleophile approaches the carbon atom as the other one leaves, and that in the transition state both nucleophiles are fairly close to the carbon atom (though further away than the other attached groups). The S_N1 mechanism requires the nucleophile leaving to be completely separated from the carbon atom before the other nucleophile begins to approach. Intermediate cases are known, and are made manifest by a mixture of inversion and racemisation during the reaction.

b) Nucleophilic Substitutions at Transition Metal Atoms

As early as 1911, Werner (44) studied nucleophilic substitutions at cobalt atoms such as



Many attempts were made to relate the steric course of reactions to those of substitutions at carbon atoms, but these were not successful. The coordination number of carbon is usually four, the bonds are arranged tetrahedrally, and there is a one to one correspondence between steric course of a reaction and mechanism (S_N1 or S_N2). However, most transition metals have octahedral coordination, and there is not a one to one correspondence of mechanism and steric course in substitution reactions.

In spite of this difficulty in determining the steric course of a reaction, the nature of reactions has been investigated, and while no one theory can be regarded as satisfactory in explaining all substitution reactions at transition metal ions, progress has been made.

Unlike the case of substitution at a carbon atom, the mechanisms of reaction are not clear for even simple cases where the rate constant does not contain terms for concentrations or active areas of catalysts, and the reaction is effectively irreversible. Consider the replacement reaction



Two simple cases arise.

- (i) The reaction is first order, i.e. $-\frac{d[RX]}{dt} = k_1 [RX]$

The reaction may be slow S_N1 heterolysis



followed by rapid attack of the ligand L on R.



or it may be slow S_N2 solvolysis of RX ,



followed by fast S_N2 attack by L on the solvated species RS .



If the measured rate of solvation of the species is the same as the rate of substitution of L into RX , then it is impossible definitely to tell which mechanism applies. This applies to the rate of chloride exchange in tetrachloroplatinate (II).



in which the aquation rate completely accounts for the chloride exchange rate (49).

For the reaction



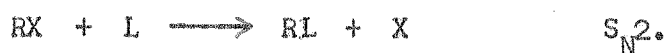
the rate of substitution was found by Grantham, Elleman and Martin (50, 51) to be much faster than the rate for the aquation



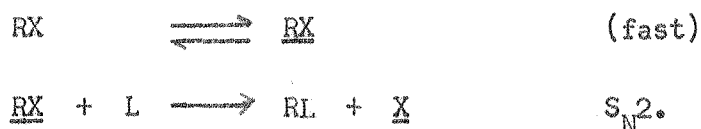
thus showing that the former did not proceed via prior solvation of the complex.

(ii) The reaction is second order.

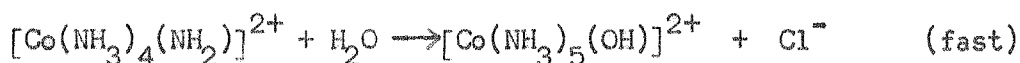
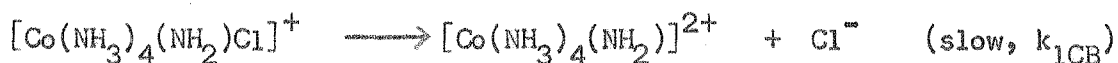
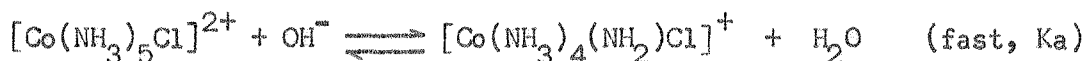
A direct bimolecular substitution may apply



A pre-equilibrium may exist, followed by a bimolecular substitution



If L is basic and RX contains an acidic proton, then we can have the mechanism exemplified by



$$k_{\text{observed}} = k_{1CB} K_a K_w^{-1}$$

This is known as the S_N1 CB (unimolecular nucleophilic substitution of the conjugate base mechanism).

Other possibilities include unimolecular substitution into ion pairs (S_N1 IP), suggested by Pearson, Henry and Basolo (52),

unimolecular substitution with second order kinetics, suggested recently by Jordan and Sargeson (53) but similar to that mentioned previously (see page 50) as a limiting case of the S_N1 mechanism, and the formation of stronger nucleophiles from reactions of basic anions and the solvent.

Brown and Ingold (6) found that the replacement by azide of chloride in cis dichlorobis(ethylenediamine) cobalt (III) in methanol showed mainly second order kinetics,



$$\text{Rate} = k_2 [\text{N}_3^-] [\text{Coen}_2\text{Cl}_2]^+,$$

and interpreted this as an S_N2 reaction.

Pearson, Henry and Basolo (54) showed the reaction was slowed by adding acetic acid, and the kinetics became first order. They suggested that the azide formed methoxide ions which substituted into the complex, the acetic acid removed the methoxide ions, and that acetate ions substituted only very slowly into the complex.

Much experimentation has been carried out in order to investigate the mechanisms of these reactions, but no conclusion has been reached. Evidence has been put forward by Basolo and Pearson (41), Jordan and Sargeson (53), and Baldwin, Chan and Tobe (11) supporting the different theories. Water has been the most common solvent, but is itself a strong nucleophile. Other solvents have

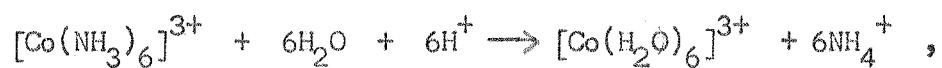
been tested in attempts to observe genuine S_N2 reactions. These also pose problems: most are dipolar and substitute into the complexes. (e.g. Tobe and Watts (55) found the presence of a solvated species when studying the isomerisation of dichlorobis(ethylenediamine) cobalt (III) in dimethyl sulphoxide), and the formation of ion pairs is often troublesome.

Most studies have been of solvation reactions, but apart from these little work has been done on non-isotopic exchanges using neutral ligands (see page 59).

Some of the most valuable work is the study of isotope exchange reactions. Most reactions take place with changes in free energy, and in a series of similar reactions the free energies of activation may parallel the free energies of the reactions. Thus the rate of reaction depends not only on the nature of the ligand to metal bonds in the reactant complex, but also on those in the product. The heat change in isotopic exchange reactions is very small, and so the free energy change is almost entirely due to the entropy of mixing.

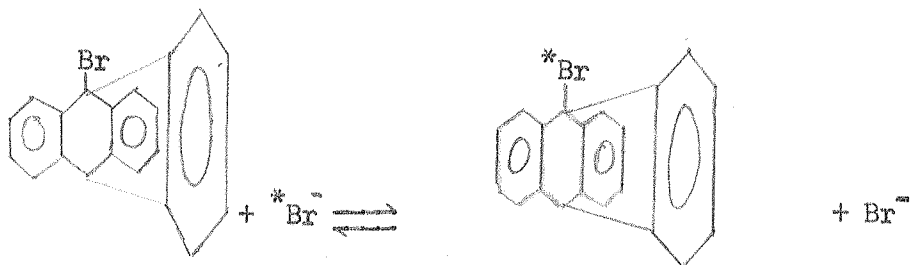
Thus the rate of an isotopic exchange reaction is a measure of the absolute kinetic lability of a complex.

When a normal chemical reaction does not appear to proceed, this may be due to an intrinsically slow reaction, such as the decomposition of hexammine cobalt (III) by dilute acids at room temperature:



or to an unfavourable equilibrium, such as the attempted solvation of chlorotriammine platinum (II) by allyl alcohol (56).

Immeasurably slow isotope exchanges can only be due to intrinsically slow reactions. e.g. the attempted bromine exchange in 1 - bromotryptycene described by Sykes (57).



PART II

EXPERIMENTAL WORK

1. Scope of The Investigation

Although many studies have been made of the rates and mechanisms of substitutions in transition metal complexes (see pages 42 and 51), very little work has been done on the reactions of complexes with neutral ligands, with the exception of solvation reactions, in which the effect of varying concentrations of the nucleophilic substituent cannot be found (see page 49).

Zvagintsev and Karandasheva (58), Banerjee, Basolo, and Pearson (56), and Banerjee and Tripathi (59) studied some substitution reactions in square planar complexes of platinum (II) and palladium (II) complexes. They found that some reactions were of first order kinetics, and some of second order.

For example, Banerjee, Basolo, and Pearson (56) studied the reactions



where X was glycine, aniline, pyridine, allyl alcohol or ammonia. They also used oxalate ion for comparison purposes. Their results showed the first three reagents gave slow first order reactions, allyl alcohol and ammonia reacted fairly slowly with second order kinetics, while oxalate reacted much more rapidly with second order kinetics.

Enthalpies and entropies of reactions have been calculated for a very few reactions of platinum (II) complexes by Zvagintsev and Karandasheva (58).

Even fewer studies have been made of the substitution of neutral ligands into octahedrally co-ordinated transition metal species (other than solvation). Bjerrum and Poulsen (60) used visual observations of the changes in colour of complexes at low temperatures (-100° to -75°C) to determine the kinetics of reactions which are too fast to measure by conventional means at room temperatures. They found that the aquated nickel (II) ion reacted slowly with pyridine and ethylenediamine at -75°C , but that the aquated copper (II) ion reacted in a few seconds with ethylenediamine at -100°C and "instantaneously" with pyridine and ammonia. Approximate Arrhenius activation energies and frequency factors were calculated.

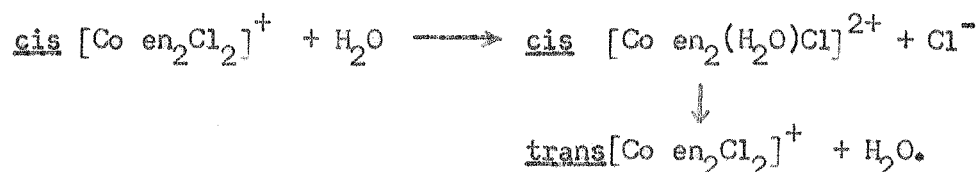
In this investigation it was decided to study the reaction of pyridine with the dichlorobis(ethylenediamine) cobalt (III) ion, $[\text{Co en}_2\text{Cl}_2]^+$, as results could then be directly compared with the many results reported on the substitution of anionic ligands into both the cis and trans isomers of this species. In order to lessen the amount of solvation, Brown and Ingold (6) used methanol as a solvent to study the reaction



where X^- was CH_3O^- , N_3^- , NO_2^- , SCN^- , Br^- , $^*Cl^-$ or $^-NO_3$, and this solvent has also been used by Pearson, Henry and Basolo (52), Chan and Tobe (61), and Sward (62).

Tobe and Watts (63, 64) studied the cis \longrightarrow trans isomerisation of $[Co\ en_2Cl_2]^+$ in other solvents; dimethyl formamide, dimethyl acetamide, and dimethyl sulphoxide, and summarised the results of other workers.

Although Pearson, Henry and Basolo (52) found that up to 0.5% water had no effect on the rate of reaction, Sward (62) considered that there was a marked acceleration of both the cis \longrightarrow trans isomerisation and chloride exchange by water. He postulated that the reaction for the isomerisation involved the steps:



As a result of these considerations, it was decided to use anhydrous methanol as the solvent in the present investigations.

It was decided to follow the substitution reactions by spectrophotometric means, if possible, and so some work was first done on the absorption spectra of cobalt complexes containing pyridine and/or ethylenediamine as ligands.

Other methods do not in general seem suitable for this type of study. Potentiometric determination of chloride ion appears impossible as pyridine forms complexes with silver/silver chloride and mercury/mercurous chloride electrodes. Simple volumetric or gravimetric methods of determining chloride are unsuitable for similar reasons. In addition, as found by Werner and co-workers (10), silver ions attack co-ordinated chloride. The method used by Baldwin, Chan and Tobe (11), viz. ion exchange followed by determination of chloride, could be used to follow the gross replacement of chloride by pyridine, but the species present in solution could not be determined.

2. Preparation, Purification and Examination of Materials

The reagents were prepared, and the expected products made directly and examined.

a) Drying of Methanol

For all substitution runs except the first, analytical reagent methanol was dried by the use of amalgamated aluminium foil by the method of Walden, Ulich and Laun (65).

b) Purification of Pyridine

Pyridine was distilled with the aid of a fractionating column, and the fraction boiling at 114-115.5°C was taken and analysed acidimetrically by potentiometric titration against standard acid. Different batches varied from 99 to 99.5% pure, and their refractive indices were about 1.506, instead of 1.5080 which is the value for pure pyridine (interpolated from values given by Timmermans (66)).

For use in substitution runs, the water present was removed by treatment with anhydrous calcium sulphate and filtered, as described by Hammond and Winthrow (67, 68). Titrations showed the pyridine content to be 100.0% to within experimental error (about $\pm 0.2\%$), while the refractive index was correct to the fourth decimal place. Evaporation of a sample of about twenty millilitres of the filtrate left no apparent residue.

c) Purification of Ethylenediamine (1, 2 diaminoethane)

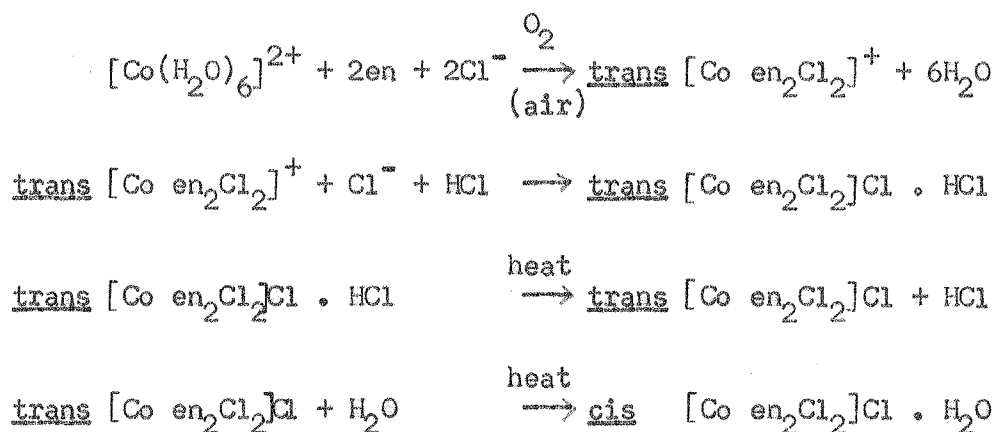
Crude ethylenediamine was fractionally distilled, and a 114-118°C cut was taken. The distillate was probably a mixture of ethylenediamine ($\text{NH}_2\text{-(CH}_2\text{)}_2\text{-NH}_2$), and its monohydrate, which have similar boiling points (116-117°C and 118°C respectively), but different densities (0.8994 and 0.963 gm/ml. at 20°C respectively) (69). The distillate had a density of 0.912 gm/ml. at 20°C, and thus a 10% W/W aqueous solution (employed for the manufacture of trans dichlorobis(ethylenediamine) cobalt (III) chloride hydrochloride) needed 72 ml of the distillate in 600 gm of solution, assuming no contraction or expansion on mixing ethylenediamine and its hydrate.

d) Preparation and Purification of Dichlorobis(ethylenediamine)

Cobalt (III) Chloride

The hydrochloride of trans dichlorobis(ethylenediamine) cobalt (III) chloride was prepared by air oxidation of an aqueous solution of cobalt (II) sulphate, ethylenediamine, and hydrochloric acid. The hydrogen chloride was removed by heating the complex, leaving crude trans dichlorobis(ethylenediamine) cobalt (III) chloride, some of which was dissolved in water and evaporated to give the crude cis isomer. The method is described by Bailar (70) who, unlike Jørgensen (71), and Chan and Tobe (61), does not mention that the cis isomer is a monohydrate; the trans isomer is anhydrous.

The reactions are, where en is ethylenediamine,



The purple cis dichlorobis(ethylenediamine) cobalt (III) chloride hydrate (hereafter cis $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ for brevity) was dissolved in the minimum volume of water at 25°C and cooled in an icebath. No crystals appeared, and so small portions of ethanol and diethyl ether were added, and the solution further cooled in an ice/ethanol bath. The resultant crystals were removed by vacuum filtration, washed with ethanol and sucked dry on the filter. The wash liquor was added, together with a little ether, to the filtrate, and the process repeated. The different crops of crystals were kept separately, and each was then examined at 8 to 160 magnifications with a stereoscopic microscope. Those crops which showed the presence of yellow crystals (probably of $[\text{Co en}_3]\text{Cl}_3$) in addition to the violet cis $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ were rejected.

	Cl	Co
Found	33.4 , 36.6	19.5, 19.7, 19.2
Calculated for $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$	35.1	19.4

The green trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ was purified in like manner.

