

CHEMICAL EFFECTS OF THE (n,γ) REACTION IN SOME SOLID
COMPLEXES OF COBALT, RHODIUM AND IRIDIUM

A thesis presented for the degree of

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in the Faculty of Science of Leicester University

by

Mary.E.Gravenor

The University

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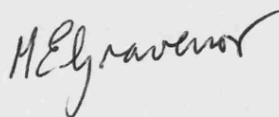
STATEMENT

All the experimental work, described in this thesis, has been carried out by the author in the laboratories of the Radiochemistry Section, School of Chemistry, City of Leicester Polytechnic between October, 1967 and the present date.

The work has not been presented, and is not being concurrently presented, for any other degree.

Dated: September, 1970

Signed:

A handwritten signature in cursive script, appearing to read "H. E. Gravener".

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SUMMARY

This research has been concerned with the chemical effects of the (n, γ) reaction in the following complexes: $[\text{M}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $\text{trans}[\text{M}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ and $\text{trans}[\text{M}(\text{en})_2\text{Cl}_2]\text{Cl}$ where M is cobalt(III), rhodium(III) or iridium(III). The work can be divided into two parts, a) the study of the fate of the recoil metal atoms following the (n, γ) reaction and b) the macroscopic effect caused by neutron-irradiation throughout the solid lattice. The methods which have been employed to study the different aspects were as follows.

a) The fate of recoil metal atoms was determined by paper electrophoresis. Several recoil species were observed, in particular for iridium complexes, and the results are explained using the hot-zone model.

b) The macroscopic effect was examined by labelling the complexes with chlorine-36, in the complex ion, prior to irradiation, and then noting any changes brought about in the distribution of the isotope as a result of neutron-irradiation. It was found that, provided the time of irradiation was long enough, almost total rupture of metal to ligand chlorine bonds occurred. The extent of the macroscopic effect was confirmed by far infrared spectroscopy and by re-irradiation of an electropherogram of irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after decay of recoil iridium-192 activity. In general, it is found that the order of stability of the complexes to metal-ligand bond rupture appears to be the reverse of that of the complexes in normal chemical reactions. An explanation is suggested for this. In order

to explain the large amount of disruption caused on a macroscopic scale, a theory is advanced of interaction of reactive species formed in the recoil zones with defects formed in the solid by the gamma radiation accompanying the thermal neutron flux.

CONTENTS

	PAGE
CHAPTER I	
1-1 Nuclear processes and their chemical effects.	1
1-2 The (n,γ) reaction.	4
1-3 Radiation effects.	6
CHAPTER II The chemical effects of the (n,γ) reaction.	10
CHAPTER III The (n,γ) reaction in transition metal complexes.	18
3-1 Ligand effects.	18
3-2 Isotopic and isomeric effects.	22
3-3 Effect of outer ions.	24
3-4 Crystal defects.	25
3-5 Retention in mixed crystals	29
3-6 Annealing	32
3-7 Szilard-Chalmers reaction in ammine complexes of cobalt(III), rhodium(III) and iridium(III).	34
CHAPTER IV Aims of research.	42
Decay schemes.	45
CHAPTER V Experimental	50
5-1 Methods available for analysis of irradiated complexes.	50
5-2 Preparation of complexes.	52

	PAGE
5-3 Analysis of complexes.	54
5-3-1 Infrared spectra.	54
5-3-2 Molar conductivity measurements.	56
5-3-3 Crystal structure.	56
5-4 Isotopic labelling of complexes.	57
5-5 Irradiation of samples.	59
5-6 Analysis of irradiated complexes.	62
5-6-1 Determination of chlorine-36 distribution.	62
5-6-2 Counting methods.	63
5-6-3 Paper electrophoresis.	65
5-6-4 Formation of sulphur-35.	69
5-6-5 Infrared spectroscopy.	70
5-7 Annealing.	70
5-8 Crystal form.	71
5-9 Mixed crystals.	71
CHAPTER VI Results.	73
6-1 Measurement of changes in chlorine-36 distribution.	73
6-2 Errors.	73
Paper electrophoresis.	79
6-3 Effects of diffusion and adsorption.	79
6-4 Cobalt complexes.	81
6-5 Iridium complexes.	88
6-6 Errors in results obtained by paper electrophoresis.	94

	PAGE
6-7 Re-irradiation of electropherogram of irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after decay of induced iridium-192 activity.	95
6-8 Infrared spectroscopy of irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.	96
6-9 Effect of crystal form.	96
6-10 Annealing.	96
CHAPTER VII Discussion.	102
7-1 Changes in chlorine-36 distribution.	102
7-2 Paper electrophoresis.	104
7-2-1 Electrophoresis of cobalt complexes.	105
7-2-2 Electrophoresis of iridium complexes.	108
7-2-3 Distribution of sulphur-35.	111
7-3 The macroscopic distribution of iridium in irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.	112
7-4 Infrared spectra of irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.	113
7-5 The influence of crystal form on recoil product distribution.	114
7-6 Annealing.	115
7-7 Recoil atom reactions.	118
7-8 Macroscopic effect.	119
7-8-1 Recoil energy effect.	120
7-8-2 Auger charging effects.	127
7-8-3 Gamma radiolysis.	129
References.	131

CHAPTER I1-1 Nuclear processes and their chemical effects.

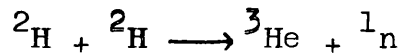
All nuclear processes and radiations emitted during these processes can bring about chemical changes in the material in which they occur. This research is concerned with the effects produced by neutron bombardment. The processes involved can be divided into two categories; neutron capture reactions and interaction of the accompanying gamma radiation with the material.

The capture of a neutron by the nucleus of an atom produces an excited compound nucleus, the energy of excitation being provided by the binding energy of the neutron and its incident kinetic energy. The binding energy of one additional neutron into a nucleus is defined as the mass of the nucleus plus the mass of the neutron minus the mass of the resultant nucleus expressed in energy units. The value of this binding energy fluctuates widely from one nucleus to the next. The value of the binding energy of a neutron to form a nucleus of even mass number is generally greater than that to form the subsequent nucleus of odd mass number and this is indicative of the greater stability of nuclei with an even number of nucleons. The binding energy of a neutron in any particular nucleus will be constant. Thus it is the incident kinetic energy of the neutron which will determine the energy of excitation of the nucleus. Neutron energies can be classified as follows:

<u>Neutron class</u>	<u>Energy(E)</u>
Slow	$E < 1\text{KeV}$
Intermediate	$1 < E < 500\text{KeV}$
Fast	$0.5 < E < 10\text{MeV}$
Very fast	$E > 10\text{MeV}$

A special class of slow neutrons are thermal neutrons. These have an energy distribution similar to that of gaseous molecules in thermal equilibrium. The mean energy of thermal neutrons at room temperature is about 0.025eV.

Neutrons can only be produced by nuclear reactions. Fast and very fast neutrons, those of energy greater than 0.5MeV, are produced using accelerators. The most common reaction used is that between accelerated deuterium nuclei, known as the D,D reaction, in which helium-3 nuclei and fast neutrons are formed.