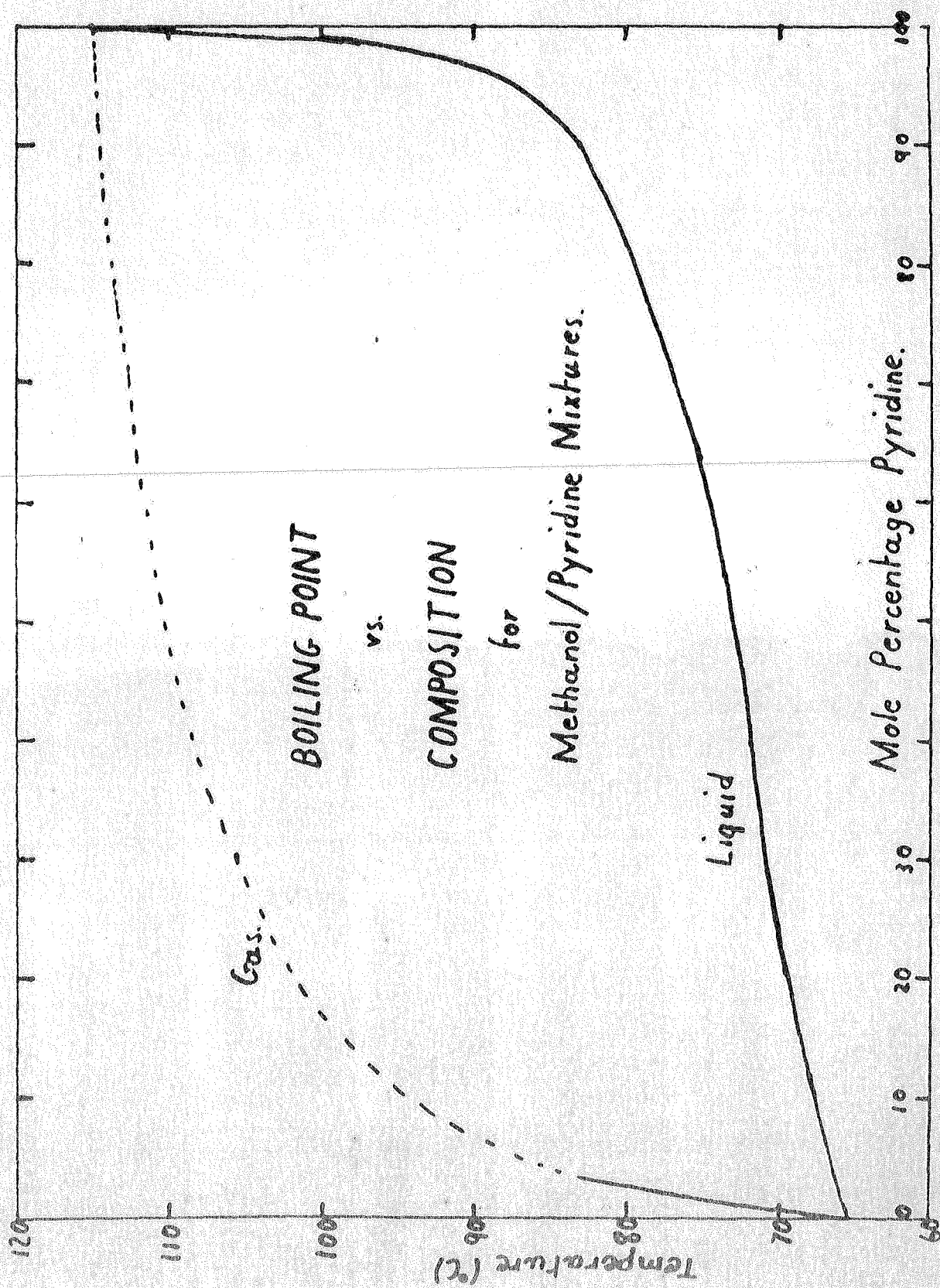
	Cl	Co
Found	38.4 , 37.8	20.2, 20.85
Calculated for $[\text{Co en}_2\text{Cl}_2]\text{Cl}$	37.3	20.65

Preparation of Pyridine Substituted Compounds

Several preparations of the expected products were made by refluxing $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ with pyridine. Sometimes charcoal was used as a catalyst, and sometimes methanol or water was used to dilute the pyridine and to lower the boiling point of the mixture. The boiling point of methanol/pyridine mixtures at one atmosphere pressure was determined by Dickenson (72) whose results are shown in figure 2. The boiling point of the azeotrope of water and pyridine, containing 57% (by weight) of pyridine is given by Timmermans (73) as 93°C at atmospheric pressure.

The preparations usually used the cis isomers. It has been found by Friend and Mellor (74) that solid trans isomer changes into solid cis isomer in hot pyridine before reacting with the pyridine.

FIGURE 2



(1) Ten millilitres of pyridine was refluxed with 0.5 gm. of cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ for seven hours. The product was washed with methanol and then with diethyl ether. Examination under a stereoscopic microscope showed it to consist mainly of a pink powder, but with yellow, purple, red, and blue crystals also present.

(2) Ten millilitres of pyridine plus ten millilitres of methanol were refluxed with 0.5 gm of cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ and a little charcoal for eleven hours. A pink powder resulted. This was purified by recrystallisation, as described for cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$. The analyses and spectra of this showed it to be cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ where py represents pyridine.

	Cl		Co
Found	29.2,	28.9	15.5 , 16.4
Calculated for $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$	29.3		16.2

(3) In order to determine whether pyridine would substitute into $[\text{Co en}_2\text{Cl}_2]^+$ in the presence of methanol only, reflux (2) was repeated, but without charcoal. After four hours a similar pink powder was filtered off from the orange solution. The filtrate was evaporated by gentle heating, and yellow and blue crystals (perhaps $[\text{Co en}_2\text{py}_2]\text{Cl}_3$, and a cobalt (II) species respectively) were deposited.

(4) Although Bailar and Clapp (75) found that $[\text{Co en}_2\text{py}_2]\text{Cl}_3$ did not form when $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ was ground with aqueous pyridine, the work by Nunn (76) and Gee (77) suggests that it may form in solution. A half gram sample of cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ was heated under reflux with twenty millilitres of pyridine and an equal volume of water, together with a little charcoal. Vacuum evaporation of the orange solution gave a small quantity (about fifty milligrams) of yellow crystals. The solution remaining was treated with ethanol and ether in an attempt to produce more crystals. However, a brown sludge formed.

No analyses were carried out on the yellow material which is thought to be $[\text{Co en}_2\text{py}_2]\text{Cl}_3$, as, after the use of some of the material for spectrophotometric work, insufficient remained for analysis.

Experimental Methods of Analysis of Cobalt Complexes

Total Chloride

Werner (44) showed that many complexes containing halogens of pseudohalogens formed addition compounds with silver ions, e.g.



and the silver halide or pseudohalide was only removable by boiling the solution of the complex. Therefore, chloride was determined gravimetrically after boiling samples of the complexes with acidified silver nitrate solution for an hour.

Free (Ionic) Chloride

Attempts were made to analyse materials for ionic chloride by cooling concentrated aqueous solutions of the complexes to 0°C , adding an acidified ice cold solution of silver nitrate in methanol plus acetone, and immediately filtering off the silver chloride and weighing it. The results were invariably high and completely unreproducible.

Cobalt

Samples of the complexes were weighed into crucibles and repeatedly evaporated to dryness with sulphuric or sulphuric plus nitric acids at 470°C . However, even seven such treatments did not suffice to oxidise all the carbon. Heating the samples with nitric acid was next tried, and it was found that two treatments removed all the carbon. The resulting cobalt nitrate samples were evaporated to dryness with sulphuric acid at 470°C and the solids weighed as cobalt sulphate.

3. Spectroscopic Examination of Materials

The complexes were examined spectroscopically in the infrared, near infrared, visible, and ultraviolet regions. The following table indicates the relationship between the present investigation and previous work.

SPECTROSCOPIC INVESTIGATIONS

	Ultraviolet 215 to 400 m μ	Visible 400 to 725 m μ	Near Infra-red 0.725 to 2.6 μ	Infrared 2.6 to 22 μ
<u>cis</u> [Coen ₂ Cl ₂]Cl·H ₂ O	2 Charge transfer Bands III and IV Band IV split	3 Spin allowed Laporte forbidden Bands I and II Slight splitting of I	4 Spin forbidden Laporte forbidden Bands A and B (0.725 to 1.1 μ)	3 Vibrations of en, H ₂ O
<u>trans</u> [Coen ₂ Cl ₂]Cl	4 Bands III and IV Band IV not split	3 Bands I and II Band I greatly split	4 Bands A and B (0.725 to 1.1 μ)	3 Vibrations of en
<u>cis</u> [Coen ₂ pyCl]Cl ₂	3 Bands III and IV Band IV not split	3 Bands I and II Band I slightly split	2 Bands A and B (0.725 to 1.0 μ) Vibrational motions of en, py (Combinations and overtones)	1 Vibrations of en, py
[Coen ₂ py ₂]Cl ₃	1 (250 to 400 m μ) Band II	1 Bands A and I	1 Overtones and combinations of vibrational motions of en, py	1 Vibrations of en, py
<u>trans</u> [Copoly ₄ Cl ₂]Cl·6H ₂ O				1 Vibrations of py, H ₂ O

1. Studied only in this investigation
2. Knowledge extended by this investigation
3. Studied by this investigation, confirming observations of other workers
4. Not studied in this investigation.

Near Infrared, Visible, Ultraviolet Spectra of Cobalt Complexes

Experimental

The spectra were measured of aqueous or methanolic solutions of the cobalt complexes within the range 215 millimicrons to 1125 millimicrons. Aqueous solutions were used for the near infrared part of the spectrum (750 to 1125 millimicrons) as the complexes were insufficiently soluble in methanol for the very weak absorptions in this region to be apparent. Reflection spectra were also measured of the complexes containing pyridine in the range 250 to 2600 millimicrons.

The machines used were a Perkin-Elmer "Spectracord" recording spectrophotometer, a Unicam S P 500 non-recording spectrophotometer, and a Bausch and Lomb "Spectronic 20 Colorimeter" (a small non-recording spectrophotometer). The ranges over which these machines can be used are respectively 215 to 2800 millimicrons, 215 to 1000 millimicrons, and 340 to 630 millimicrons. As discussed later, the Perkin-Elmer "Spectracord" was not sufficiently accurate in measurements of optical density. Because of this and the fact that the Bausch and Lomb uses a fairly large band-width (about 20 millimicrons), the spectra shown come from measurements using the Unicam S P 500 wherever possible, but with the observed wavelengths corrected to true wavelengths by the use of spectra of standard materials (rare earth glasses).

For spectra embracing a wide range of densities, a simple optical density versus wavelength or frequency graph is unsuitable. The regions of high optical density completely overshadow those of low optical density. The extinction coefficients of the absorption bands for the solutions considered range from about 0.5 to about 25,000, and only a logarithmic scale can give a reasonable graph of such extreme values. Also when the wavelength considered varies from 250 millimicrons to 2.5 microns (or wavenumber from 40000 cm^{-1} to 4,000 cm^{-1}) neither a scale linear in wavelength nor a scale linear in wavenumber is suitable. The former compresses the ultraviolet end of the spectrum and unduly emphasises the near infrared, while the latter has the reverse effect. In order not to have to change the scale of the abscissa or the ordinate partway through a graph, logarithmic scales have been used for some graphs. When it was required to use a logarithmic scale for the abscissa, the octaval of the radiation was plotted. The definition of octaval given by Shurcliff (78) is

$$\text{Octaval (in CRU)} = 100 (\log_2 \frac{\text{wavelength in millimicrons}}{375} + 2)$$

Discussion of the Near Infrared, Visible, and Ultraviolet Spectra of Cobalt Complexes

The energy diagram for the d^6 configuration, due to Tanabe and Sugano (79) and reproduced from Dunn (80) is shown

There are two very weak transitions ($\log \epsilon = -0.6$ to $+1.5$) usually in the infrared or red known as Bands A and B. These are respectively due to the ${}^3T_1 \leftarrow {}^1A_1$ and the ${}^3T_2 \leftarrow {}^1A_1$ transitions. These are Laporte forbidden, as there is no change in electric dipole moment as a result of the transition, and also spin forbidden, as the spin multiplicity changes from one to three. The B band, which is at the higher frequency of the two spin forbidden bands, cannot always be observed because it is often overlain by a stronger band which is known as Band I and is the lower frequency of the two spin allowed bands in the visible region. These bands are of moderate intensity only ($\log \epsilon = 1.4$ to 2.1) as they are still Laporte forbidden.

Lowering of the symmetry of the environment of the atom, by replacing two of the six equivalent ligands in a regular species such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ results in an observable splitting of the first (${}^1T_1 \leftarrow {}^1A_1$) but usually not the second (${}^1T_2 \leftarrow {}^1A_1$) band. The splitting is greater for the trans isomer. Laporte's rule applies to environments with a centre of symmetry, which is the case with the trans isomer of complex $[\text{Co } X_4 Y_2]$, but not with the cis isomer. Thus the intensities of the A, B, first, and second bands are usually greater for the cis isomer.

In the ultraviolet region two charge transfer bands occur. The one at longer wavelength (band III) has $\log \epsilon \approx 3$, while the one at shorter wavelength (band IV) is fully allowed with $\log \epsilon$ greater than 4.

The spectra of ions of the type $[\text{Co en}_2(\text{amine})(\text{halide})]^{2+}$ have been discussed by Yasui and Shimura (83), who assign the bands in these species in a similar manner.

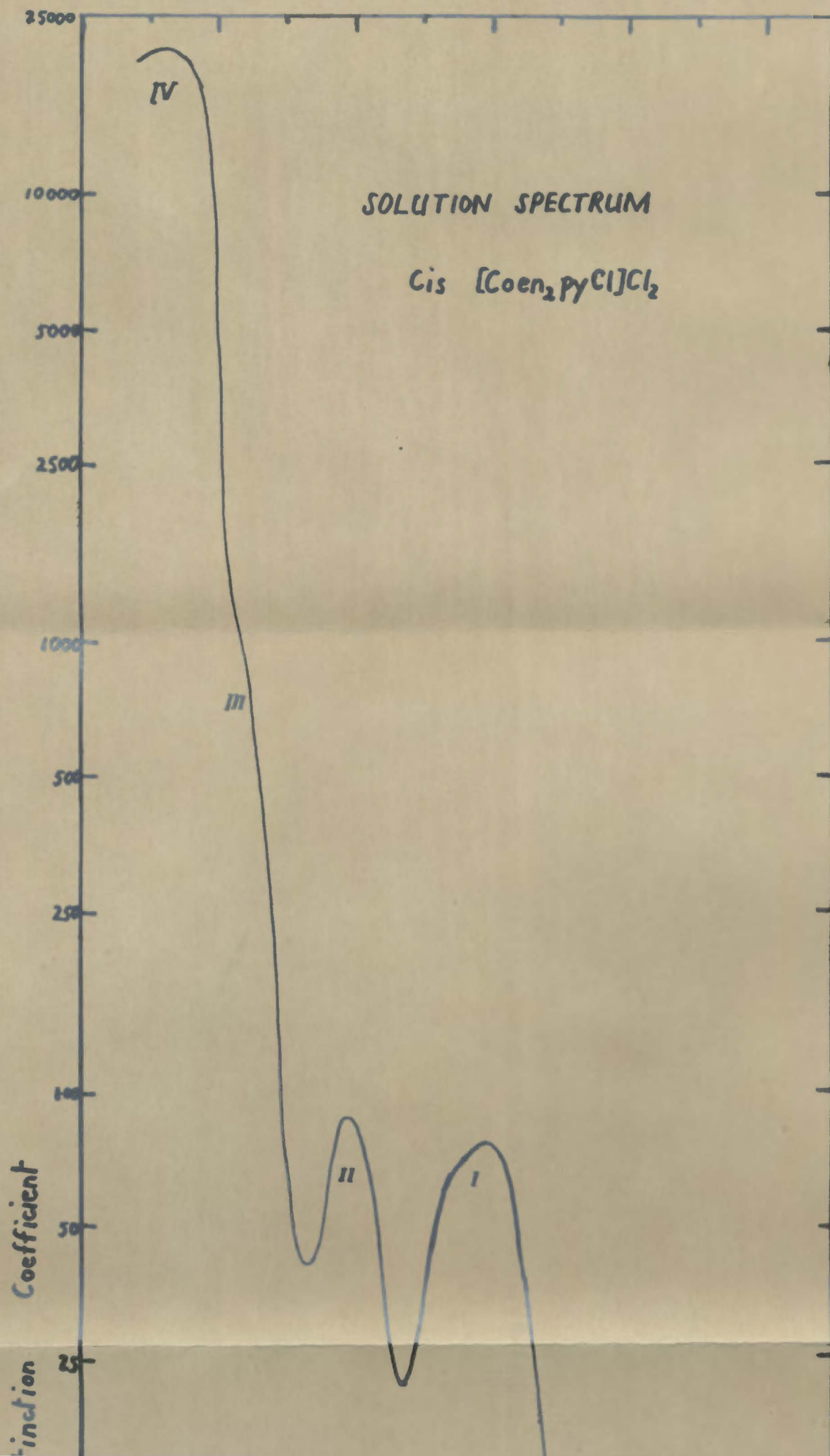
Results and Discussion

Cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$.--The solution spectrum of this material was measured in the ultraviolet, visible, and near infrared regions from 215 to 1125 millimicrons (figures. 4, 5, 6).