The potential barrier for the reaction is low and good neutron yields can be obtained with deuterons of relatively low energies, 100 to 200KeV. Lower energy neutrons, down to 30KeV, can be produced by the ${}^7\text{Li}(p,n){}^7\text{Be}$ reaction and if protons of well defined energy are available from the accelerator, monoenergetic neutrons can be obtained. Fast neutrons are also produced during the fission processes occurring in nuclear reactors. Generally two to three neutrons are emitted for each fission occurring. Neutrons from all nuclear reactions are initially fast neutrons. These lose energy rapidly in inelastic collision with heavy nuclei until intermediate energies are reached. Energy is then lost by elastic collisions which are most effective

with light nuclei and therefore hydrogen containing substances such as water make effective media for slowing down neutrons to thermal energies. A steady flux of thermal neutrons is available in the thermal column of a nuclear reactor. The thermal column is made of a moderating material such as water or graphite and is usually situated outside the biological shield of the reactor. A steady flux of thermal neutrons is obtained in the column by moderation of fast neutrons from the pile.

The manner in which an excited compound nucleus, produced by neutron capture will decay depends on the energy of excitation, and therefore on the kinetic energy of the incident neutron. In the majority of cases, capture of slow neutrons results in the emission of gamma radiation and the process is known as the (n,γ) reaction. With target materials of low atomic number the emission of a proton, i.e. the (n,p) reaction, or of an alpha particle, the (n,α) reaction, can occur though the latter does not generally occur for thermal neutron capture. At neutron energies of several MeV, (n,p) reactions become prevalent and as the energy increases $(n,2n)$, (n,α) and (n,np) reactions occur. In general, the higher the energy of the captured neutron the more complex the possible nuclear reactions become.

1-2

The (n, γ) reaction

The gamma rays which are emitted following thermal neutron capture have a total energy of ΔMc^2 , where ΔM is the change in the nuclear mass. The emission is almost instantaneous and the time lapse is even shorter than the vibration times of atoms in a solid. The emitting nucleus receives a recoil momentum which is equal and opposite to the vector sum of the momenta of the emitted gamma rays. Usually several gamma rays are emitted for each nuclear event, but single gamma ray emission does occur in certain cases, in particular for the lighter elements. A gamma ray of energy E_γ has a momentum $p = E_\gamma/c$. The recoiling atom will have the same momentum, and the recoil energy R is thus given by

$$R = \frac{(p_\gamma)^2}{2M} = \frac{(E_\gamma)^2}{2Mc^2} \quad \dots \dots \dots 1$$

where M is the atomic mass. For M in atomic mass units and E_γ in MeV:

$$R = \frac{537 E_\gamma^2}{M} \text{ eV} \quad \dots \dots \dots 2$$

For two gamma rays emitted at an angle θ to each other

$$R = \frac{(p_{\gamma 12})^2}{2M} = \frac{(E_{\gamma 1})^2}{2Mc^2} + \frac{(E_{\gamma 2})^2}{2Mc^2} + \frac{E_{\gamma 1} E_{\gamma 2} \cos \theta}{Mc^2} \quad \dots 3$$

If no angular correlation exists between gamma rays and all angles are equally probable, there will be a spread of

possible recoil energy between fixed limits.

$$R_{\max}(\theta = 0^\circ) = \frac{(E_{\gamma_1} + E_{\gamma_2})^2}{2Mc^2} \dots\dots\dots 4$$

$$R_{\min}(\theta = 180^\circ) = \frac{(E_{\gamma_1} - E_{\gamma_2})^2}{2Mc^2} \dots\dots\dots 5$$

For several gamma rays emitted in cascade the situation becomes more complex. However, the recoil energy distribution following the (n, γ) reaction can be calculated from neutron capture gamma ray spectra. Usually a compound nucleus formed by thermal neutron capture has an excess energy of about 8MeV and the majority of this is dissipated by emission of gamma rays in a cascade. Unless all these gamma rays are very low in energy, which is unlikely to occur, the recoil energy will be well in excess of that necessary to bring about bond rupture. Bond energies are of the order of 1 to 5eV. Emission of a gamma ray of energy only 2MeV from a heavy nucleus of say 200 atomic mass units will give that nucleus a recoil energy of 11eV and a light nucleus of 20 atomic mass units a recoil energy of 107eV. Thus, in the majority of cases, the recoiling atom has sufficient energy to break one or more bonds in the molecule of which it is a part. If the molecule is not immediately dissociated as a result of the (n, γ) reaction, the whole molecule will then suffer recoil. The molecular recoil energy is shared between the internal energy, R_i , and the energy of translation, R_t . The proportion of the total

energy which exists as internal energy is given by:

$$\frac{R_i}{R} = \frac{m}{M+m} \quad 6$$

where M is the mass of the recoil atom, and m is the mass of the remainder of the molecule. The increase in internal energy is certain to cause molecular dissociation unless R_i is very small when compared to R . This will only be the case when m is very small i.e. when the atom which suffers the (n, γ) reaction is bonded only to a light atom such as hydrogen or deuterium.

1-3

Radiation effects

As has already been mentioned neutron bombardment, in the thermal column of a nuclear reactor, is always accompanied by gamma irradiation. Radiation will generally result in excitation, ionisation and dissociation of molecules in the irradiated media. In gases the effects produced are independent of the type and energy of the ionising radiation and depend only on the total energy absorbed by the system. In the condensed phase about half the energy of the radiation is used for ionisation and the other half for molecular excitation. Both these processes may be followed by dissociation, and the production of radicals in the medium is probable. Much work has been done on the radiation chemistry of aqueous solutions where H and OH radicals are thought to be involved as intermediates. Radiation studies in organic compounds show the formation

of fragments smaller than the original molecule, H_2 , CO etc. and polymerisation induced by free radicals formed by the radiation.

In crystalline solids radiation will generally result in excitation and ionisation of the atoms in the lattice. As a result of excitation some atoms will be displaced and the degree of disorder in the crystal will increase. Ionisation will release electrons into the lattice and if these are trapped in interstitial positions luminescence and colour phenomenon will result. However, if valency changes are possible these will occur in preference to electron displacement. The crystal defects produced can be divided into two types; fixed defects due to foreign atoms or accidental irregularities, and mobile defects. The latter can be further classified as follows:

- 1) The ion or atom leaves its lattice position for an interstitial position. This is a Frenkel defect.
- 2) The ion or atom leaves its lattice position and migrates to the surface, or to a discontinuity, leaving a vacancy in the lattice known as a Schottky defect.

When an atom is displaced to an interstitial position both defects will be present and the process is reversible.

Gamma emission from the radioactive nuclei must also be considered. The energies of these gamma rays are much lower than those emitted in the (n, γ) reaction, being generally of the order of 100KeV and rarely above 500KeV. A 100KeV gamma ray would give a nucleus of mass 100 a recoil energy of only 0.05eV, much too small for bond

rupture. Internal conversion of the gamma rays results in electron emission which will impart a recoil energy about ten times that of gamma emission, i.e. 0.5eV which is still below bond energies. However, the vacancy left in the inner electron shell by internal conversion leads to electron rearrangement and emission of Auger electrons. The atom will thus obtain a high positive charge and as a result of this valency changes and molecular dissociation will certainly occur. Gamma rays emitted in the isomeric transition process are generally low in energy and can undergo internal conversion. Thus, isomeric transitions will give rise to chemical effects due to both gamma and Auger emission.

The chemical effects of beta decay processes are dependent on the following factors:

- a) The recoil energy of the daughter atom acquired by emission of beta particles, internal conversion and Auger emission.
- b) The charge on the daughter atom as a result of these three processes.
- c) The electronic excitation produced in the daughter atom by the sudden change in nuclear charge.
- d) The chemical state of the parent atom and the conditions under which the parent molecule breaks down.

The energy of the recoiling nucleus due to emission of an electron can be calculated from relativistic theory.

However, for any given transition the recoil energy has a spectrum of energy values as beta emission is not mono-

energetic. Valency changes are bound to occur in the recoil atom as a result of electron emission but experimental difficulties are found in measuring charge variation because of recombination and neutralisation reactions which occur.

The extent to which beta and gamma decay processes, following the (n, γ) reaction, are responsible for the chemical changes which occur can be determined by measuring the recoil product distribution at various times. Any marked variation in results with time must be due to decay effects. In the majority of cases, decay effects are negligible when compared to the effects of nuclear recoil.

CHAPTER II

The Chemical Effects of the (n, γ) Reaction

The effect of bond rupture following the (n, γ) reaction was first noted by Szilard and Chalmers in 1934, 1, in their work on neutron-irradiated ethyl iodide. Following irradiation they were able to extract iodine-128 into aqueous solution as iodide ion, showing that carbon-iodine bonds had been broken. The iodine-128 remaining in the organic phase was found as ethyl iodide and also as other organic iodine compounds, which could only have been formed by reactions following neutron capture. Szilard and Chalmers concluded that bond rupture was due to recoil of the iodine nucleus induced by the incident neutron. However, it was later shown, 2, that the momentum of the incident thermal neutron was insufficient to cause a recoil of the necessary magnitude, but that emission of gamma rays could supply the required momentum to the nucleus.

The question arises that, if the recoiling atom possesses sufficient energy to break several chemical bonds, why are a certain proportion of the radioactive product nuclei retained in the original compound. This proportion is generally referred to as the "retention" value. It should be noted that the term "retention" has been used with other meanings by some writers. For instance, in much of the early work on these processes in organic systems the retention value was the proportion of the recoil atoms which were found in the organic phase, not

necessarily all in the parent compound. However, retention now almost always refers to retention in the original form. The magnitude of the retention depends very largely on the phase of the irradiated substance. For gases retention is very low or zero, the activity being mainly found in some new chemical form. This is attributable to the long free path in the gaseous state which allows the recoil atom to escape from the neighbourhood of the remainder of the parent molecule. Thus recombination of the fragments of the molecule to produce the parent is very unlikely. The free path is much reduced in the liquid and solid states, making recombination of the fragments of recoil a more probable occurrence. There is therefore a tendency for retention values to increase through the range gas-liquid-solid.

Most of the early work carried out on effects of the (n, γ) reaction was concerned with the gaseous and liquid phases and interest in the solid phase was not aroused until the 1950s. Thus the first theories of recoil atom behaviour following the (n, γ) reaction were based on results found in gases and liquids only. Many theories have been advanced concerning the mechanism by which recoil atoms dissipate their excess energy by interaction with other entities in the medium, such as atoms, molecules, ions and radicals. In this section the basic principles of the various theories will be outlined together with the supporting experimental evidence. The theories are based on studies of changes in product distribution with neutron

energy, chemical environment or phase, and annealing.

The first ideas on recoil atom behaviour were based on simple collision theory and were put forward by Libby and other workers, 3,4,5. Libby's model envisaged the recoil atom losing its energy in elastic and inelastic collisions with surrounding molecules. Retention was explained by assuming that the recoil atom could undergo an elastic collision with a similar atom in a nearby molecule, rupturing the bond between this atom and the rest of the molecule. Having lost most of its energy in this way the recoil atom would be unable to move further in the medium. It could then react with the molecular fragment it had produced, by the elastic collision, to give a molecule exactly similar to the parent molecule but containing a radioactive atom. Elastic collisions occur while the atom has more than about 100eV of kinetic energy. Below this energy the recoil atom will suffer inelastic collisions with molecules causing rupture of other bonds e.g. carbon-carbon and carbon-hydrogen bonds in organic molecules. Such reactions are probable at about 10eV and are called epithermal reactions.

The Libby model was found to be inapplicable to recoil atom behaviour in several organic systems, although it was successful in explaining effects in alkyl halides. For this reason a further modification was made to the theory by Miller and Dodson, 6, in particular to explain the behaviour of recoil chlorine atoms in liquid hydrocarbon media. They postulated that each recoil atom combined

with a hydrocarbon molecule to produce an excited complex which could then decompose in a number of different ways. The proportions of the products would be dependent on the competing reactions of the excited molecules in the epithermal region.

Besides the original results obtained for alkyl halides, several experimental observations have been explained using the collision model. The majority of successful applications of this theory have concerned recoil reactions in organic systems. An attempt has been made to apply the theory to organometallic 'sandwich' compounds with rather doubtful results, 7. Saito et al, 8. were able to explain the replacement of ligands in cobaltamine complexes using Libby's model.

As a realistic model of the course of events in recoil atom reactions the collision theory leaves much to be desired. To begin with, it considers atoms as hard spheres which interact by 'billiard-ball' collisions, an idea which is totally unacceptable in modern theories of atom interactions. In addition to this many of the predictions made using the model have been experimentally disproved. For example, the distribution of products is solely dependent on the energy of the recoil atom. Thus recoil atoms having different energies should give rise to different product distribution. Saito et al, 9,10, found that radioactive bromine produced by the $(n,2n)$ reaction and that produced by the (n,γ) reaction had very similar recoil behaviour in spite of the difference in recoil energy.

As a result of his work on recoil halogen atoms in liquid systems, Willard proposed an alternative to the Libby model, 11. He suggested that the recoil atom loses its energy in a two stage process. At first, while its energy is high, the atom will dissipate its energy in a series of inelastic collisions producing free radicals and excited atoms in a purely random fashion. In the second stage, when the energy has fallen below the level necessary for bond rupture, the recoil atom will combine with radicals in its path, a process which will be dependent on the rate of diffusion of the atom. Willard also reached the conclusion that for organic systems, where a large number of reactions are possible, the chemical characteristics of the medium are more important than physical factors such as the energy of recoil or the masses of the atoms involved. Using the Willard model product distribution can be predicted but these results are not generally in agreement with experimental determinations.

The most successful and currently the most widely accepted theory of recoil atom reactions is the 'hot-zone' model, proposed by Yankwich, 12, and Harbottle and Sutin, 13,14. They based their ideas on the original 'thermal spike' theory of Seitz and Koehler, 15, who assumed that the recoil atom was slowed down in the lattice by elastic collisions with a small number of atoms in a limited region.

In the 'hot-zone' model the energy of the recoil atom is envisaged as being used in heating a small region of the

lattice to a temperature above its melting point. Harbottle and Sutin considered the case of a recoil atom of initial energy 300eV and mass 100. They estimated the mean free path of the atom in an ionic crystal to be about $5r_s$ where r_s is the atomic radius. Since the atom will lose around half of its energy in each collision, about four collisions are necessary to reduce the atom to thermal energies below 25eV. This slowing down process will take approximately 10^{-13} sec. This rapid loss of energy in a sphere of radius $5r_s$ will produce a very high temperature. In fact it is more realistic to envisage about five to ten separate hot spots in a sphere of radius $5r_s$ which merge to form the hot-zone after 10^{-12} sec. If the melting point of the solid is around 1000 K, calculation using the specific heat, density and thermal diffusion coefficient of the solid shows that the heat produced in the original hot-zone will heat a sphere of radius ten times $5r_s$ i.e. about 1000 atoms and that the time for the temperature to fall below 1000°K will be 100 times the time of hot spot production i.e. 10^{-11} sec. During the short time the hot-zone is in a molten state high-energy chemical reactions will occur but, as cooling is very rapid, they are unlikely to go to completion. After cooling the hot-zone will be a small region of the lattice containing a conglomeration of very reactive species (molecular fragments, radicals, ions etc.) stabilised by the rapid cooling process.