NEAR INFRARED TO ULTRAVIOLET SPECTRUM OF $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ IN SOLUTION:

BAND POSITIONS, INTENSITIES AND ASSIGNMENTS

<u>Yasui and Shimura</u>			<u>This Work</u>			
Wavelength (m μ)	Extinction Coefficient	Assignment	Wavelength (m μ)	Octaval (CRU)	Extinction Coefficient	Assignment
			1040	347	0.25	Ethylenediamine vibration (see page)
842	0.54	A	850	318	0.53	Band A. ${}^3\text{T}_1 \leftarrow {}^1\text{A}_1$
525.5	76	Ia	525	248.5	77	Band Ia. ${}^1\text{T}_1 \leftarrow {}^1\text{A}_1$. This
466	31	Ib				band showed marked lack of
						symmetry and indicated the
						presence of Band Ib at
						about 470 millimicrons.
368	81.5	II	368	197	81	Band II. ${}^1\text{T}_2 \leftarrow {}^1\text{A}_1$
281	870	III	285	160	900	Band III. Charge transfer.
						Only a small variation in
						slope is present so the
						position and intensity can-
						not be determined precisely
						without mathematically sep-
						arating curves. (The position
						is similar in Band I)
233	2.4×10^4	IV	232	131	2.2×10^4	Band IV. Charge transfer



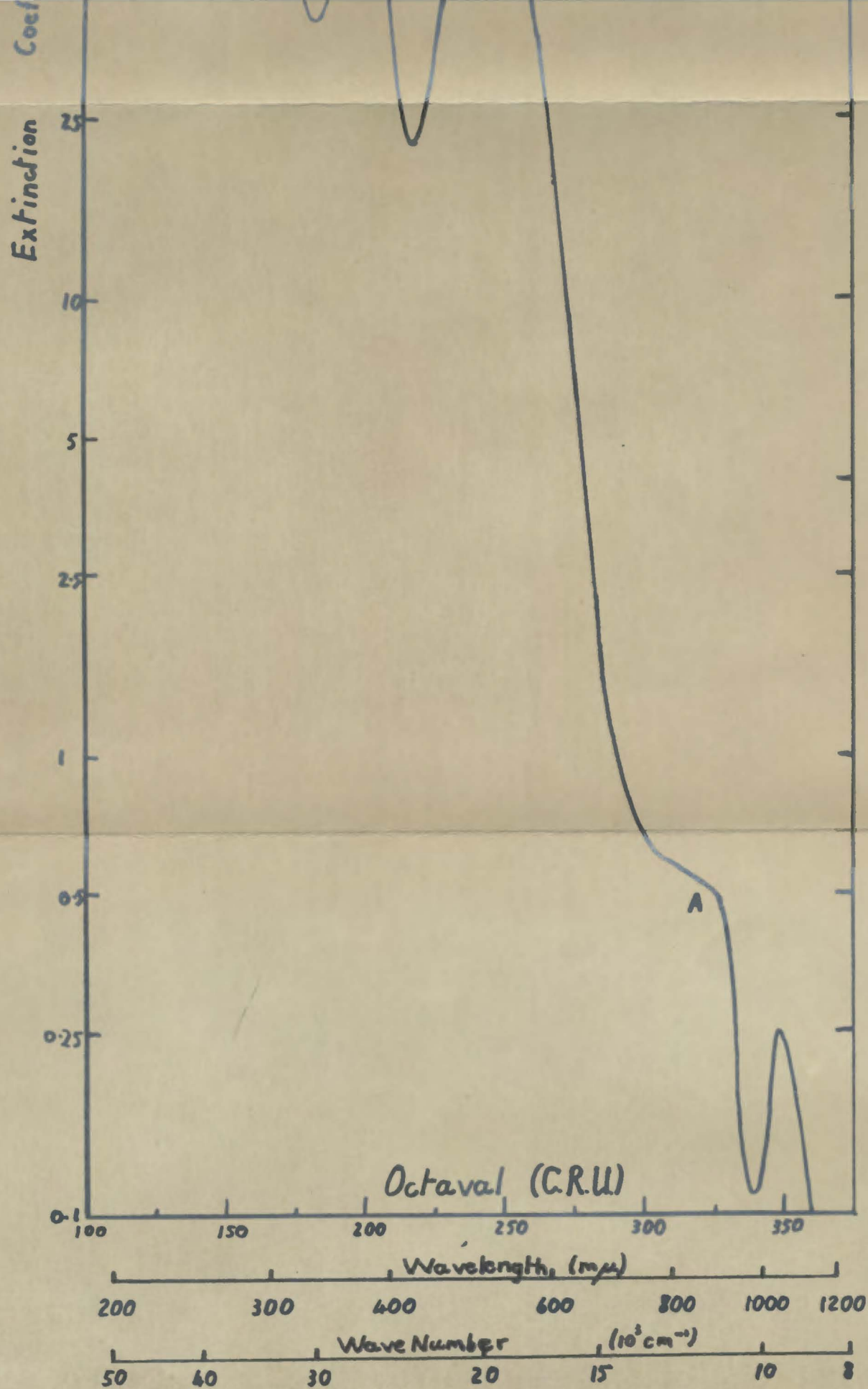


FIGURE 5

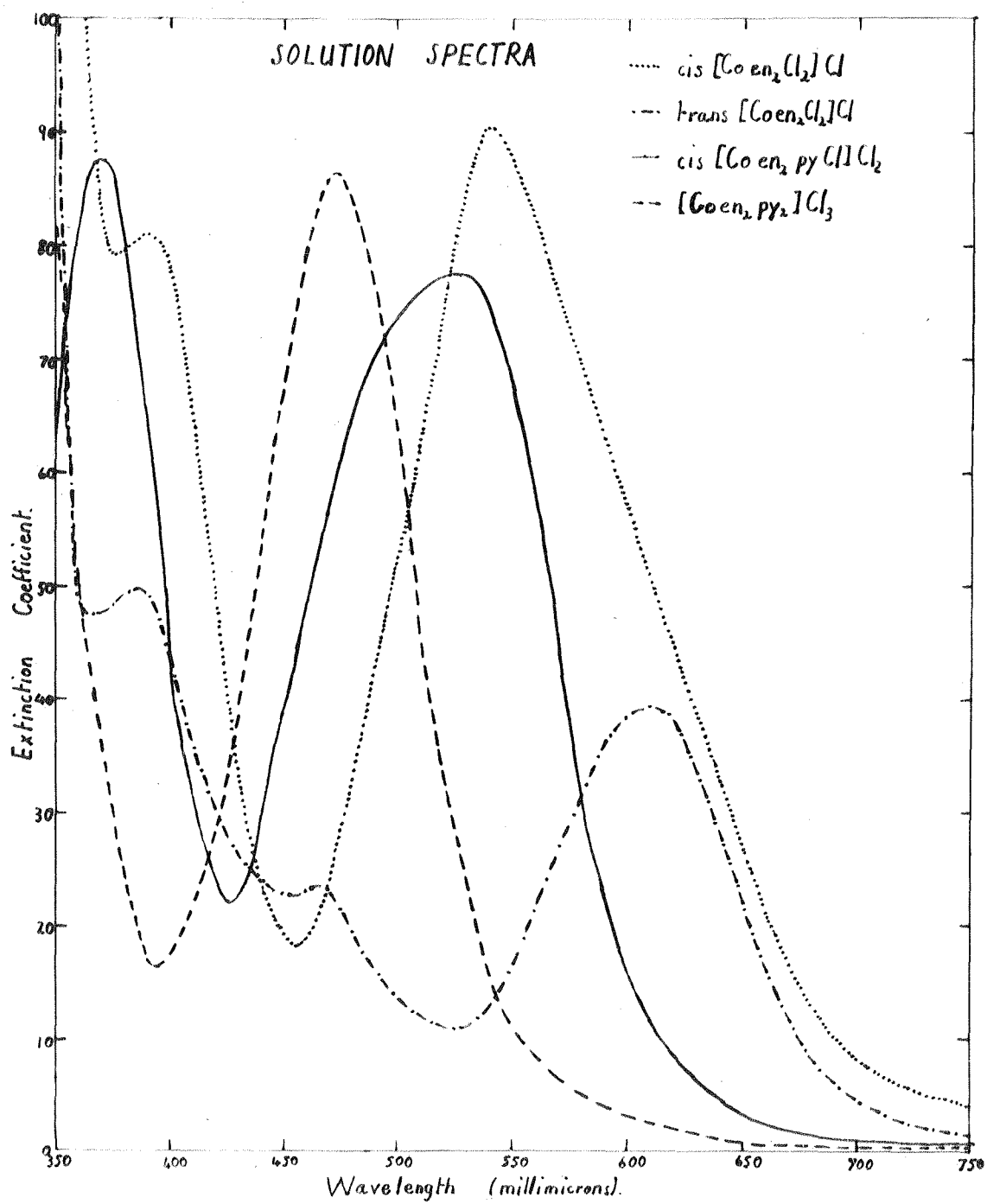
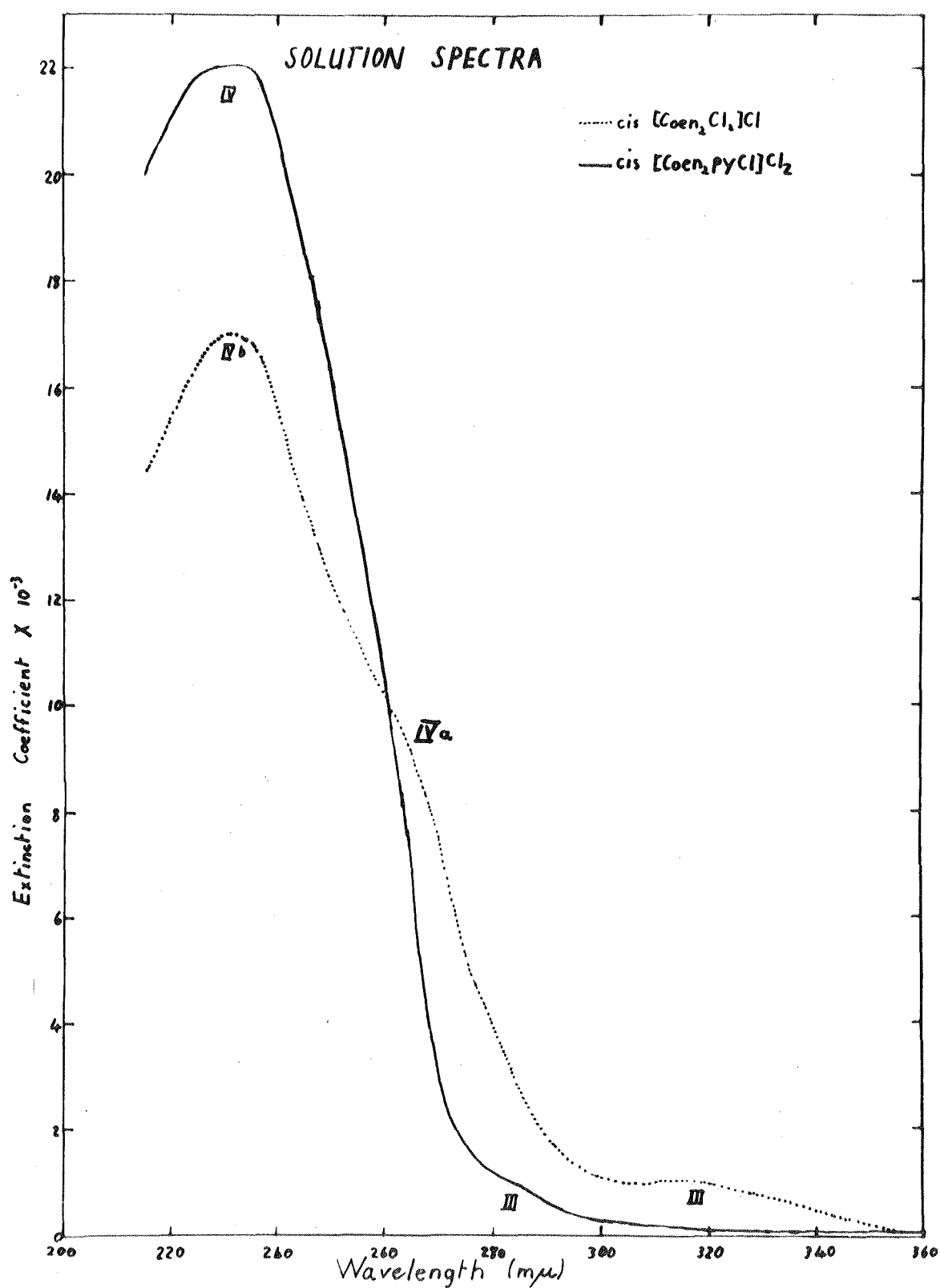


FIGURE 6



These results quite well agree with those of Yasui and Shimura (83), but they did not report a band at 1040 millimicrons. The maximum extinction coefficient of the band is lower even than the extinction coefficient of the minimum between any other two bands, and the band is off the scale of their graphs. At first the writer thought it could be the doubly spin forbidden $^5T_2 \leftarrow ^1A_1$ transition, but its intensity seems too large for this. It is now thought to be a vibrational motion of ethylenediamine. A vibration of ethylenediamine with optical density of 0.95 in a one centimetre cell was found at 1040 millimicrons for ethylenediamine (see page 92). This corresponds to a molar extinction coefficient of 0.065. As there are two ethylenediamine groups in the complex, a molar extinction coefficient of 0.13 would be expected for $[Co en_2pyCl]Cl_2$, but the actual value is higher, being 0.25. Apparently the altered environment on co-ordination results in the vibration being less forbidden than in the free material.

The near infrared portion of the spectrum required the use of concentrated solutions (of the order of 0.1 molar) even in cells of ten centimetres path-length. The literature (81, 82) indicated that the other complexes likely to be present also have only very weak near infrared absorption. None of the complexes is very soluble in methanol. These two facts showed that the reaction scheme could not be investigated by the use of near infrared spectra, and so the infrared solution spectra of the other complexes were not determined.

The reflectance spectrum (figure 7) was taken in the region 250 to 2550 millimicrons. It is qualitatively similar to the solution spectrum and shows the following electronic transitions.

Wavelength (m μ)	Octaval (CRU)	Classification	Assignment
820	313	shoulder	Band A
495	240	strong	Band I
\sim 375	\sim 200	shoulder	Band II
\sim 292	\sim 164	shoulder	Band III

The weak band at 1050 millimicrons was not observed. However, as well as the bands due to electronic transitions in the complexes, other relatively narrow bands were observed in the near infrared.

Cis and trans [Co en₂Cl₂]Cl.---The solution spectra of cis and trans [Co en₂Cl₂]Cl were measured in the visible region, 350 to 750 millimicrons, and that of cis [Co en₂Cl₂]Cl was also measured in the near ultraviolet, 215 to 350 millimicrons (figures 5 and 6). These are similar to those of Sward (62), Linhard and Weigel (81, 82), and Brown and Nyholm (84). Unless otherwise indicated, the values given below for these workers are read from their graphs (in the case of Linhard and Weigel a logarithmic graph). They are therefore approximate only.

VISIBLE AND ULTRAVIOLET SPECTRA OF CIS AND TRANS $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ IN SOLUTION:
BAND POSITIONS, INTENSITIES AND ASSIGNMENTS

This Work			Linhard and Weigel			Sward		Brown and Nyholm	
Cis	Trans	Assignment	Cis	Trans	Assignment	Cis	Trans	Cis	Trans
Wavelength ($m\mu$)	Wavelength ($m\mu$)		Wavelength ($m\mu$)	Wavelength ($m\mu$)	Wavelength ($m\mu$)	Wavelength ($m\mu$)	Wavelength ($m\mu$)	Wavelength ($m\mu$)	Wavelength ($m\mu$)
Extinction Coefficient	Extinction Coefficient		Extinction Coefficient	Extinction Coefficient	Extinction Coefficient	Extinction Coefficient	Extinction Coefficient	Extinction Coefficient	Extinction Coefficient
600 X	610 38	Ia	590 55	625 40	Ia		610 37.8 *	608 40	
540 91	465 27	Ib	545 90	455 32	Ib	*	455 25	460 25	
390 82	375 50	II	377 85	385 37	II	380 100	385 45	390 110	385 45
314 10^3		III	307 7.1×10^2	300 1.4×10^3	III				
270 9×10^3		IVa		250 2.7×10^4	IV				
232 1.7×10^4		IVb							

* Tabulated by writer.

X Unsymmetry in larger, neighbouring peak, apparent, due to weaker band.

The present work shows the previously unobserved second charge transfer band (Band IV) in cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}$. The lower symmetry of the cation, compared with trans $[\text{Co en}_2\text{Cl}_2]^+$ and $[\text{Co en}_3]^{3+}$ results in the splitting of the band into two components. The band at the longer wavelength is here called Band IVa, and the band at the shorter wavelength Band IVb. Band IVa is centred at about 270 millimicrons, with an extinction coefficient of approximately 9×10^3 . Its exact position is hard to find as it is overlain by the stronger Band IVb, with maximum extinction coefficient of 1.7×10^4 at 232 millimicrons. The splitting of Band IV into Bands IVa and IVb as a result of low symmetry of the molecules has not previously been observed.

It was found by the writer to be very difficult to measure the extinction coefficients of the complexes in the ultraviolet region to better than $\pm 10\%$, most probably because of the extremely low concentrations needed (of the order of two milligrams per hundred millilitres of solution).

Pyridine absorbs in the ultraviolet, and in addition any ion pairs formed in solution would alter the ultraviolet absorption spectrum of a reaction mixture. For these reasons it was decided to follow the reactions by measurements of the change of the visible spectrum only. Therefore the visible absorption spectrum only of $[\text{Co en}_2\text{py}_2]\text{Cl}_3$ was determined (figure 5).

It shows only one absorption maxima in the visible region at 472 millimicrons, of extinction coefficient 86.5. This is most probably Band I in the above classification, corresponding to the ${}^1T_1 \leftarrow {}^1A_1$ transition. It is not noticeably split, as pyridine and ethylenediamine have very similar positions in the spectrochemical series. The position of this band is very close to that of the first band (465 millimicrons) in $[\text{Co en}_3]\text{Cl}_3$ as found by Linhard and Weigel (81, 82).

The very weak A and B bands are probably in the visible region, at similar wavelengths to those for $[\text{Co en}_3]\text{Cl}_3$, which were found by Linhard and Weigel (82) to be at 720 millimicrons and 605 millimicrons respectively, but no attempt was made to find these by the use of concentrated aqueous solutions.

The reflectance spectrum was taken in the range 250 to 1125 millimicrons (figure 8). It shows that the band shown by the solution spectrum is Band I as expected. The electronic transitions indicated are:

Wavelength (m μ)	Octaval (CRU)	Classification	Assignment
650	280	Weak	Band A
470	233	Strong	Band I
342	287	Strong	Band II

As was the case with $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$, other bands were present at longer wavelengths arising from vibrational transitions.

As mentioned previously, narrow bands were observed in the near infrared region of the reflectance spectra. An attempt was made to assign these bands to specific ligand (pyridine and ethylenediamine) vibrations, or to vibrations of any water present. The spectra of these three liquids were measured, but only those of water and ethylenediamine are shown (figures 9 and 10). Most bands of the pyridine showed too much fine structure to be readily reproduced by hand.