An attempt to decide the shape of the hot-zone has been made by Rosenberg and Sugihara, 16. The shape will depend on the energy of the recoil atom and the efficiency

with which it is transferred to other atoms. Using this hypothesis the authors made a qualitative assessment of the shape of the hot-zone in various transition metal complexes. The physical significance of the results is questionable.

A large number of the chemical effects of the (n, γ) reaction can be explained using the hot-zone model, 17-23.

An adaptation of the hot-zone model was suggested by Müller as a result of his work on mixed crystals, 24,25. Homogeneous mixed crystals of $K_2ReBr_6 - K_2SnCl_6$ and $K_2ReCl_6 - K_2SnBr_6$, with the rhenium complex at low concentration, were irradiated with neutrons and the products of the $^{185}Re(n, \gamma)^{186}Re$ process were determined by electrophoresis. Müller found that the recoil atom showed a preference for the ligands to which it was originally attached whether those ligands were bromine or chlorine. He deduced from this that the recoil range and the reaction zone were small and that the reaction zone was centered around the site of recoil. Assuming the original ligands remain in this reaction zone, and using the knowledge that the unit cell contains 24 halogen atoms Müller was able to calculate, from the ligand enrichment in the recoil products, the size of the reaction zone to be about 500\AA^3 and its radius 5\AA assuming it to be a sphere. As to the nature of the reaction zone, Müller rejected the idea of a melt as in the hot-zone model. He reasoned that if the reaction zone is a homogeneous melt the product distribution would be purely statistical, and the results he obtained were far from those predicted in this way. Müller put forward a

new 'disorder' model. The recoil atom penetrates only a short distance into the lattice producing temporary deviations of atoms from their equilibrium positions, to give vacancies and interstitials. It comes to rest in a near perfect lattice and reacts with the ligands around it. Thus in mixed crystals of this type, the further the recoil atom travels the more ligands of the non-Szilard-Chalmers component will become attached to it. The disorder model differs from the hot-zone model in two main features. First the size of the reaction zone is at least ten times greater in the hot-zone model. And secondly, the hot-zone is a melt where much disruption of the lattice occurs while the disorder model envisages only small changes in the structure of the solid.

Müller discounted the hot-zone model on the assumption that the reaction zone was a homogeneous melt which would give rise to a statistical distribution of products. However, as the hot-zone is only molten for 10^{-11} sec. it is unlikely that homogeneity will be obtained and so a purely statistical product distribution would not be expected. Thus Müller's results do not invalidate the hot-zone model.

CHAPTER III

The (n,γ) Reaction in Transition Metal Complexes

The chemical effects of the (n,γ) reaction in transition metal complexes have been studied from a number of different viewpoints. In this chapter these various aspects will be described with reference to the experimental work done in this field up to the present time.

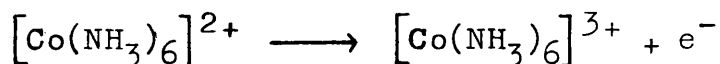
3-1

Ligand effects

Much of the work carried out on the Szilard-Chalmers reaction in transition metal complexes has been concerned with the effect of alterations in the ligand arrangement on the distribution of recoil products. It is obvious that if the recoil atom is the central metal atom of the complex ion, its behaviour will be dependent, at least to a small extent, on the arrangement of ligands around it and on their chemical nature.

An example of the effect of ligand variation on product distribution is given in the work of Harbottle on nitrate-ammine complexes of cobalt(III), 19. A series of complexes containing varying numbers of nitrate and ammine ligands, (i.e. $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$ etc.) were subjected to irradiation with thermal neutrons and the distribution of cobalt-60 radioactive products was studied by paper electrophoresis. In most cases, the major proportion of the products was made up of the parent ion or retention product, and the cobalt(II) ion or reduced product.

The change in product distribution on thermal annealing was also studied. The general conclusions of the work were that $[^{60}\text{Co}(\text{NH}_3)_6]^{3-}$ was only produced in systems where it was the parent ion, or in other words, addition of an ammine ligand did not occur. Displacement of ammine ligands did occur but the effect was reversed by annealing. In $[\text{Co}(\text{NH}_3)_6]^{3+}$ the major annealing reaction was the disappearance of cobalt(II) ion. This was explained by assuming that cobalt(II) ion was produced in solution by the decomposition of the reduced form $[\text{Co}(\text{NH}_3)_6]^{2+}$. This entity is removed on annealing the solid by the reaction,



In contrast to Harbottle's results, Yasukawa, 26, showed, using ion exchange and precipitation methods, that in the neutron irradiation of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ some of the radiocobalt was found as $[\text{Co}(\text{NH}_3)_6]^{3+}$. It may be that the larger nitrate ion will hinder the entry of ammonia molecules into the ligand sphere, while the more mobile bromide ions may allow diffusion of ammonia molecules and the formation of the Co-NH₃ bond.

The value of choosing a simple ligand system, where only two or three types of ligands compete, is obvious from these results. However, the work is complicated by the method of analysis in that reactive entities in the solid lattice will interact with water upon dissolution. Complex ions of the type $[^{60}\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ are therefore also found by the electrophoretic method, which presumably result from the reaction of ligand deficient species in the

crystal with water molecules. These problems of hydration are always encountered when studying recoil products by methods which require dissolution.

The effect of altering only one ligand and keeping the remainder of the co-ordination sphere constant was investigated by Saito et al, 27. The distribution of radiobromine in the products of the (n,γ) reaction of bromine atoms in complexes of the type $[\text{Co}(\text{NH}_3)_5\text{X}]\text{Br}_2$ was studied. It was found that the fraction of the total radiobromine, which entered the co-ordination sphere in place of the ligand, X, increased with the mass of the donor atom in that ligand. This suggests that the recoil reactions are dependent on the kinetics of the reaction of the molecular fragment $[\text{Co}(\text{NH}_3)_5]^{3+}$ and the competing ligands. In other words, the lighter and hence more mobile the ligand, the more rapidly it will react with the fragment. Whether these reactions occur in the lattice, or only upon dissolution is uncertain.

A comprehensive study of the effect of ligand denticity on recoil atom reactions was made by Shankar and Shankar, 28. They made the following generalisations for cobalt(III) complexes.

- 1) Monodentate ligand complexes produce several recoil species.
- 2) Bidentate ligand complexes produce mainly cobalt(II) and retention products.
- 3) Sexadentate ligand complexes produce numerous recoil species.

Similar work was later carried out by Stucky and Kiser, 29. They found numerous products in all three cases. In addition, they were able to correlate a decrease in the cobalt(II) fraction with an increase in gamma dose, and suggested that radiation damage could be the main factor in this, and not recoil effects.

At a much earlier date Sue and Kayas, 30, had studied the effect of the Szilard-Chalmers reaction in the series $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$, $[\text{Co}(\text{en})_3](\text{NO}_3)_3$ and $[\text{Co}(\text{dien})_2](\text{NO}_3)_3$. The retention value was found to increase with the ligand denticity, and this was explained as due to increased screening of the central cobalt atom by the more complex ligands. Nath and Shankar, 31, divided metal chelates into two classes; a) a group with low initial retention, and b) a group with high initial retention. In class a) complexes the recoil atom is not hindered by the ligands and is easily ejected. 'Sandwich' compounds such as cyclopentadienyls fall into this group, which are referred to as 'open-type' complexes. Octahedral complexes fall in the second class, and here the hindrance is large. The difference between the two groups is stereochemical.

Steric effects are of prime importance in recoil atom reactions. Both the configuration of the molecule and the steric properties of the crystal as a whole have a large influence on retention values. The influence of crystal structure will be discussed later in considering crystal defects. The extent to which molecular configuration is retained, following the (n,γ) reaction, has been studied

for both geometric and optical isomers. Rauscher et al, 17, 18, studied dextro-tris-ethylenediaminecobalt(III) nitrate, and cis- and trans-dichlorobisethylenediaminecobalt(III) nitrate. In all cases they found that to a very large extent configuration was preserved, i.e. very little cis isomer was found in the recoil products of the trans isomer and vice-versa. For some reason it appears that the complex ion 'remembers' its original configuration. It could be that only two metal-ligand bonds are broken in which case recombination would be most likely to occur in the original configuration. Annealing studies showed an increase in retention and decrease in the cobalt(II) fraction. This suggests that more than two bonds are broken in most cases and the recoil fragment is reduced to cobalt(II) ion. In annealing, the various recoil fragments recrystallise on the pattern of the surrounding crystal, thus restoring the original configuration. Stereospecificity of this kind was also observed by Jagannathan and Mathur, 23, in their study of neutron irradiated cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$. The large increase in retention of configuration on annealing is convincing evidence for the validity of the hot-zone model.

3-2 Isotopic and isomeric effects

Different isotopes and isomers of the same element are known to behave differently on recoil. The first evidence for a direct relationship between nucleogenesis and retention values was found by Apers and Capron, 22, in their work on recoil zinc-65 and zinc-69.

In this particular field the work of Lazzarini and co-workers is perhaps the most outstanding, 32-39. They have studied the isomeric effect in Szilard-Chalmers recoil of cobalt-60m and cobalt-60g in various cobalt(III) complexes. The results of their work showed that cobalt-60m and cobalt-60g have different recoil behaviour. The ratio of the retention of cobalt-60m to that of cobalt-60g depended on the chemical constitution of the target. The ratio is linearly dependent on the magnitude of the splitting of the 3d-orbitals of the cobalt(III) by the ligand field, and on the ability of the ligands to promote back-donation from the cobalt atom, 32, 33. The isomeric effect was found to be essentially an additive property of the ligands, 34. The effect of the crystal structure beyond the first co-ordination sphere of cobalt, and that of cis-trans isomerism, on the magnitude of the retention ratio were very small, 35, 36. Other conditions being constant, the isomeric effect is dependent on $\sigma_m/(\sigma_m + \sigma_g)$, where σ_m and σ_g are the cross sections of formation of cobalt-60m and cobalt-60g by the (n, γ) reaction, 37. In the last two papers, 38, 39, the authors have measured the variation of the retention ratio with irradiation time, storage time and storage temperature, and attempted to explain these using annealing parameters. Stucky and Kiser, 29, also studied the isomeric effect in cobalt complexes. They concluded that retention values could not be correlated with ligand field only but were also dependent on other factors such as the extent of π -bonding and back-donation, and the polarisability and dielectric constant of the ligands.

A good example of the large amount of work done on outer ion effects is to be found in a series of publications on the distribution of recoil iridium-192 in neutron irradiated hexachloro complexes of iridium(IV) with Na^+ , K^+ , $(\text{NH}_4)^+$, Rb^+ and Cs^+ as outer cations. Herr and Heine studied the recoil species formed in all five complexes, 40, 41, and found that the retention varied markedly for the different salts, even though only the sodium salt has a different crystal structure. Six radioiridium anionic complexes were found on electrophoresis. The sodium salt was examined further by Bell and Herr, 42, who found thirteen iridium-192 recoil species. They suggested formulae for each of these, mostly as complex ions of iridium(III) and iridium(IV) with Cl^- , H_2O and OH^- ligands. Cabral, 43, 44, pointed out that sodium hexachloroiridate is always hydrated in the crystalline form, and water of crystallisation will complicate the recoil processes. He therefore carried out neutron irradiation of both the hydrated sodium salt and the anhydrous ammonium salt. The number of recoil species found for the sodium salt was in good agreement with the results of Bell and Herr. For the ammonium salt all these species were found, plus three new species, which Cabral concluded were ammine complexes of iridium. The latest work in this field is by Cabral and Maddock, 45. They investigated the role of water of crystallisation using hydrated and anhydrous sodium salts. In the anhydrous salts, the percentage of iridium(III)

species is reduced and that of iridium(IV) species increased. They explained this by assuming that OH and H radicals were formed in $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ which reduce iridium(IV) atoms.

The effect of outer anions on recoil processes in complexes was investigated by Saito et al, 46, using complexes of the type $[\text{Co}(\text{NH}_3)_6]\text{X}_3$ containing nine different anions, X. The distribution of cobalt-60 recoil species varied with the nature of the outer anion and, in general, retention tended to increase as the stability of the Co-X bond decreased, i.e. as competition from the anion, X, for a place in the co-ordination shell decreases, the probability of the complex reforming with its original ligands is increased.

3-4

Crystal defects

The importance of crystalline structure in determining the distribution of recoil products following the Szilard-Chalmers reaction in solids was first appreciated by Maddock and Vargas, 47, when they noticed that exactly similar irradiation conditions of temperature, gamma dose rate etc. did not give results with the degree of reproducibility expected. They suggested that this might well be due to defects in the crystal structure of the solids irradiated. Sutin and Dodson, 48, had shown earlier that if crystals were exposed to gamma radiation before neutron irradiation, the rate of thermal annealing of the products was accelerated. Single crystals and powdered crystals showed different initial retention values, following

irradiation under the same conditions, 47. Also pre-irradiation with gamma rays decreases initial retention.

In subsequent work, Maddock et al, 49, irradiated potassium chromate in various crystal forms, i.e. a) large crystals, b) crystals powdered before irradiation, c) crystals powdered after irradiation and d) crystals powdered and thermally annealed before irradiation. Powdering of the crystals before irradiation was found to produce the same results as pre-irradiation, i.e. lower retention but faster annealing. Harbottle and Sutin, 14, had suggested that gamma-irradiation might produce radicals in the crystal lattice. These would lower retention by reacting rapidly with recoil fragments and preventing reformation of the parent molecule. Powdering of the crystals could not produce radicals but on the other hand it would increase the surface area and facilitate reaction with the atmosphere. However, experiments performed in vacuo on powdered crystals showed the same decrease in initial retention and atmospheric effects must therefore be ruled out. Powdering and pre-irradiation have only one effect in common, they increase the density of defects in the crystal lattice.