FIGURE 7

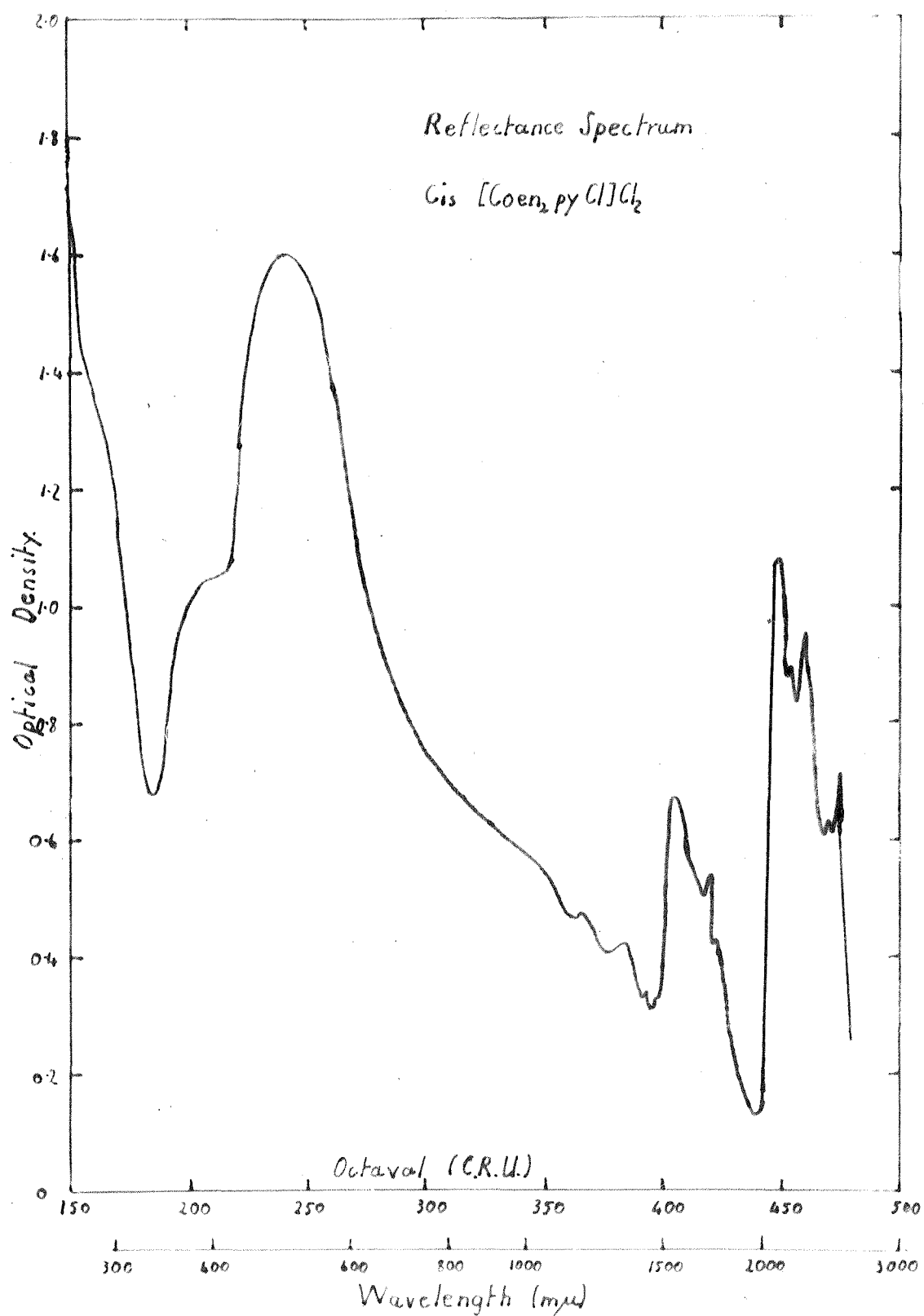


FIGURE 8

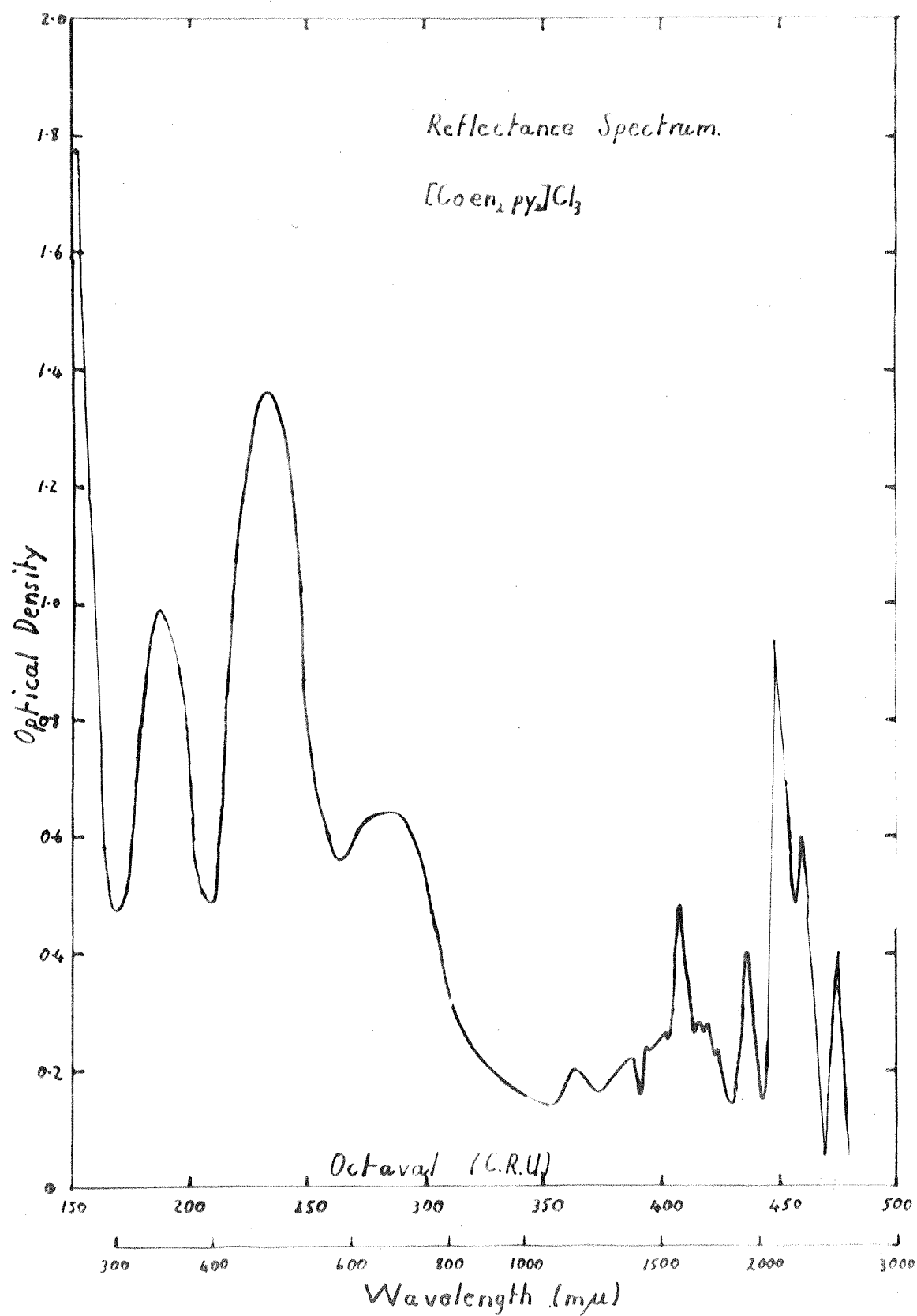


FIGURE 9

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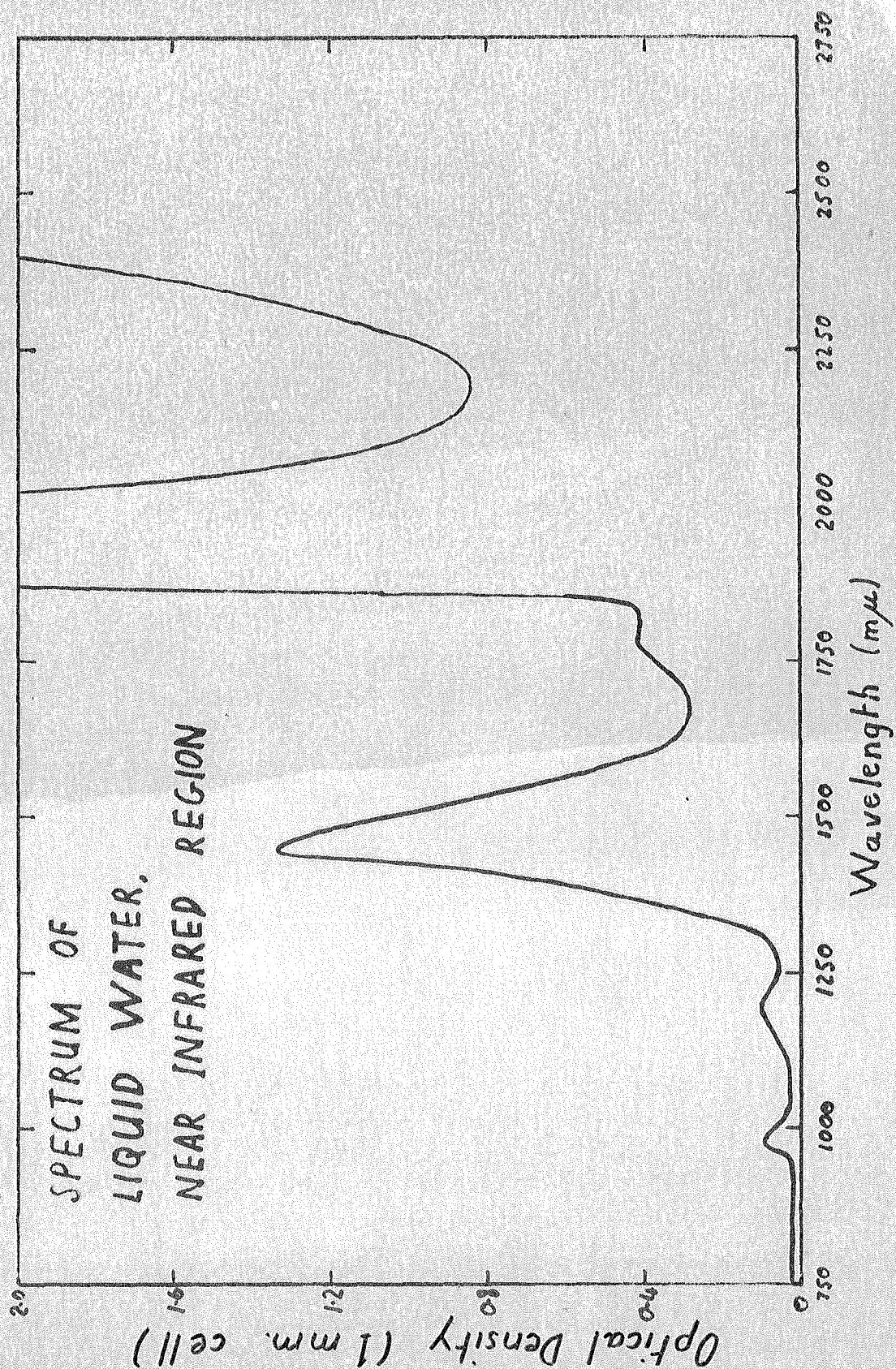
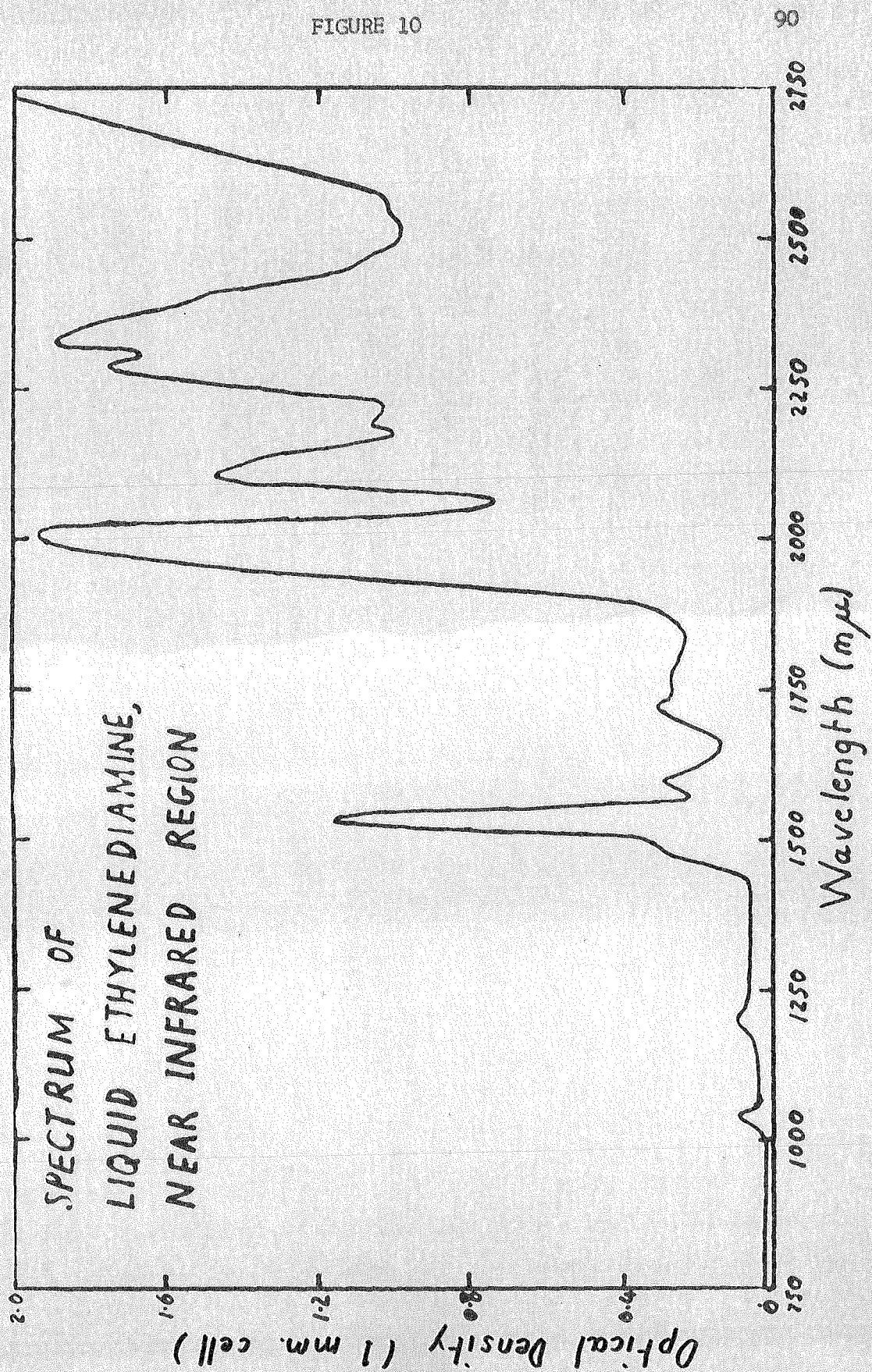


FIGURE 10



NEAR INFRARED SPECTRA OF PYRIDINE, ETHYLENEDIAMINE AND WATER

BAND POSITIONS AND INTENSITIES

Pyridine

Wavelength (μ)	Optical Density of 1 cm Sample
0.870	0.03
1.14	0.58
1.15	0.46
1.40	2.5
1.43	2.8
1.45	3.0
1.47	3.0
1.63	1.4
1.68	7.0
1.71	3.9
1.74	1.1
1.75	0.9
1.76	0.74
1.78	0.84
1.79	0.71
1.80	0.76
1.82	0.64
1.90	1.28
1.94	4.3
2.15	12.0
2.18	10.0
2.20	9.2
2.23	6.9
2.27	4.2
2.29	4.0
2.35	6.0
2.36	6.4
2.38	6.6
2.45	>20
2.51	8.8
2.54	6.3
2.67	11.4
> 2.7	>20

Ethylenediamine

Wavelength (μ)	Optical Density of 1 cm Sample
1.04	0.95
1.19	0.8
1.21	1.0
1.48 (shoulder)	2.8
1.53	11.8
1.59	2.3
1.715	3.5
1.78	2.8
2.01	19.4
2.11	14.8
2.20	10.6
2.29	17.7
2.33	19.0
2.37 (shoulder)	17.8
2.41 (shoulder)	15
2.47 (shoulder)	10.7
2.55 (shoulder)	10.2
>2.7	>20

Water

Wavelength (μ)	Optical Density of 1 cm Sample
0.97	0.5
1.19	0.8
1.45	13
1.95	>20
>2.4	>20

The positions of these bands of water agree with the results of Collins (85), but the intensities are not the same. This is probably related to poor performance of the Spectracord, as noted on page 134.

The extremely weak bands ($E 1 \text{ cm} \approx 0.03$ and 0.04) at 0.76 and 0.85 microns found by Collins were not observed, as a one millimeter cell was used, and the peak heights would have been less than the instrument noise.

Assignment of the bands to specific vibrations is generally impossible as they are overtone and combination bands, and not all the bands in lower energy regions than the present study have been unambiguously assigned even in the free bases. Partial assignments of the bands in pyridine have been made by Kline and Turkevich (86), by Corrsin, Fax, and Lord (87), and by Wilmshurst and Bernstein (88).

The infrared spectra of co-ordinated pyridine have been studied by Gill, Nuttall, Scaife, and Sharp (89) in the range 400 to 1700 cm^{-1} .

No detailed infrared study of ethylenediamine appears to have been made. The peak at 1.53 microns is clearly an N-H stretching overtone. Its intensity of an optical density 1.2 in a one millimetre cell corresponds to a molar extinction coefficient of 0.76 or an equivalent extinction coefficient (i.e. extinction coefficient per N-H group) of 0.19 . Liddell and Wulf (90) found

equivalent extinction coefficients of between 0.3 and 0.6 for aliphatic monoamines, and 0.18 for ammonia. The result observed here is thus of the same order as for other amines, though rather low.

The near infrared reflectance spectrum of cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$, together with that of the yellow product from prolonged reflux, is discussed below. On the basis of the reflectance spectrum and the infrared absorption spectrum (see page 99) the yellow material is considered to be bis(pyridine) bis(ethylenediamine) cobalt (III) chloride. The near infrared reflectance spectra of two pyridine complexes, $[\text{Mo py}_3\text{Cl}_3]$ and $[\text{Cr py}_3\text{Cl}_3]$, have been discussed by Wedd (91).

NEAR INFRARED SPECTRA OF COMPLEXES AND THEIR CONSTITUENT GROUPS:
BAND POSITIONS (μ) AND ASSIGNMENTS

Wedd		Collins	This Work					Assignment
[Mo py ₃ Cl ₃]	[Cr py ₃ Cl ₃]	Water	Water	Ethylenediamine	Pyridine	[Co en ₂ py ₂]Cl ₃	[Co en ₂ pyCl]Cl ₂	
				1.04		1.04 (solution only)	1.04 v.w.	en
1.15 w	1.15 v.w.	1.195	1.19		1.14	1.175 v.w.	1.175 v.w.	?
				1.21		1.27 v.w. 1.33 v.w. 1.37 v.w.	1.23 v.w. 1.35 v.w.	en ? ? ?
	1.40 v.w.	1.44	1.45		1.40 1.43 1.45 1.47	1.45 v.w.	1.42 w. 1.44 v.w.	py
				1.53		1.59 s.	1.59 s.	N-H stretch overtone in en
1.67 w.	1.67 w.				1.68	1.68 w.	1.66 m.	py

NEAR INFRARED SPECTRA OF COMPLEXES AND THEIR CONSTITUENT GROUPS (Cont.)