Andersen and Maddock, 50, extended this work further by introducing irregularities into the potassium chromate lattice by two other methods, quenching and incorporation of multicharged impurities e.g. Cu, La or Tl for potassium. Quenching was found not to alter the initial retention, although defects must be produced. Crystals doped with

copper and lanthanum ions showed increased retention, while thallium ions decreased it. In all cases thermal annealing was accelerated by the introduction of defects.

Machado et al, 51, carried out similar work using the trisacetylacetonates of cobalt(III) and chromium(III). They found that the introduction of defects prior to irradiation always reduced the retention of ^{60}Co and ^{51}Cr . They reached the conclusion that defects must compete with the recoil atom for the capture of a third body which is necessary for the reformation of the parent molecule. Even when the density of such defects is small, the retention is decreased suggesting that the third body is easily captured and therefore very mobile. They have suggested that the third body might well be a free electron.

3-5

Retention in mixed crystals

In 1961 Maddock and Vargas published results of their studies of the retention of radiochromium as chromate ion in mixed crystals of potassium chromate and potassium fluoroberyllate, 52. They found that a linear relationship existed between the retention observed, R_o , and the percentage of potassium chromate in the mixed crystals, such that $R_o = (29.5 \pm 1.29) + (0.38 \pm 0.07)x$, where x is the percentage of chromate. They advanced the theory that the observed retention, R_o , could be considered as the sum of four independent terms;

$$R_o = R_n + R_c + R_r + R_a$$

where R_n is the retention due to the proportion of nuclear

events which fail to rupture the target molecule; R_c is due to the rapid reformation of the parent molecule while the recoil atom is held in a reaction 'cage'; R_r is due to the reformation of target molecules by epithermal reactions of recoil fragments with inactive molecules in the hot-zone; and R_a is the retention due to thermal or radiative annealing during or after irradiation. R_n will be independent of the environment of the nucleus undergoing the (n,γ) reaction and will be, generally, only a small fraction of R_0 . Similarly under the conditions of irradiation used, R_a will be very small. Changes in R_c with composition of the mixed crystals are expected to be small since the effectiveness of the 'cage' will depend on forces in the lattice and not on the actual ions present. However, R_r will be expected to decrease linearly as the concentration of chromate ions decreases since it depends on recoil chromium fragments encountering inactive chromate ions.

Perhaps the best example of the use of effects in mixed crystals to elucidate the course of recoil reactions is the work of Müller, 24,25, in which homogeneously mixed crystals of K_2ReBr_6 and K_2SnCl_6 were irradiated with neutrons to bring about the $^{185}Re(n,\gamma)^{186}Re$ reaction. Using the billiard ball theory, at very low rhenium concentrations, the complexed radiorhenium will mostly be in the form $[^{186}ReCl_6]^{2-}$ because the recoil atom will generally replace only tin atoms. However, if the hot-zone model is applied, the complexed radiorhenium should be in seven different forms, $[^{186}ReCl_nBr_{6-n}]^{2-}$ ($6 \leq n \leq 0$), provided the concentration of

$[\text{ReBr}_6]^{2-}$ is not too low. The products were analysed by electrophoresis and the results are shown in fig.3-1. As all seven species are present the results would appear to support the hot-zone model. However, Müller carried his analysis of the results a stage further. If the reaction zone is a melt he decided that the distribution of products would be purely statistical. (This may be an erroneous assumption, since the hot-zone will cool very rapidly, probably before a statistical distribution is reached.) On comparing the statistical yield of the various complex ions with the experimental yield, no correspondence of values was obtained, as can be seen in table3-1. On this basis Müller rejected the hot-zone model and formulated his own 'disorder' model which has been discussed in the preceeding chapter, p.16.

FIGURE 3-1

Electrophoretic separation of neutron-irradiated

$\text{K}_2\text{ReBr}_6 - \text{K}_2\text{SnCl}_6$ mixed crystals, as determined

by H.Müller, 24.

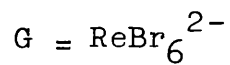
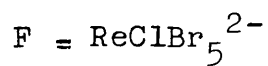
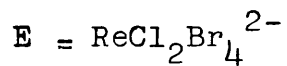
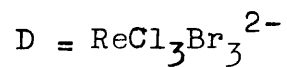
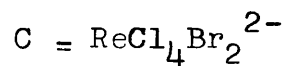
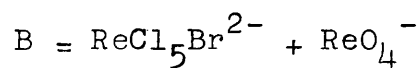
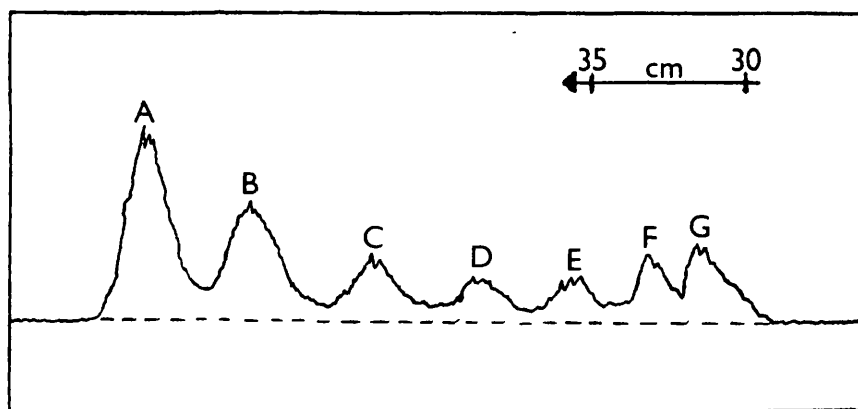


TABLE 3-1

Comparison of the experimental and the calculated yield
of hexa(chlorobromo)rhenates for $K_2ReBr_6 - K_2SnCl_6$, as
determined by H.Müller, 24.

System	Experimental (%)	Calculated (%)
$ReBr_6^{2-}$	15.3	0.2
$ReClBr_5^{2-}$	7.9	3.0
$ReCl_2Br_4^{2-}$	7.4	12.0
$ReCl_3Br_3^{2-}$	9.0	26.5
$ReCl_4Br_2^{2-}$	13.0	32.0
$ReCl_5Br^{2-}$	13.5	21.0
$ReCl_6^{2-}$	33.8	5.5

Much of the information so far obtained on the chemical effects of the (n,γ) reaction has been the result of post-irradiation annealing studies on the solids concerned. Of several methods of annealing the most widely used is that of thermal annealing. In this process the irradiated solid is heated at a constant temperature. Samples can be removed at set times and the proportions of radioactive products determined, so that the kinetics of thermal annealing can be followed. In the majority of cases thermal annealing, to reform the parent species containing the radioactive atom, proceeds rapidly at first, followed by a much slower annealing rate, giving rise to a pseudo-plateau. Examples of this type of behaviour can be found in the work of Maddock et al, 53, and Bell and Herr, 42. The order of the thermal annealing reaction is still undecided. Maddock and Apers, 54, derived zero order for the annealing reaction, Shankar et al, 20, first order and Harbottle and Sutin, 14, bimolecular kinetics. It appears that different mechanisms operate in different systems.