1.73 sh.				1.715 1.78		1.72 w. 1.77 v.w.	1.72 w. 1.78 v.w.	en
	1.95 v.w.	1.96	1.95		1.94	1.92 m.	1.93 w.	water or py
				2.01				?
				2.11		2.10 s.	2.10 s.	en
2.16 w.	2.16 w.				2.15 2.18 2.20 2.23 2.27	2.17 sh. 2.25 m.	2.17 w. 2.265 m.	py
2.22 sh 2.27 sh	2.22 sh.							
				2.29	2.29		2.29 sh.	?
				2.33		2.33 sh.		en
2.44 w.	2.38 w.			2.37 sh 2.41 sh 2.47 sh 2.55 sh	2.35 2.36 2.38 2.45 2.51 2.54	2.52 s.	2.42 w. 2.515 s.	py

Infrared Spectra of Cobalt Complexes

Experimental

The infrared spectra of trans $[\text{Co py}_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$, cis $[\text{Co en}_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$, trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$, cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$, and $[\text{Co en}_2\text{py}_2]\text{Cl}_3$ were taken in the range two to twentyfive microns, using a Grubb-Parsons spectrophotometer. Nujol mulls were used, and hexachlorobutadiene mulls were used in the regions where Nujol (a heavy paraffin oil) absorbs.

Results and Discussion

The spectra of cis and trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ agree with those found by Morris and Busch (93) who discussed the infrared spectra of cobalt (III) species of the type $[\text{Co en}_2\text{X}_2]$, where X_2 was en, $(\text{NO}_2)_2$, or Cl_2 . The infrared spectra of pyridine in different environments (but not in any cobalt (III) complexes) have been studied by Gill, Nuttall, Scaife, and Sharp (89), who concluded that, with the exception of the pyridine in the pyridinium ion, the spectrum of pyridine is changed only slightly by co-ordination: one new band at about 1235 to 1255 cm^{-1} appears, and other bands shift slightly.

An attempt was made by the writer to assign the observed bands in the infrared absorption spectra of trans $[\text{Co py}_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ and $[\text{Co en}_2\text{py}_2]\text{Cl}_3$. This was partially successful, but it was complicated by the fact that the absorption bands of the pyridine and ethylenediamine parts of the molecules

overlapped. The spectrum of $[\text{Co en}_2\text{py}_2]\text{Cl}_2$ was poorly resolved, as the material did not mull properly. This was particularly troublesome with the hexachlorobutadiene mull, and it is probable that many smaller peaks in the 6.5 to 9.5 microns (1535 to 1050 cm^{-1}) and 2.5 to 4 microns (4000 to 2500 cm^{-1}) regions exist but were not observed. All peaks observed for this material were very weak.

The bands which could be assigned to specific vibrations are shown below. The observed spectra of cis and trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ are similar to those of Morris and Busch (92).

INFRARED SPECTRA OF COMPLEXES
BAND POSITIONS (cm^{-1}) AND ASSIGNMENTS

<u>Trans</u> [Co pyCl ₂] ₂ Cl·6H ₂ O	<u>Trans</u> [Co en ₂ Cl ₂] ₂ Cl	<u>Cis</u> [Co en ₂ Cl ₂] ₂ Cl·H ₂ O	<u>Cis</u> [Co en ₂ pyCl] ₂ Cl ₂	[Co en ₂ py ₂] ₂ Cl ₃	Group undergoing vibration ¹	Assignment of vibration ²
644			645	645	py	6a
696			705	703	py	11
763			763	760		4
	778	769 787	800	782	en	NH ₂ rock
	851	893	877 896	890	en	CH ₂ rock
1017			1020		py	1
	1053	1053	1057	1053	en	C-N stretch
	1005	1005	1000			
	1085	1090	1106		en	CH ₂ twist
	1118	1109 1133	1135			
1037					py	12
1064					py	18a

INFRARED SPECTRA OF COMPLEXES (Cont.)

	1198	1190	1198	1250		
	1274	1212	1274	1278	en	CH ₂ wag
	1307	1232	1282	1326		
		1276	1311			
		1316				
1212					py	9a
1235					py	co-ordinated py
1350					py	6a + 10b
	1363	1359	1360	1363	en	NH ₂ deformation
	1399		1389	1391		(symmetric)
	1449	1430	1460	1460	en	CH ₂ bend
1449			1443	1440	py	19b
1475			1490		py	19a
1563					py	8b
	1575	1563		1553	en	NH ₂ deformation
		1627				(antisymmetric)
1600					py	8a
1631						1 + 6b or 6a + 12

INFRARED SPECTRA OF COMPLEXES (Cont.)

2959	2851	2850		en	CH ₂ stretch
2985	2920				
	2950				
3012	3090	3070	3078		
3226	3190	3175	3200	en	NH ₂ stretch
3279	3260				
3478 w	3416 s	3355	3375	water	OH ₂ stretch
3571 w		3495			

1. Ethylenediamine is represented by en, and pyridine by py.
2. Numbers refer to the vibrations of pyridine and follow the scheme of Kline and Turkevich (86). Their scheme, which is also followed by Gill, Nuttall, Scaife, and Sharp (89), writes, for example, ν_4 as 4 for simplicity.

In addition some bands were observed which cannot be assigned.

INFRARED SPECTRA

UNASSIGNED BANDS IN COMPLEXES
BAND POSITIONS (cm^{-1}) AND COMMENTS

Trans $[\text{Co py}_4\text{Cl}_2]\text{Cl}\cdot 6\text{H}_2\text{O}$	Trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$	Cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot \text{H}_2\text{O}$	Cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$	$[\text{Co en}_2\text{py}_2]\text{Cl}_3$	Comments
	575	580	579	578	Related to band at 506 cm^{-1} in free ethylenediamine?
			1216	1218	CH_2 wag in en, or 9a in py.
			1232	1233	CH_2 wag in en, or co-ordinated pyridine
			1576	1576	NH_2 deformation (asym) in en, or vibration 8b in py.
			1613		NH_2 deformation (asym) in en, or vibration 8a in py.
		2275		2275	Combination or overtone?
	2355			2355	Combination or overtone?

4. Kinetics and Mechanism of Replacement of Chloride

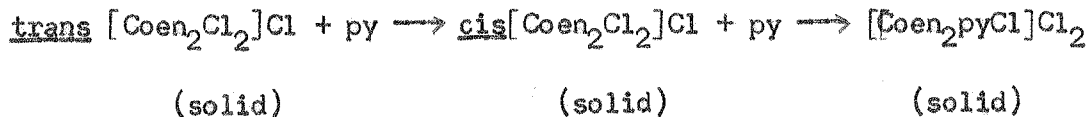
in $[\text{Co en}_2\text{Cl}_2]^+$ by Pyridine

Experimental

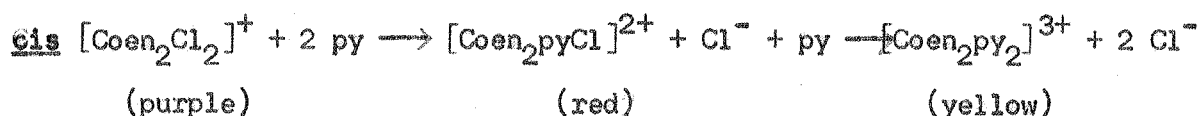
For each run several samples were bottled and then suspended in a darkened oilbath, maintained at various temperatures ($\pm 0.05^\circ\text{C}$). Samples were withdrawn one at a time at intervals of usually about thirty minutes. After its removal from the bath, each sample was immediately transferred to the cell of a visible region spectrophotometer. The optical density at a number of wavelengths was determined, and from these results the concentrations of the reactant and the products were determined (see page 128).

The spectrophotometers used were a Perkin-Elmer Spectracord recording double beam spectrophotometer, a Unicam S P 500 non-recording single beam spectrophotometer, and a Bausch and Lomb Spectronic 20 Colorimeter (a simple single beam non-recording spectrophotometer).

It was found by Friend and Mellor (74) that the reaction of solid trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ with pure pyridine involved the prior formation of the cis compound.



For the first run, cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ was used in a 5×10^{-4} molar solution. This was a preliminary run to see what reactions occurred. The solvent, which was not anhydrous, was a mixture of equal volumes of pyridine and methanol, which was therefore about 6.2 molar in methanol. The complex did not dissolve rapidly, and hence zero-time was not established accurately. The appearance of the solutions, which turned yellow brown, showed that the reaction scheme

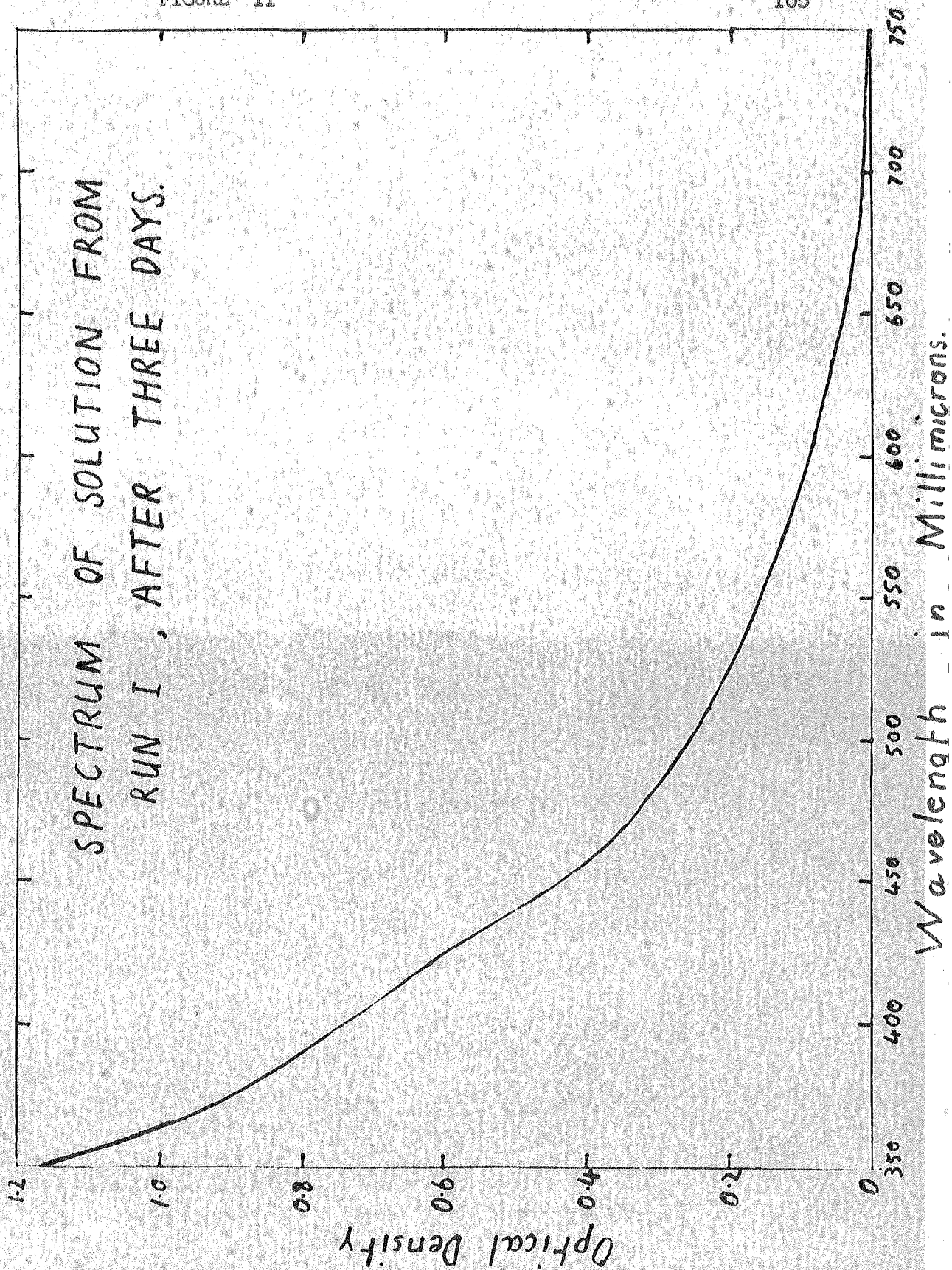


could not be correct, and this was borne out by the measurements of optical densities at the binary isosbestic points 416, 436, and 613 millimicrons. Results calculated on the assumption that the only coloured species were cis $[\text{Co en}_2\text{Cl}_2]^+$, cis $[\text{Co en}_2\text{pyCl}]^{2+}$, and $[\text{Co en}_2\text{py}_2]^{3+}$ were ridiculous, with the apparent concentration of one of the species becoming minus twenty times that of the original concentration of starting material. The product at three days had an absorption spectrum characteristic of an indefinite mixture (figure 11).

In order that zero-time should be established more accurately and to avoid attack of the complexes by water, it was decided to dissolve the cobalt complex in anhydrous methanol first, bring it to temperature, and then add anhydrous pyridine. The cis \longrightarrow trans isomerisation was found to proceed quite rapidly (half life about

FIGURE 11

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ten minutes at 55°C) in dry methanol. It was at least as fast as the replacement of chloride by pyridine, and so the stable trans isomer was used for all further work. A solution of trans

[Co en₂Cl₂]⁺Cl⁻ was prepared in methanol, pyridine added, and the mixture boiled under reflux for twelve hours. The visible region spectra of the liquid and of a solution of the solid which had formed were measured (figures 12 and 13). The former was almost a linear combination of the spectra of trans [Co en₂Cl₂]⁺ and cis [Co en₂pyCl]²⁺, but the latter showed some other species to be present in small amount. This suggested that the reaction



could be the main reaction, with some other reaction of lesser importance.

Several runs were made with solutions of trans [Co en₂Cl₂]⁺Cl⁻ (3 x 10⁻³ molar) and pyridine (usually 0.3 molar, but in one case 0.8 molar). The spectra of samples were taken on the Spectracord. In order to use a large number of points on each spectrum, and so damp out errors in reading only two or three points from each, a method of calculating concentrations of m components from n readings (n ≫ m) was developed by the writer (see page 128).

Graphs of the logarithm of the concentration of [Co en₂Cl₂]⁺ against time were linear for the first few percent of the reaction, but the slope of these lines varied depending upon the wavelengths at which measurements were taken to calculate the concentration.