Various workers, 19, 21, have suggested the participation of electrons, and defects which act as electron traps, in thermal annealing of transition metal complexes. A model for thermal annealing was proposed by Shankar et al, 55. Defects are produced in the lattice by gamma radiation and fast neutrons in the reactor, and also by fragmentation and Auger emission in the path of the recoil atom. These defects together with those already present in the crystal,

form traps for electrons in the lattice. In annealing electrons are released from the traps, with half-times dependent on the trap depths, to take part in the annealing process.

In many experiments neutron irradiated solids have been annealed using gamma radiation. The extent of annealing depends on the gamma dose rate and the time of irradiation. It is generally agreed that gamma annealing is an electronic process as suggested by Maddock and Müller.⁵⁶ Several mechanisms are possible; local hot-spots may be produced by secondary electrons in which the various molecular and recoil fragments can react. Alternatively, gamma radiation may re-excite the recoil fragments which can then combine with each other.

During neutron irradiation, samples will undergo a certain amount of thermal and gamma annealing, dependent on the temperature and gamma dose rate in the reactor at the time of irradiation.

Several other methods of annealing besides thermal and gamma annealing can be applied but their use has been more limited. The effect of compression on irradiated solids was noted by Andersen and Maddock,⁵⁰ They found that a threshold pressure existed, below which annealing would not occur, and above this the increase in retention varied linearly with the logarithm of the pressure. Other less common methods of annealing are irradiation using ultra-violet and visible light,^{51, 57} and ultrasonic radiation,⁵⁸

3-7 Szilard-Chalmers reaction in ammine complexes of
cobalt(III), rhodium(III) and iridium(III).

Szilard-Chalmers reactions in transition metal complexes, where the recoil atom is the central metal or one particular ligand, are more easily studied when atoms of the remaining ligands do not suffer recoil. Ammine ligands, being composed of carbon, nitrogen and hydrogen are ideal for this purpose, because of the low cross sections of these atoms for neutron capture. The range of stable ammine complexes of transition metals is wide, and in general they are easily prepared.

Ammine complexes of cobalt in particular have been extensively studied, mainly because of their ease of preparation, and, provided the irradiation dose is large enough, the distribution of the recoil cobalt-60 can be determined. Harbottle, 19, examined the distribution of cobalt-60 recoil species in the products of the neutron irradiation of several nitrateammine complexes of cobalt(III) using paper electrophoresis as a means of separating the products. The products were identified by comparing their migration distances with those of prepared complexes, labelled with cobalt-60. As an example of the type of complex ions formed, the results for irradiated $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ are given in table 3-2. The significance of Harbottle's results, and also those of Yasukawa, 26, on similar compounds has already been discussed in considering ligand effects, p.18. The presence of NO_2^- must be due to reduction of NO_3^- in the hot-zone. Species

TABLE 3-2

Percentages of ^{60}Co -labelled species after dissolution of
irradiated hexaamminecobalt(III) nitrate as determined by
G.Harbottle, 19.

Products	Percentage
cis- & trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	0.5
unknown	0.7
Co^{2+}	22.4
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$	1.4
$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$	18.2
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	0.9
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	5.2
$[\text{Co}(\text{NH}_3)_6]^{3+}$	48.8

such as $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ must arise from the interaction of ligand deficient ions e.g. $[\text{Co}(\text{NH}_3)_5]^{3+}$ with water on dissolution.

To determine the extent of the role played by the solvent, Stucky and Kiser, 29, dissolved irradiated $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ in non-aqueous solvents, such as N,N-dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO), before electrophoretic analysis. They found larger retention values using these solvents than when using water and attributed this to the lesser extent of solvation or redox reactions occurring in these media. In addition they found that the distribution of products depended on the pH of the electrolyte used. (This was in agreement with the results obtained by Shankar and Shankar, 28, on the effect of electrolyte pH on the product distribution in neutron-irradiated $\text{NaCo}(\text{III})\text{EDTA}$.) At pH 3 and pH 5.4 cationic species predominated, whereas at pH 10 most activity was found in anionic form.

Most of the cobalt complexes formed with NO_2^- and NH_3 as ligands have been studied by Saito et al, 59. In particular they investigated the effects of neutron-irradiation on cis- and trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$. In contrast to other works on geometric isomers they found that an appreciable amount of the cobalt-60 activity was in the other isomeric form. For irradiated cis- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$, 20.5% of the cobalt-60 activity was in the cis- form and 11.9% in the trans- form. In addition they showed that, the ratio of the initial yield of products

containing one more anionic ligand than the target complex, to that of the radioactive parent complex, increased with the positive charge on the original complex ion.

Maddock et al, 53, suggested that the results of Saito et al, given above might be uncertain because of impurities in the original complex salts. They studied the thermal annealing behaviour in several nitroamminecobalt(III) complexes. The outstanding results of their work are as follows. In annealing the re-attachment of ligands is not sequential, but cobalt(III) ion is converted to the parent molecule by what appears to be a one-step process. Relatively little stereospecificity was found for cis- and trans- isomers, in agreement with Saito's work. To interpret the one-step annealing process, Maddock et al suggested that the cobalt atom returns to a more or less empty octahedral array of ligands, which they called the 'cavity complex'. This ligand arrangement will present a low activation energy to ligand re-arrangement and hence non-stereospecificity can be explained.

It should be noted in this section that the work of Lazzarini on the isomeric effect in cobalt(III) complexes was carried out almost entirely with various ammine complexes, because such a large variation of ligand field can be obtained using ammonia and ethylenediamine in conjunction with other ligands.

Complexes of cobalt(III) containing chelating amine ligands have not been studied as extensively as those with simple ammonia ligands. Rauscher et al have investigated

the radiocobalt and radiochlorine distribution in neutron-irradiated cis- and trans- $[\text{Co}(\text{en})_2\text{X}_2]\text{NO}_3$, 17, 18. Most of the product was in the form of cobalt(II) ion and there was very little change in isomeric form. Radiative annealing of cis- and trans- $[\text{Co}(\text{en})_2\text{X}_2]\text{NO}_3$, where $\text{X} = \text{Cl}$ or Br , by Dimotakis and Maddock, 60, showed that the trans- salts were fairly resistant to gamma radiolysis while the cis- salts readily decomposed.

The (n,γ) reaction in cobalt(III) and rhodium(III) complexes with tetradentate ligands has been studied by Gardner et al, 61, using cis- and trans- dichlorotriethylene-tetraminecobalt(III) chloride and the corresponding cis-rhodium salt. A higher retention value was observed for the trans-complex than for the related cis-complex, which might be regarded as tenuous support for the 'cavity complex' theory.

Very little detailed work has been done with rhodium(III) and iridium(III) complexes. The only publication of note is that of Schmidt, 62, on recoil reactions in bromopentamminerhodium(III) nitrate and chloropentaammineiridium(III) chloride. The product distribution was determined by paper electrophoresis, using the radiobromine activity in the case of the rhodium complex and radioiridium activity in the case of the iridium complex. The electropherograms obtained using an acetate buffer solution ($\text{pH} = 5.4$) as electrolyte, are shown in figures 3-2 and 3-3. Both complexes showed only small retention values, 5% for the rhodium complex and 3.8% for the iridium complex. By

FIGURE 3-2

Paper electrophoretic separation of ^{82}Br recoil products
in neutron-irradiated $[\text{Rh}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ as determined
by G.B.Schmidt, 62.