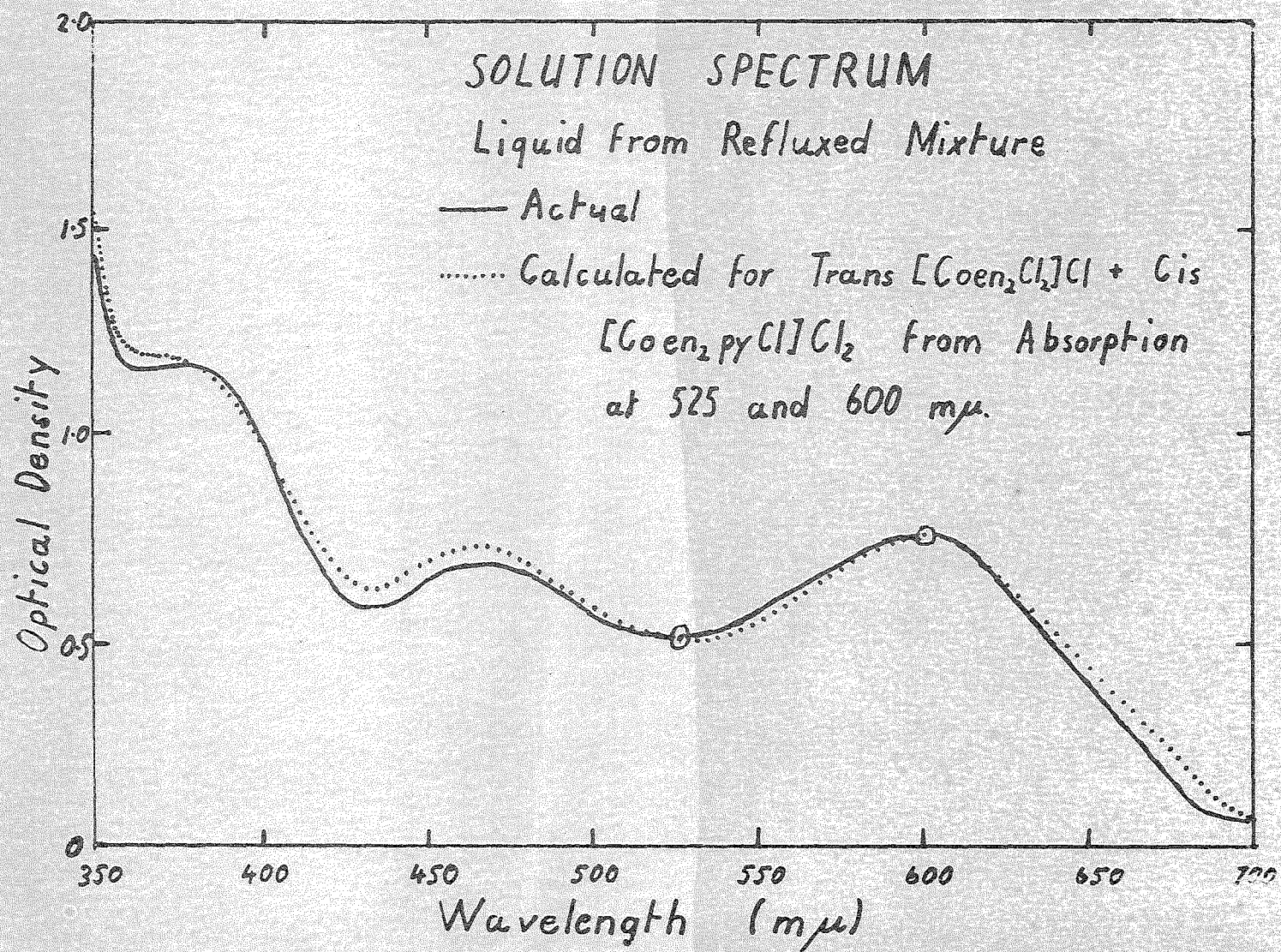
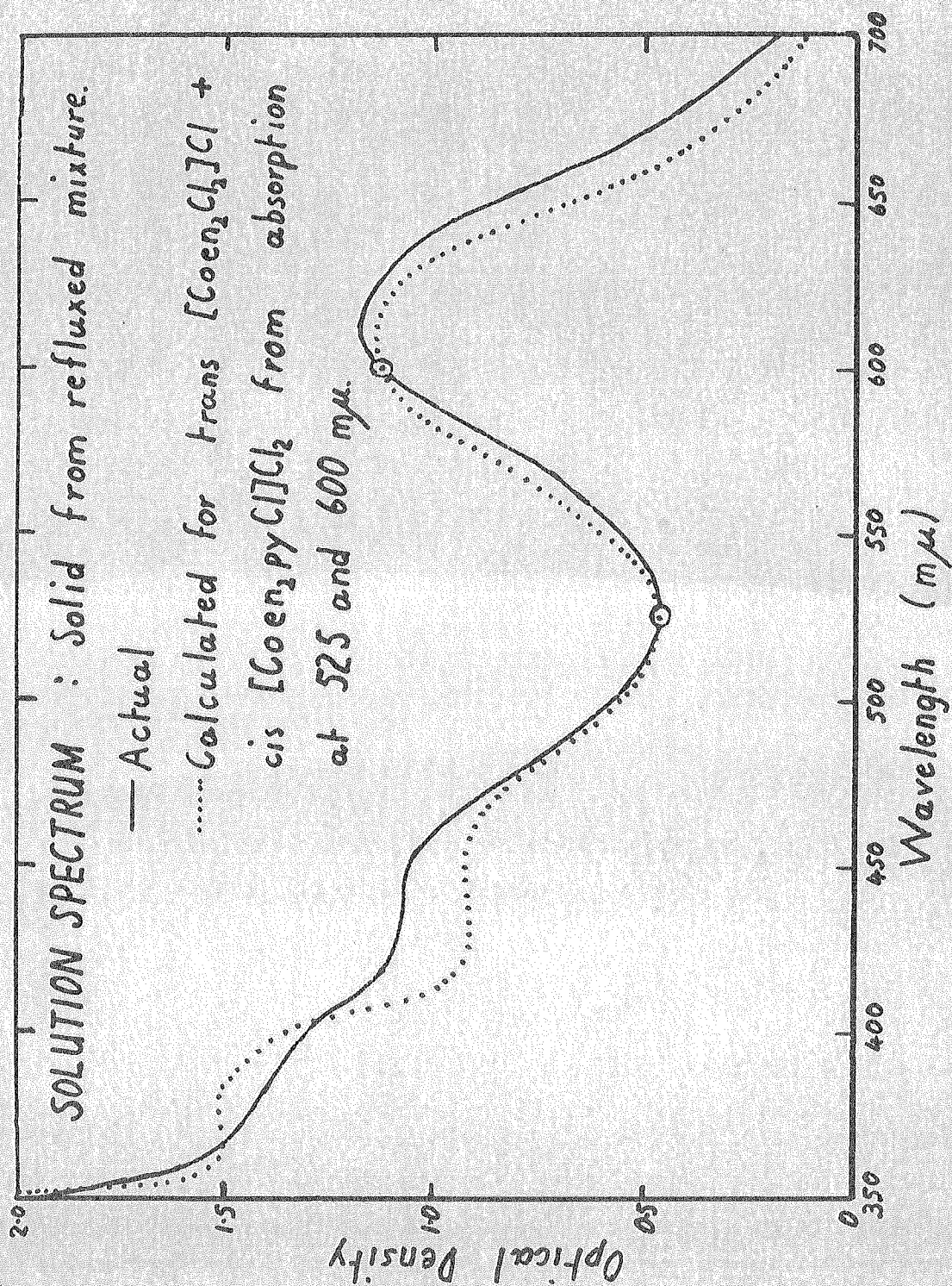


FIGURE 12

FIGURE 13

108



This showed that even in the first few percent of the reaction, during which time it was thought that very little of other products such as $[\text{Co en}_2\text{py}_2]\text{Cl}_3$ would be present, the observed spectrum was not a linear combination of the spectra of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ and cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$.

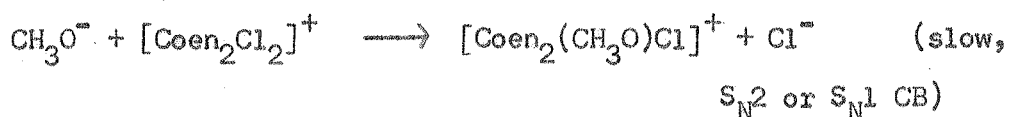
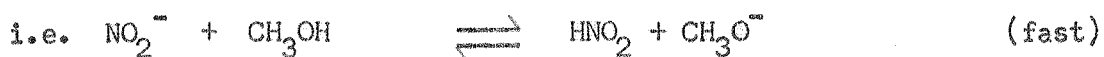
The writer had previously found that Beer's Law was obeyed both for the reactant, trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$, and the product, cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ (using the Unicam S P 500 single beam spectrophotometer). Beer's Law obedience had also been found by Yasui and Shimura (83) for cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ and by Nunn (76) for $[\text{Co en}_2\text{py}_2]\text{Cl}_3$. Thus the observed spectra were anomalous, and checks were made of the Spectracord. These showed systematic, but rather unreproducible deviations from the correct results (see page 135). It was found impossible to obtain sufficiently accurate or precise results from this instrument, and later runs were followed by the use of the Unicam single beam spectrophotometer.

Even using this instrument, systematic deviations from linear combinations of the spectra of trans $[\text{Co en}_2\text{Cl}_2]^+$ and cis $[\text{Co en}_2\text{pyCl}]^{2+}$ were observed. For example, the results for run VIII showed that the mixtures absorbed more at 436 millimicrons and less at 525 and 610 millimicrons than mixtures of trans $[\text{Co en}_2\text{Cl}_2]^+$ and cis $[\text{Co en}_2\text{pyCl}]^{2+}$. From the calculated concentrations $\log \frac{c}{c+p}$ was calculated, where c is the concentration

of trans $[\text{Co en}_2\text{Cl}_2]^+$ and p is the concentration of cis $[\text{Co en}_2\text{pyCl}]^{2+}$. The second, third, fourth, fifth, and sixth points could be fitted to a straight line, of slope corresponding to a first order rate constant of $5.2 \times 10^{-4} \text{ min}^{-1}$. However, the first and seventh points are not on this line, and it did not pass through the origin (see figure 14).

Other runs gave even more ridiculous results. For example, the calculated values for run IX, at 47.8°C , are shown on figure 15. Values for run VIII are tabulated (see page 136).

As mentioned previously (see page 55) basic substituents may react with the solvent to form more strongly nucleophilic species. For example, Brown and Ingold (6) found that the substitution of nitrite and azide in cis $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ in methanol followed second order kinetics, and from this suggested an $\text{S}_{\text{N}}2$ mechanism. However, it was shown by Pearson, Henry, and Basolo (54) that the second order kinetics was due to formation of methoxide ion, its attack on the complex, and its fast replacement by azide or nitrite.



In order to determine whether the substitution of pyridine into trans $[\text{Co en}_2\text{Cl}_2]^+$ was methoxide catalysed, run XI employed

FIGURE 14

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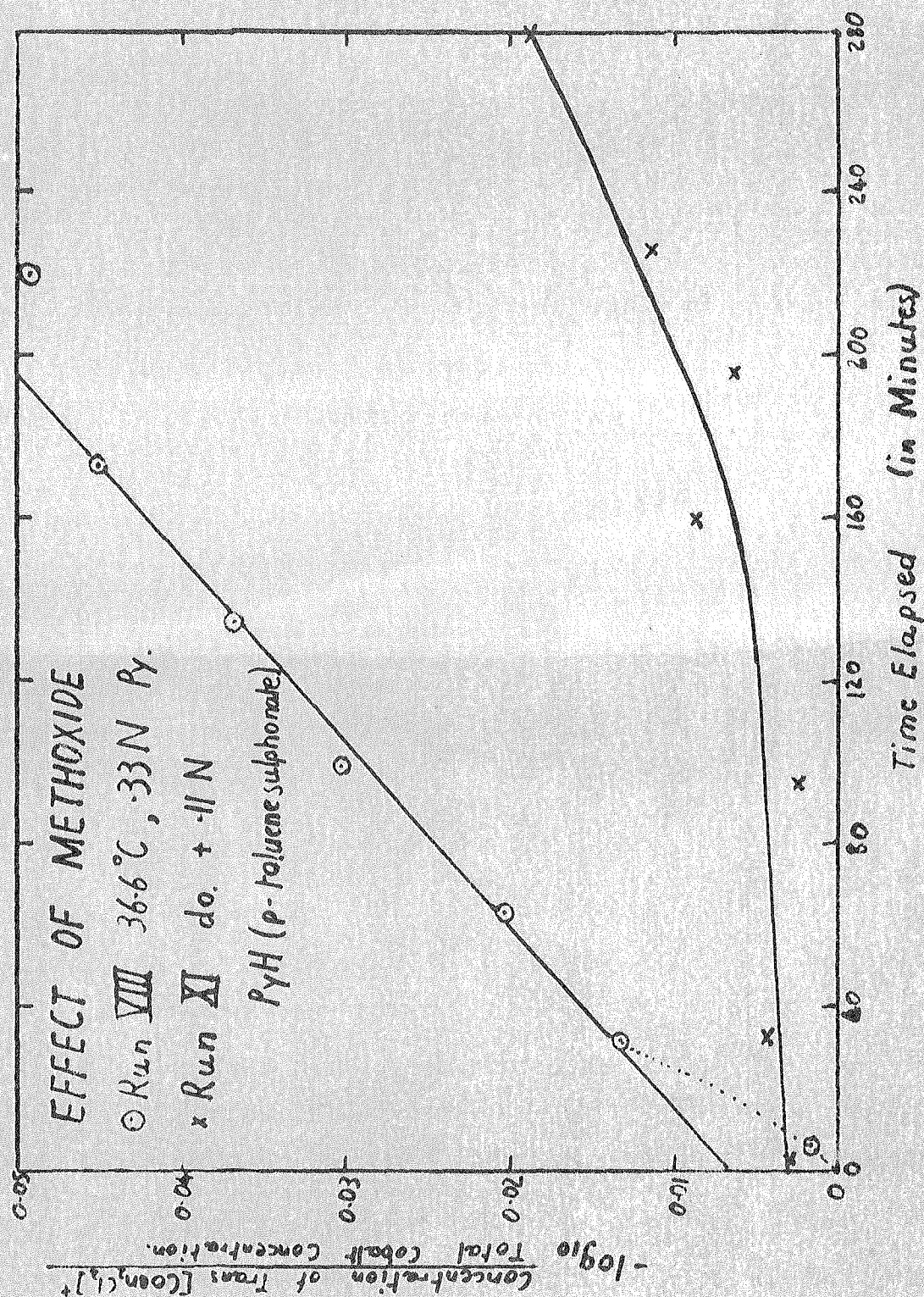
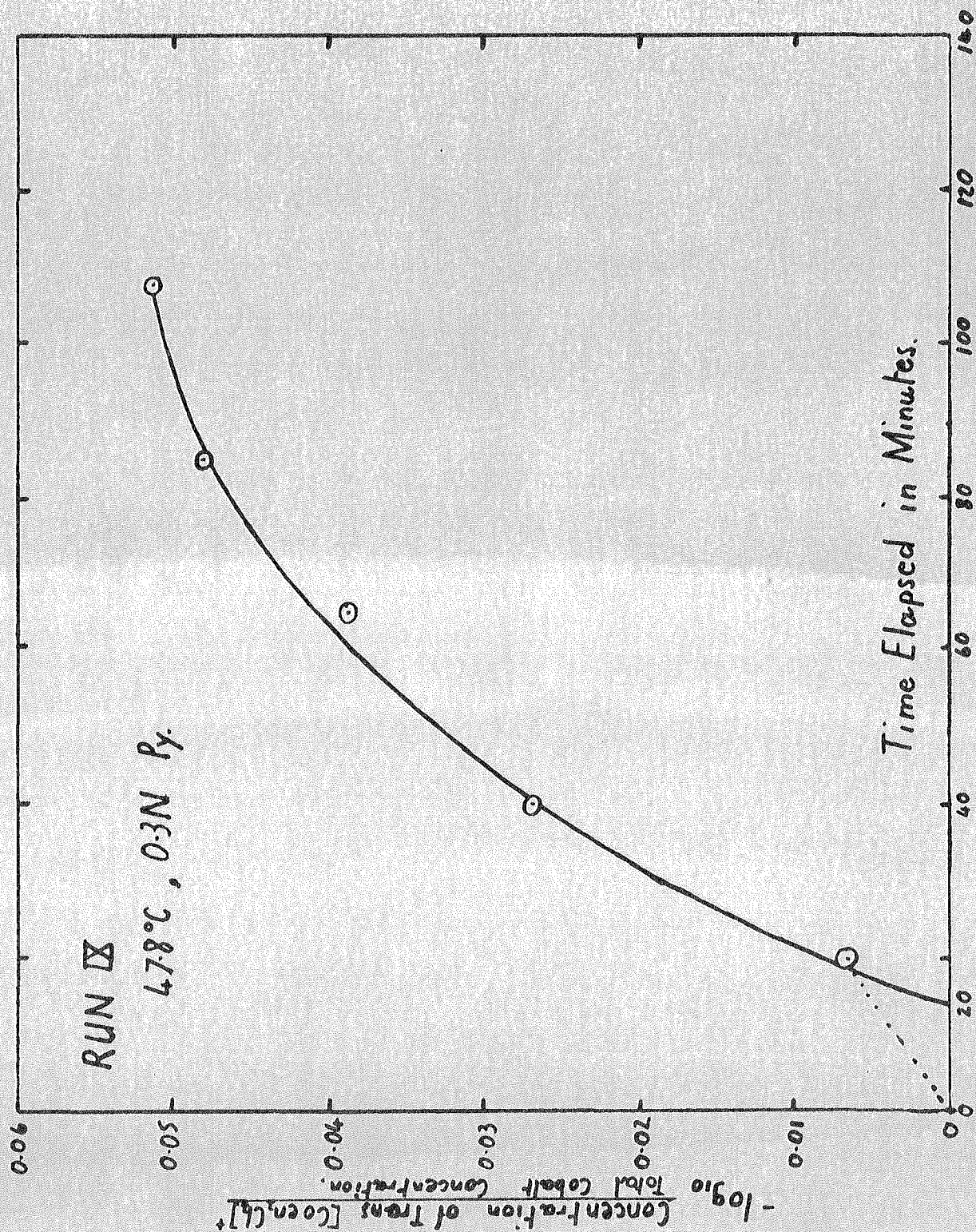


FIGURE 15

112



the same conditions as run VIII, except that acid was added.

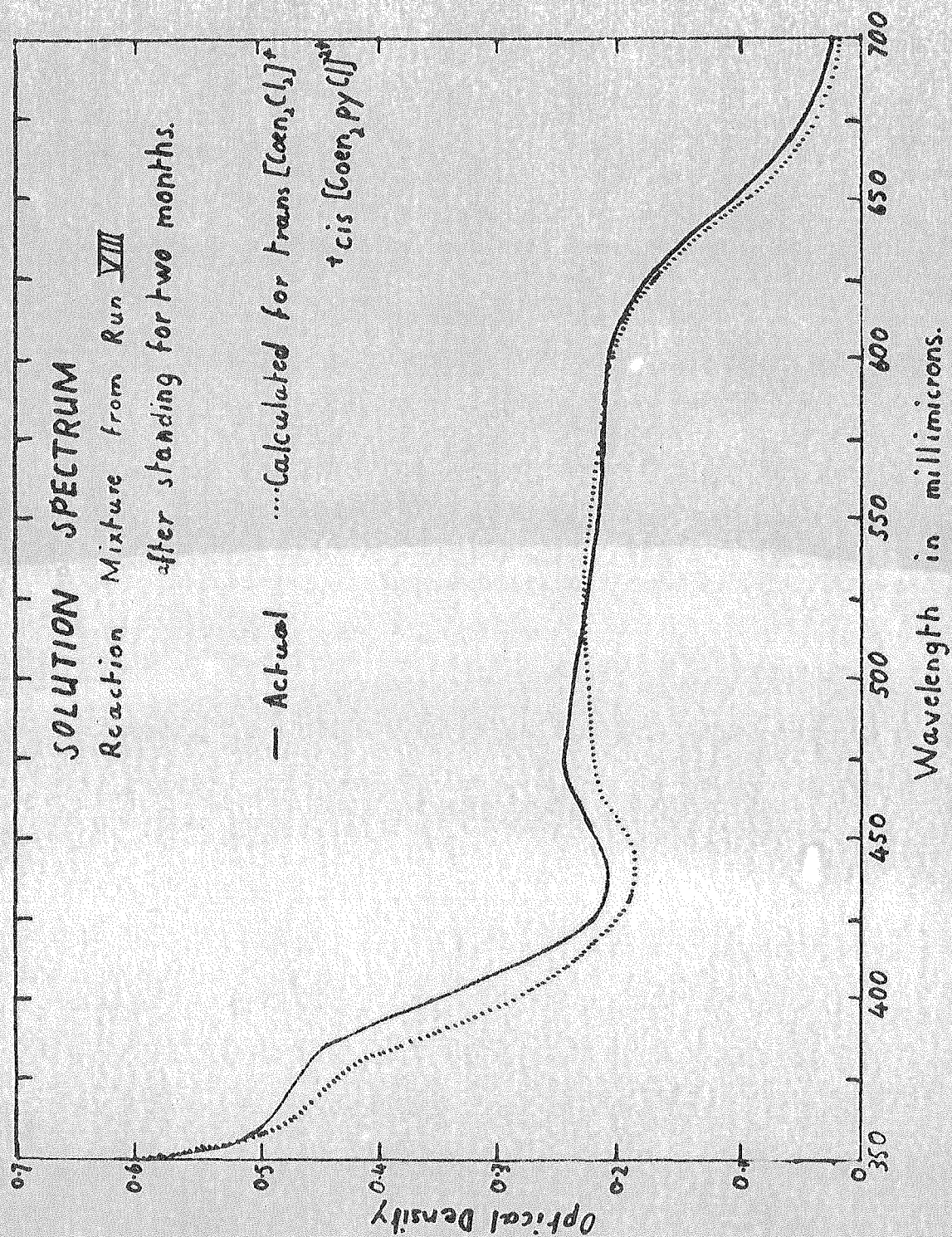
The conditions for these runs were:

Temperature: 36.6°C
 Concentration of complex: 3×10^{-3} molar
 Free pyridine concentration: 0.33 molar

Run XI was 0.44 molar (total) in pyridine, but was also 0.11 molar in para toluenesulphonic acid. This acid was found by Watts (94) not to noticeably substitute into $[\text{Co en}_2\text{Cl}_2]^+$ or similar species.

It was found that only an extremely slow reaction took place in run XI, this being characterised by an induction period of about two hours (see figure 14). The reaction thus appeared to take place via methoxide catalysis.

The spectrum of the solution of run VIII was taken again after several weeks. It showed a mixture of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$, cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$, and some other material. (see figure 16) To three samples of the solution were added some tetraethylammonium chloride, lithium chloride, and hydrochloric acid (one of these in each). The solutions turned cloudy, and so it was impossible to tell if cobalt (II) species were present. If there had been cobalt (II) species it was expected that they would have combined with the added chloride to form deep blue tetrahedral species such as $[\text{Co py}_2\text{Cl}_2]$ or $[\text{CoCl}_4]^{2-}$. Lacking centres of symmetry,

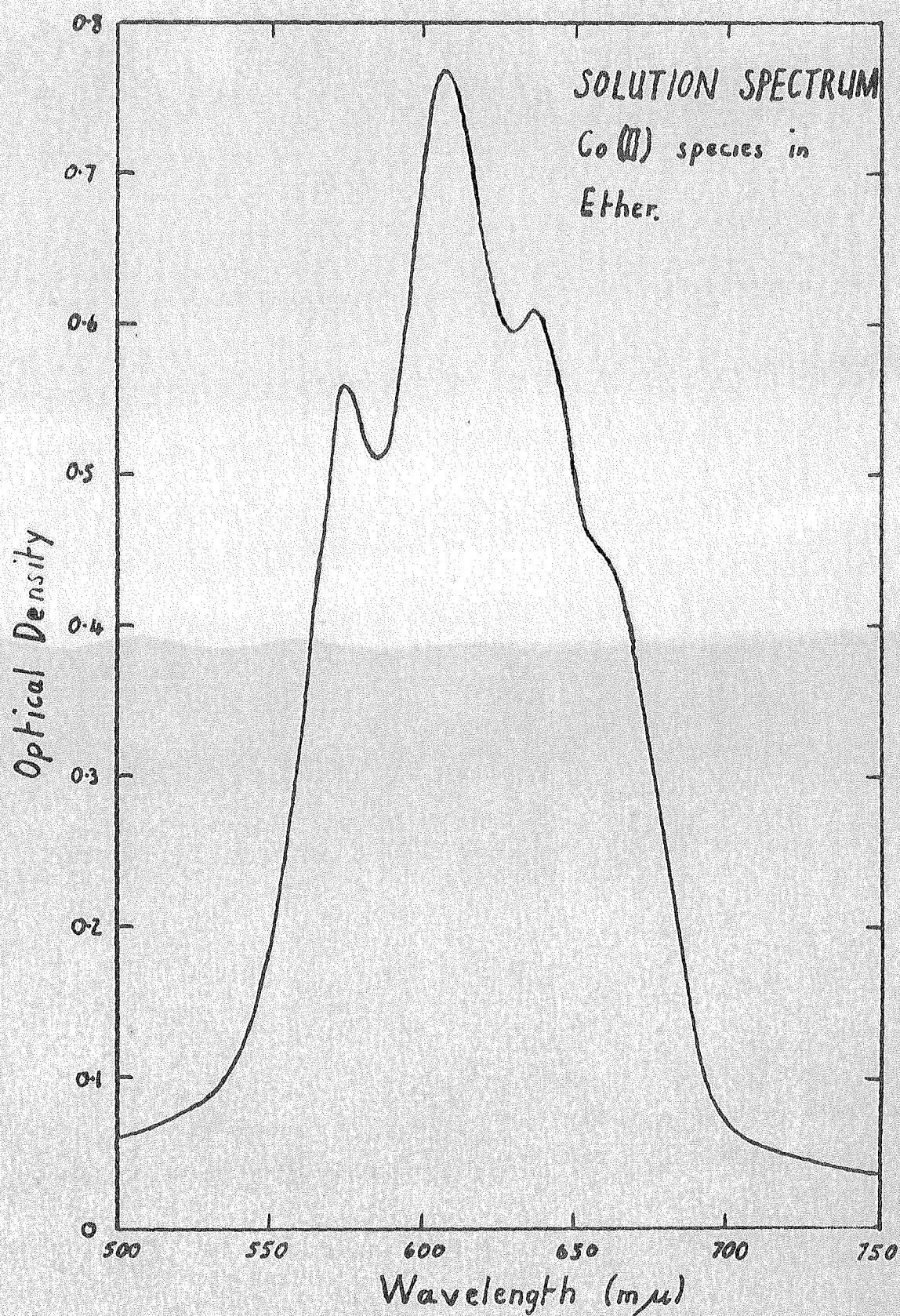


these species show intense bands (ϵ_{max} of the order of 500) at between 600 and 680 millimicrons, as shown by Katzin and Gebert (94).

To further test the effect of basic ions on the substitution reaction, a concentrated solution of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ was made in water plus pyridine at room temperature. A few millilitres of sodium hydroxide solution were then added. The solution turned brown and became cloudy. About five minutes after adding the sodium hydroxide the mixture was filtered and a small amount of yellow-brown residue was retained. The brown solution had turned red by the time another five minutes had elapsed, but still had a brownish tinge.

To a sample of this solution was added some lithium chloride. The solution turned purple, indicating the probable presence of cobalt (II) compounds. Methanol and ether were added to another sample, and a pink precipitate formed. This appeared to be cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$, and the infrared spectrum confirmed that it was. After the cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$ had precipitated, a small quantity of a green precipitate was formed. The infrared spectrum showed this to be trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$.

The filtrate was a clear blue. Its visible absorption spectrum was run, and it showed only one absorption band, from 570 to 670 millimicrons (half peak heights), and peaks at 575, 607, 637, and 665 millimicrons. (see figure 17). This definitely shows the presence of a tetrahedral cobalt (II) species in solution.



It was clear that the reaction



and also the reduction of cobalt (III) to cobalt (II) were accelerated by hydroxide ions in water. A solution of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ was made in methanol (not anhydrous) and a few millilitres of pyridine, followed by alcoholic sodium hydroxide, were added. Within a few minutes the solution (at room temperature) changed colour from green to red. The addition of ether and petroleum spirit to a sample of the solution caused the precipitation of a small amount of a pink powder, most probably cis $[\text{Co en}_2\text{pyCl}]\text{Cl}_2$.

The spectrum of the solution was run in the visible region after the addition of concentrated hydrochloric acid. This reagent would convert cobalt (II) to the deep blue $[\text{CoCl}_4]^{2-}$. The spectrum showed an absorption band centred at 620 millimicrons after allowance for the absorption due to cis $[\text{Co en}_2\text{pyCl}]^{2+}$ and a small amount of trans $[\text{Co en}_2\text{Cl}_2]^+$.

Discussion

Brown and Ingold (6) found that in damp methanol the rate of racemisation of optically active $[\text{Co en}_2\text{Cl}_2]^+$, the rate of cis \longrightarrow trans isomerisation, the rate of chloride exchange, and the rate of substitution by nitrate, bromide, and thiocyanate were all equal, of rate constant $1.4 \times 10^{-4} \text{ sec}^{-1}$ at 35.8°C . This corresponds to a half-life of 1.4 hours.

The rate found by the writer for the cis \longrightarrow trans isomerisation in anhydrous methanol is similar to what would be expected for the reaction in wet methanol at the same temperature. This result shows that the cis \longrightarrow trans isomerisation of $[\text{Co en}_2\text{Cl}_2]^+$ does not, as is claimed by Sward (62) proceed via an aquated species. It could proceed via a penta co-ordinated species, as suggested by Brown and Ingold (6), or via an unstable methanol complex. The methanol complex would be expected to have a visible region absorption spectrum like the corresponding aqua complex, and this could explain the "aquo species" in solution reported by Sward.

The substitution of pyridine into $[\text{Co en}_2\text{Cl}_2]^+$ has been shown by the writer not to be a simple one stage reaction:



Other reactions take place, including the reduction of some cobalt (III) to cobalt (II). The substitution and the reduction are both catalysed by methoxide ion.

Further discussion of substitution and reduction reactions is given in Chapter 6 of Part II of this thesis (see page 125).

5. Reduction of Cobalt (III) to Cobalt (II) by Pyridine

As stated above the writer has found that alkaline aqueous or methanolic pyridine reduced cobalt (III) in the form of trans dichlorobis(ethylenediamine) cobalt (III) to cobalt (II).

Previously it had been found by Friend and Mellor (74) that pure pyridine reduced a number of cobalt (III) chloro complexes to cobalt (II) with the evolution of chlorine gas. They suggested that an unstable complex, perhaps $[\text{Co py}_5\text{Cl}]^{2+}$ or $[\text{Co py}_6]^{3+}$, formed and then oxidised chloride ion to chlorine.

Tobe and Watts (63), when studying the isomerisation of $[\text{Co en}_2\text{Cl}_2]^+$ in dimethyl formamide and dimethylacetamide, found that cobalt (II) species were slowly formed, but did not investigate the mechanism of the reduction.

The reduction of cobalt (III) in complexes of the type $[\text{Co}(\text{AB})_3]\text{Cl}_3$, where AB is ethylenediamine (1, 2 diaminoethane), 1, 2 diaminopropane, or 2, 3 diaminobutane, has been studied by Klein and Moeller (95), and Taylor and Moeller (96). The products observed were aldehydes, amines and diamines, but not chlorine. The solutions were orange to red and showed general absorption in the visible region. They suggested the reaction was a photochemical oxidation-reduction reaction with cobalt (III) and the

diamine, accompanied by reaction with the solvent.

It was decided to investigate whether the reduction of cobalt (III) to cobalt (II) compounds by pyridine was also photochemical. Dichlorobis(ethylenediamine) cobalt chloride was unsuitable, as a mixture of products forms, and so trans dichlorotetrakis(pyridine) cobalt (III) chloride was used instead.

A small sample ($\frac{1}{4}$ gm) of this compound $[\text{Co py}_4\text{Cl}_2]\text{Cl}$ was heated in pyridine under reflux in the dark, and concurrently a similar sample was heated under similar conditions but in laboratory light.

The compound dissolved to give green solutions. After $2\frac{1}{2}$ hours reflux, both solutions were clear blue, and the reaction appeared not to be photochemical.

This blue solution turned green, then orange-brown on cooling. Reheating to 40°C reversed the colour changes. Evaporation of the cold or the hot solution gave pink crystals which turned green and then blue as they dried. These blue crystals turned pink when moistened with water, but again became blue when the solvent evaporated.

Both the dry (blue) and damp (pink) crystals were soluble in benzene, toluene, ethanol, chloroform, butanol, pyridine, and water. The solutions in benzene, toluene, and ethanol were coloured blue from 0°C to the boiling point of the solution; the solution in butanol was yellow-green at 0°C , blue-green at room

temperature, and blue at about 30°C and over; the solution in pyridine was orange-brown at room temperature and below, but turned green and then blue on warming to 40°C; the solution in water was orange-brown at all temperatures from 0°C to 100°C.

The spectrum of the orange-brown solution in pyridine at room temperature was run in the visible region. It showed traces of the maxima at 595, 630, and 665 millimicrons overlain by general absorption, which increased with decrease in wavelength.

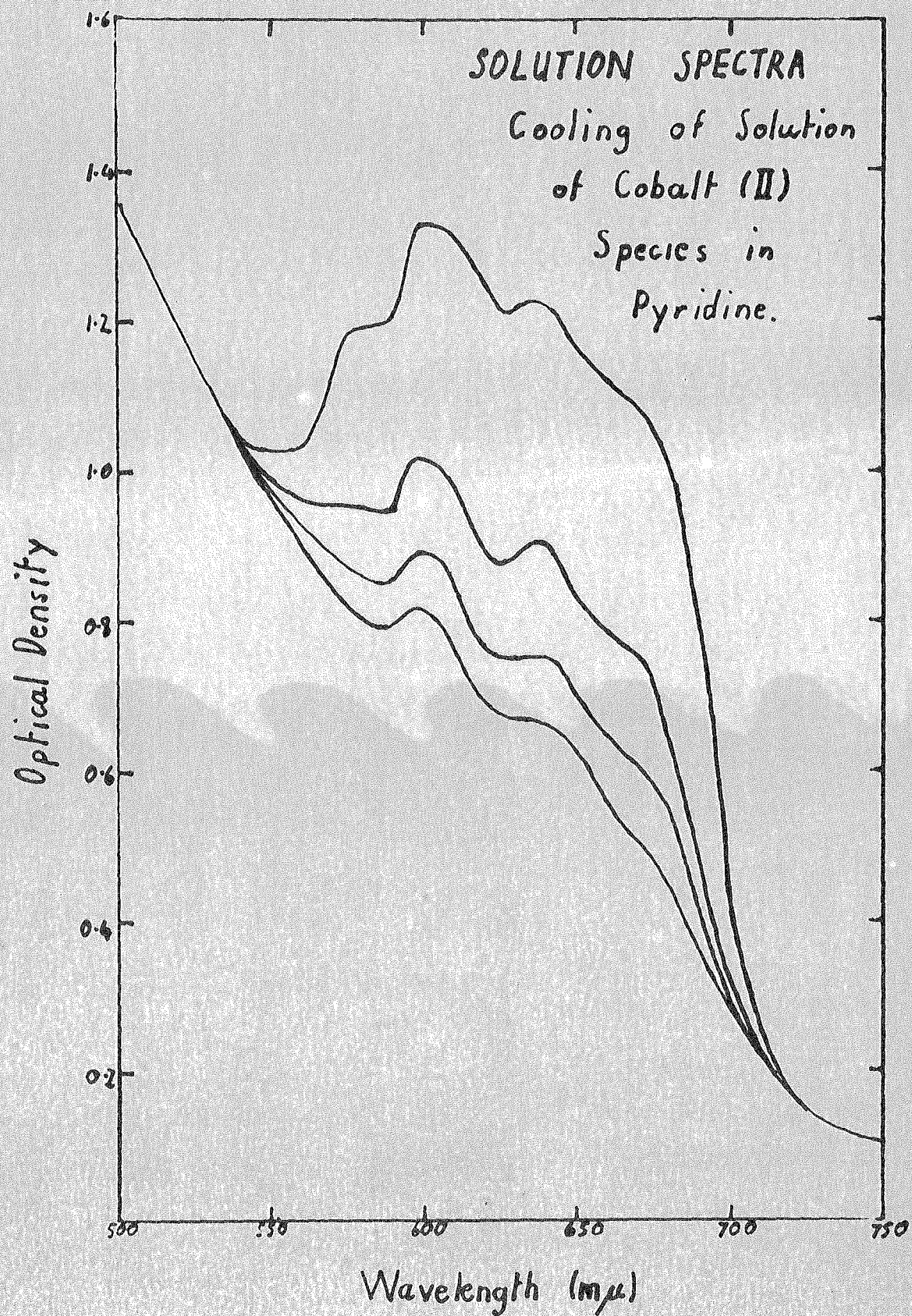
The spectra of a solution in pyridine (which was green when the first run was made) were recorded repetitively as the sample cooled. They clearly showed the disappearance of the (probably tetrahedral) blue species as the temperature fell (see figure 18).

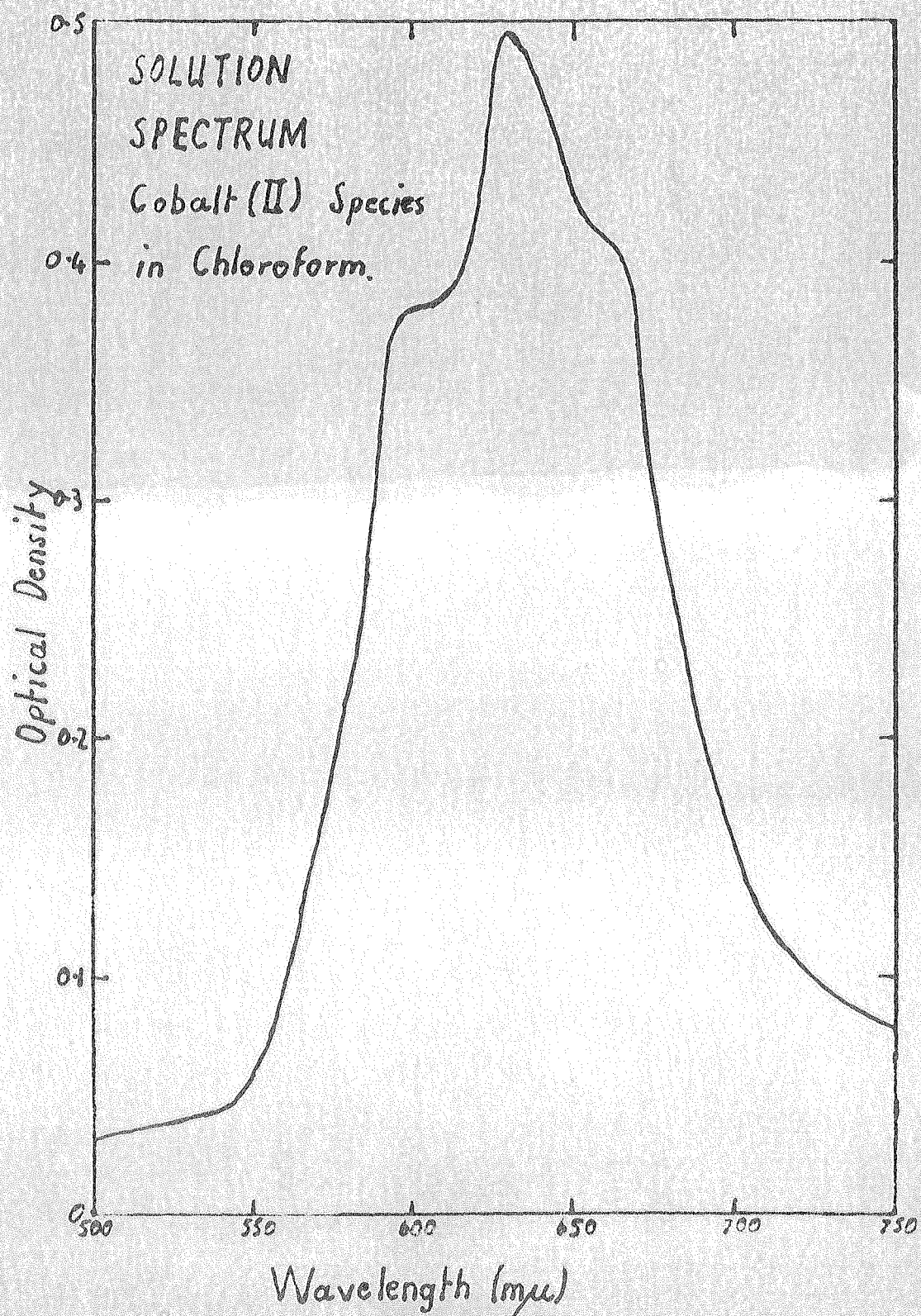
The equilibria between the blue and red forms of cobalt (II) in different solvents as a function of temperature has been studied to a small extent by MacWalter and Barratt (97) and Ablov and Nazarova (98). They find the concentration of the blue form increases with increase in temperature, in agreement with the present observations.

The spectrum of the blue solution in chloroform was determined in the ultraviolet and visible regions. In the visible region it shows an absorption band with half peak height wavelengths of 585 to 685 millimicrons with peak positions at about 595, 630, and 665 millimicrons. In the ultraviolet region it shows a band with peak positions at 251, 256, and 263 millimicrons. This visible

region spectrum (figure 19) is similar to the spectrum of the reduction product of $[\text{Co en}_2\text{Cl}_2]\text{Cl}$, but with a slight shift to longer wavelengths. Probably the species formed are similar, and the variation is due to solvation.

Work by Katzin and Gebert (93), Furlani and Geroni (99), Porai-Koshits and Antsishkina (100), Antsishkina (101), and Gill and Nyholm et al (102) indicates that blue cobalt (II) species are those in which the cobalt has a tetrahedral arrangement of ligands, while violet or red species are those in which the cobalt is octahedrally co-ordinated.

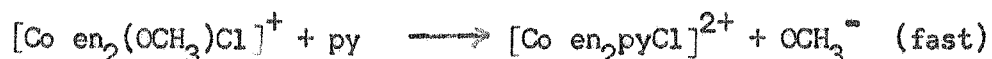




6. Final Discussion

It has been found by the writer that the cis \longrightarrow trans isomerisation of $[\text{Co en}_2\text{Cl}_2]^+$ in methanol does not proceed via an aquo intermediate.

The substitution of pyridine into trans dichlorobis (ethylenediamine) has been found to proceed, in the main at least, by methoxide ion catalysis. The reaction may be



It could be studied further by buffering the mixture to different methoxide concentrations and observing the rate as a function of methoxide concentration. For a simple scheme like that shown above, the rate would be expected to vary directly with the methoxide concentration.

The catalysis by hydroxide or methoxide of the reduction of cobalt (III) to cobalt (II) by pyridine was also observed, while the reduction was found not to be photochemical. In view of the differences between the reduction of cobalt (III) to cobalt (II) by different organic compounds, as found by Tobe and Watts (63), Friend and Mellor (74), Klein and Moeller (95), Taylor

and Moeller (96), and the writer, it would be of interest to try the reduction using different agents and analysing the products in detail.

Another possible mechanism for substitution is the alkali catalysed formation of a cobalt (II) species, reaction of this to give $[\text{Co en}_2\text{pyCl}]^+$, (this step would be fast as Co(II) complexes react much more rapidly than the analogous Co(III) complexes), followed by electron exchange between $[\text{Co en}_2\text{pyCl}]^+$ and $[\text{Co en}_2\text{Cl}_2]^+$. Ellis, Wilkins and Williams (103) found the exchange of $[\text{Co}(\text{phen})_3]^{3+}$ and $[\text{Co}(\text{dipy})_3]^{3+}$ (where phen is ortho phenanthroline and dipy is ortho dipyridyl) with isotopically labelled phen or dipy took place by catalysis with cobalt (II) as an impurity, acting through rapid Co(II)/Co(III) electron transfer.

This mechanism could be checked by introducing a cobalt (II) species (e.g. CoCl_2) into a buffered solution of trans $[\text{Co en}_2\text{Cl}_2]^+$ and pyridine in methanol and observing if reaction takes place.

APPENDICES

1. Calculations of Concentrations

The calculation of the concentration of materials from the least possible number of observations suffers from the disadvantage that a single small error (e.g. random fluctuation in measurement) can exert a large effect on the result, and so scatter results which could otherwise be concordant. If, however, more than the minimum possible number of observations are made and the concentrations worked out from all the possible combinations of the observations, then a number of slightly varying answers will probably be found. A satisfactory method of averaging the results and expressing them as a single result, together with the discrepancies between the observed and calculated results, is needed. A "least squares" fitting method was devised by the writer, and has been converted to a computer programme by Baxter (104). Since its writing, a similar calculation has been made and a computer programme published by Blackburn (105).

If Beer's Law applies to the solutions, the absorption spectrum of a mixture of components is a linear combination of the absorption spectra of the components. That is

$$y(\lambda) = a f(\lambda) + b g(\lambda) + c h(\lambda) + \dots$$

where $y(\lambda)$ is the optical density of the mixture at wavelength λ ,

$f(\lambda)$ is the extinction coefficient of component A at wavelength λ

$g(\lambda)$ is the extinction coefficient of component B at wavelength λ

$h(\lambda)$ is the extinction coefficient of component C at wavelength λ

.....

a is the concentration of component A

b is the concentration of component B

c is the concentration of component C

.....

If the optical densities are measured at n different wavelengths, λ_j , $j = 1(1)n$, then

$$y_j \approx a f_j + b g_j + c h_j + \dots,$$

where $y_j = y|_{\lambda = \lambda_j}$

$$f_j = f|_{\lambda = \lambda_j}$$

$$g_j = g|_{\lambda = \lambda_j}$$

$$h_j = h|_{\lambda = \lambda_j}$$

.....

(The approximation sign replaces the equality above as y_j , f_j , g_j , h_j are experimentally measured quantities).

We wish to find the "best" values of a , b , c , ... to satisfy the equations

$$y_j = a f_j + b g_j + c h_j + \dots, \quad j = 1(1)n,$$

as nearly as possible.

$\sum_{j=1}^n$ will be written below as \sum .

Put $G = \sum [y_j - (a f_j + b g_j + c h_j + \dots)]^2$, and minimise G . That is, we minimise the sums of the squares of the discrepancies between observed and calculated values.

G has a stationary value when all its partial derivatives (with respect to a, b, c, \dots) are zero.

$$\begin{aligned} G &\stackrel{\text{def}}{=} \sum [y_j - (a f_j + b g_j + c h_j)]^2 \\ &= \sum y_j^2 + a^2 \sum f_j^2 + b^2 \sum g_j^2 + c^2 \sum h_j^2 + \dots \\ &\quad + 2ab \sum f_j g_j + 2bc \sum g_j h_j + 2ac \sum f_j h_j + \dots \\ &\quad - 2a \sum f_j y_j - 2b \sum g_j y_j - 2c \sum h_j y_j - \\ \frac{\partial G}{\partial a} &= 2a \sum f_j^2 + 2b \sum f_j g_j + 2c \sum f_j h_j + \dots \\ &\quad - 2 \sum f_j y_j \end{aligned}$$

= 0 when

$$a \sum f_j^2 + b \sum f_j g_j + c \sum f_j h_j + \dots = \sum f_j y_j.$$

Similarly, $\frac{\partial G}{\partial b} = 0$ when

$$a \sum f_j g_j + b \sum g_j^2 + c \sum g_j h_j + \dots = \sum g_j y_j,$$

and

$$\frac{\partial G}{\partial c} = 0 \text{ when}$$

$$a \sum f_j h_j + b \sum g_j h_j + c \sum h_j^2 + \dots = \sum h_j y_j.$$

Thus a stationary value of G is given by solving the $m \times m$ matrix shown below (m is the number of components assumed present, $m \leq n$).

$$\begin{pmatrix} \sum f_j^2 & \sum f_j g_j & \sum f_j h_j & \dots \\ \sum f_j g_j & \sum g_j^2 & \sum g_j h_j & \dots \\ \sum f_j h_j & \sum g_j h_j & \sum h_j^2 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ \dots \end{pmatrix} = \begin{pmatrix} \sum f_j y_j \\ \sum g_j y_j \\ \sum h_j y_j \\ \dots \end{pmatrix}$$

As this is a set of linear equations, it has, providing the equations are linearly independent, one and only one solution.

Also

$$\frac{\partial^2 G}{\partial a^2} = 2 \sum f_j^2 > 0, \text{ and similarly } \frac{\partial^2 G}{\partial b^2}, \frac{\partial^2 G}{\partial c^2}, \dots$$

are all intrinsically positive.

Thus the solution to the matrix is unique, and corresponds to the minimum. For the case $m = 2$, calculations can be carried out by hand, but for $m > 2$, this is excessively tedious. The programme of Baxter (105) can be used for $m = 3$ or 4, while that of Blackburn (106) can be used for even more complex systems. The former programme also calculates the variance, $\frac{G}{n-1}$, to show if

the fit of calculated results to observed results is reasonable, and, if desired, prints out the order pairs (y_j ; $a f_j + b g_j + c h_j + \dots$) i.e. the observed and calculated optical densities.

As this uses discrete values, f_j , g_j , etc. there is no need for them to come from continuous curves or, indeed, to be anything but independent observations. All that is required is that the property is additive (for example, melting point is not a suitable property). Any property p should be divided by a fixed number, N_p , such that for all p , the absolute error in $\frac{N_p}{p}$ is approximately constant. This appropriately weights each set of observations.

Putting $f = 1 = \lambda^0$, $g = \lambda = \lambda^1$, $h = \lambda^2$, $i = \lambda^3$, etc. gives a vertical least squares fit of a polynomial, $y \simeq a + b\lambda + c\lambda^2 + \dots$

An interesting case is for refining values for A , B , and C , the cell constants for an orthorhombic cell, where, h, k, ℓ , are the indices of the lines, and δ is the systematic error.

$$A h^2 + B k^2 + C \ell^2 + D \delta \simeq \sin^2 \theta$$

On the basis of the first few lines, h, k, ℓ indices are derived. We wish to find A, B, C , and D , such that

$$G = \sum [\sin^2 \theta_j - (A h_j^2 + B k_j^2 + C \ell_j^2 + D \delta_j)]^2 \text{ is minimised.}$$

This is exactly analogous to the general case, except that h_j, k_j , and ℓ_j are always integral.

2. Spectrophotometer Checking

Wavelength Check

As most measurements of optical density were made on sloping parts of the spectral curves, uncertainty in the wavelengths could cause considerable error in the calculations. The spectra were thus run twice of two rare earth glasses. The results were in reasonable agreement with each other, and also with similar spectra run on the same machine a year previously. The observed values, together with the accepted reference values of Dodd and West (106) are tabulated below.

SPECTRA OF RARE EARTH GLASSES:
POSITION OF ABSORPTION MAXIMA (m μ)

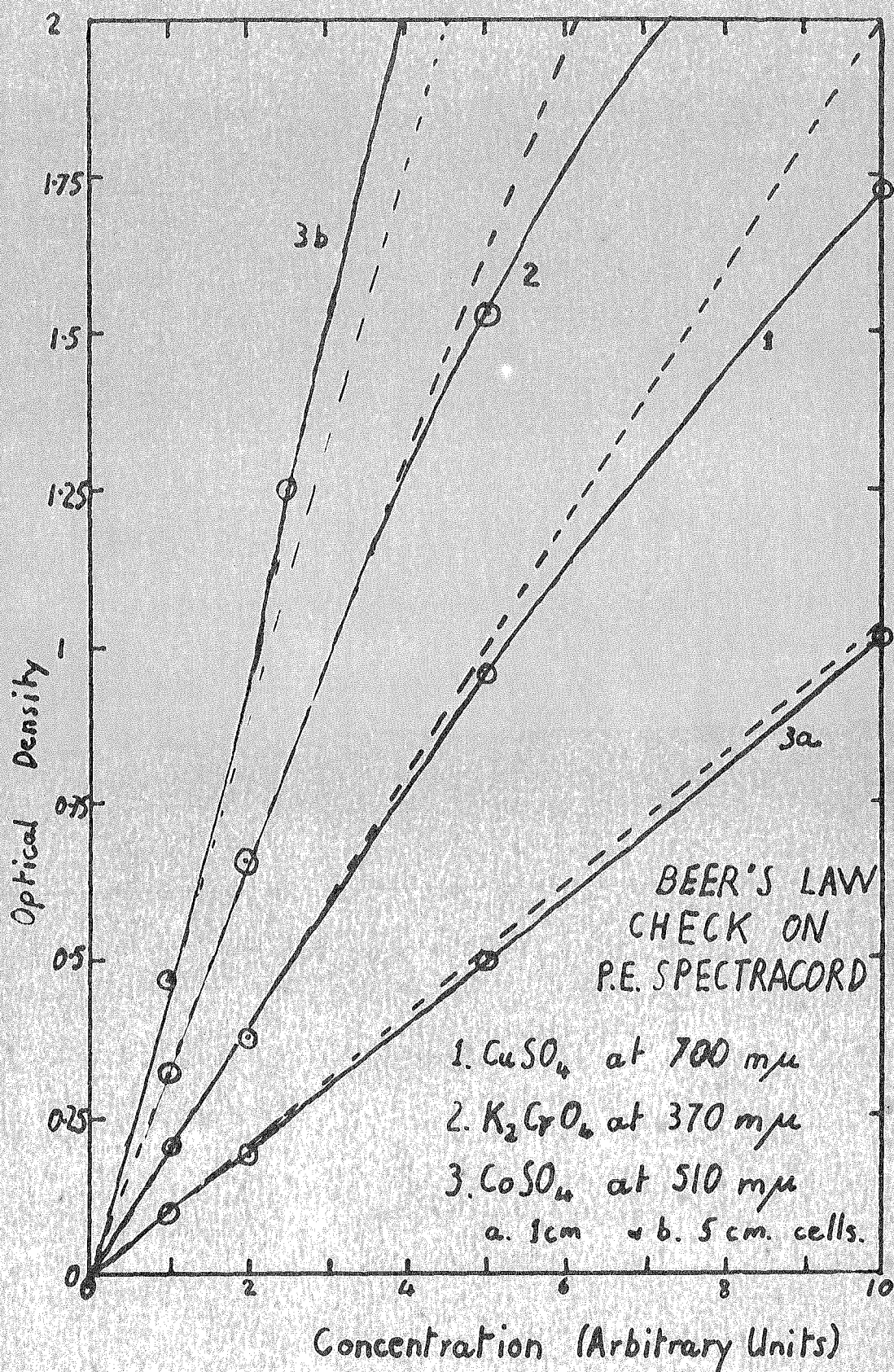
Dodd and West	17/7/64	29/7/65	29/7/65
402.4	402	403	402.5
430.9	430	431.5	431
445.6	443.5	445.5	445.5
453.4	452.5	453.5	453
459.7	458.5	460	460
572.8	571	572	572
585.1	583	586	583

Extinction Check

As stated above, Beer's Law was found to hold for the complexes being considered. Solutions of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ of different concentrations were run on the Spectracord. It was found that Beer's Law was not obeyed; the discrepancy was greatest for optical densities greater than 1.1. For further checking, the spectra of standard substances were run. Those solutions used as standards were copper sulphate in a 1% solution of sulphuric acid in water, cobalt ammonium sulphate in a similar solution, and potassium chromate in 0.5 normal aqueous potassium hydroxide solution. These three substances are recommended in a volume edited by Mellon (107). Florkin and Stotz (108) also recommend alkaline potassium chromate and aqueous potassium nitrate as standards. As the latter absorbs in the ultraviolet but not in the visible region of the spectrum, and only visible region spectra were dealt with, it was not used as a further check. The results show clearly that the measured absorbance does not vary directly with the concentration, even with these substances which are known to obey Beer's Law. Typical values are shown in figure 20.

Adjustments were made to the Spectracord controls, but the trouble persisted, and it was apparent that the Spectracord was not suitable for the precise measurements necessary.

FIGURE 20



3. Typical Results for Run

Run VIII

Temperature:		36.6°C				
Molarity of pyridine:		0.33				
Molarity of <u>trans</u> $[\text{Co en}_2\text{Cl}_2]^+$:		3×10^{-3}				
Elapsed Time in Minutes	Extinction Coefficients			Calculated Concentrations (molarity $\times 10^3$)		$-\log_{10} \frac{c^*}{c+p}$
	440 $m\mu$	535 $m\mu$	625 $m\mu$	<u>trans</u> $[\text{Co en}_2\text{Cl}_2]^+$	<u>cis</u> $[\text{Co en}_2\text{pyCl}]^{2+}$	
6	0.308	0.120	0.447	2.942	0.011	0.0017
32	0.312	0.145	0.447	2.913	0.089	0.0131
63	0.303	0.155	0.433	2.799	0.132	0.0201
97	0.315	0.178	0.435	2.806	0.204	0.0304
135	0.305	0.188	0.427	2.721	0.241	0.0368
173	0.311	0.202	0.420	2.678	0.292	0.0450
220	0.312	0.212	0.423	2.681	0.321	0.0492

* c = molarity of trans $[\text{Co en}_2\text{Cl}_2]^+$

p = molarity of cis $[\text{Co en}_2\text{pyCl}]^{2+}$

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