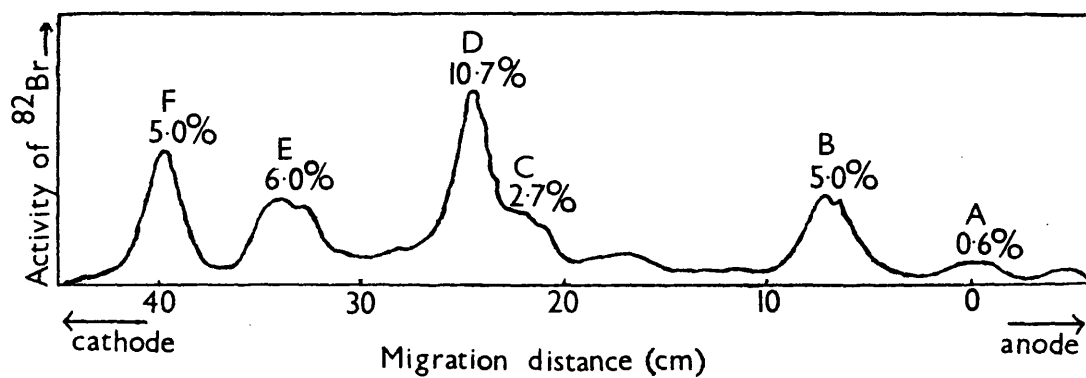
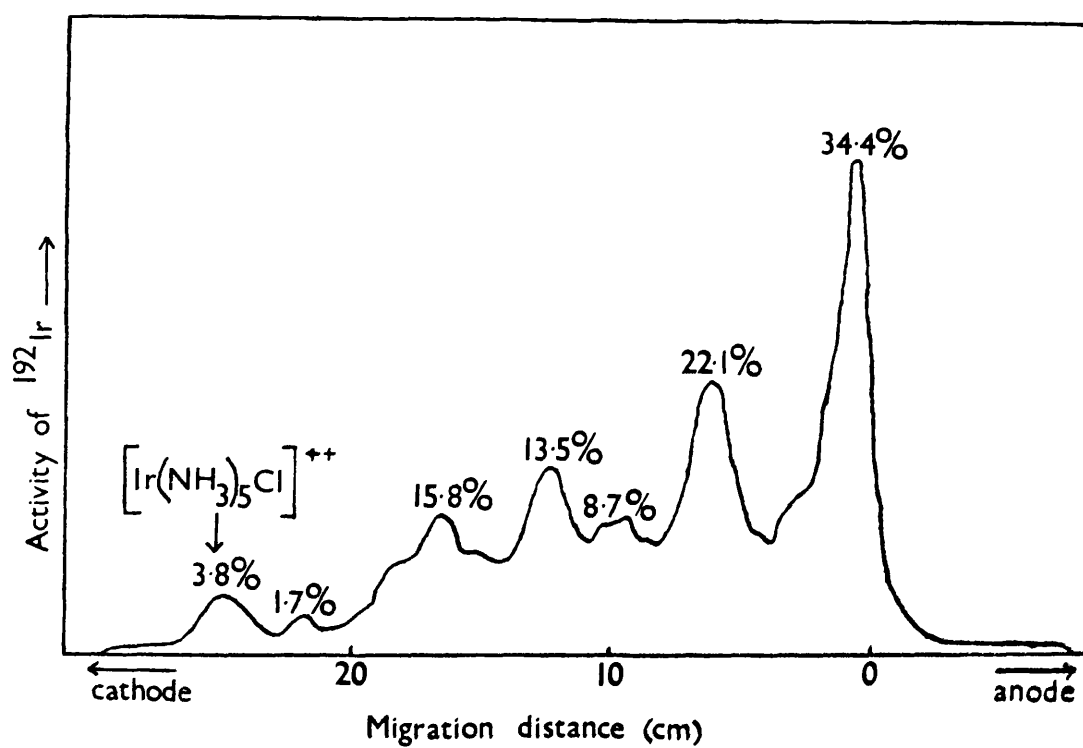


FIGURE 3-3

Paper electrophoretic separation of ^{192}Ir recoil products
in neutron-irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as determined by
G.B.Schmidt, 62.



preparing labelled complexes, Schmidt was able to identify three of the rhodium species as $A = [\text{Rh}(\text{NH}_3)_3\text{Br}_3]$, $D = [\text{Rh}(\text{NH}_3)_4\text{Br}_2]^+$ and $F = [\text{Rh}(\text{NH}_3)_5\text{Br}]^{2+}$. For the iridium complex only the parent ion could be identified in this way. However, Schmidt did suggest that the neutral iridium species could be some form of oxyhydrate.

CHAPTER IV

Aims of Research

The work carried out to date on the chemical effects of nuclear transformations has been primarily concerned with the fate of the recoil atom itself. Macroscopic effects in the solid as a whole have not usually been considered. Knowledge of the processes which occur in molecules, whose atoms do not suffer recoil themselves, as a result of the transfer of energy from the recoil atom would be useful in understanding the principles of recoil behaviour. This macroscopic effect can be investigated by isotopic labelling prior to irradiation and study of the change in distribution of the radioisotope caused by neutron bombardment.

In studies of transition metal complexes the effect of ligand variation on the distribution of recoil metal atoms has been the most common system for investigation. The fate of recoil ligand atoms has also been considered. However, the effect of varying the central metal atom while the ligand arrangement is unchanged has not been investigated.

It is the aim of this research to study these two, hitherto neglected, aspects of recoil chemistry: the macroscopic effect and the effect of metal atom on product distribution. Complexes with ammonia and ethylenediamine ligands have been chosen, as the constituent atoms, nitrogen carbon and hydrogen have low cross sections for thermal neutron capture. In most cases the complexes are easy to prepare and a wide range of such complexes can be obtained.

The central metal atom will be varied through the group cobalt, rhodium, iridium. In order to study the macroscopic effect the fate of one of the ligands will be determined. Chloride ligand, isotopically labelled with chlorine-36 has been chosen for this purpose. Chlorine nuclei will suffer Szilard-Chalmers recoil on neutron capture and this must be considered in analysis of the results. Chlorine-36 is a convenient tracer for chlorine ligands as it has a long half-life (3.03×10^5 years) making decay corrections unnecessary. Chlorine-36 is a pure beta emitter allowing the activity to be measured using a Geiger-Muller counter. The amount of radiolabelled chlorine in the form of free chloride ion can be measured by precipitation of silver chloride. When the time of irradiation is short, the macroscopic effect can also be studied, in cobalt complexes by labelling with cobalt-60 (half-life 5.2 years) prior to irradiation. Labelling of iridium complexes with iridium-192 cannot be used to study macroscopic effects as a large amount of the isotope is produced by the (n, γ) reaction and masks any iridium-192 introduced before irradiation.

The following complexes have been selected for this research:

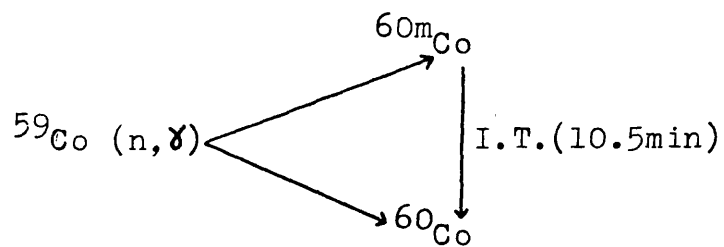
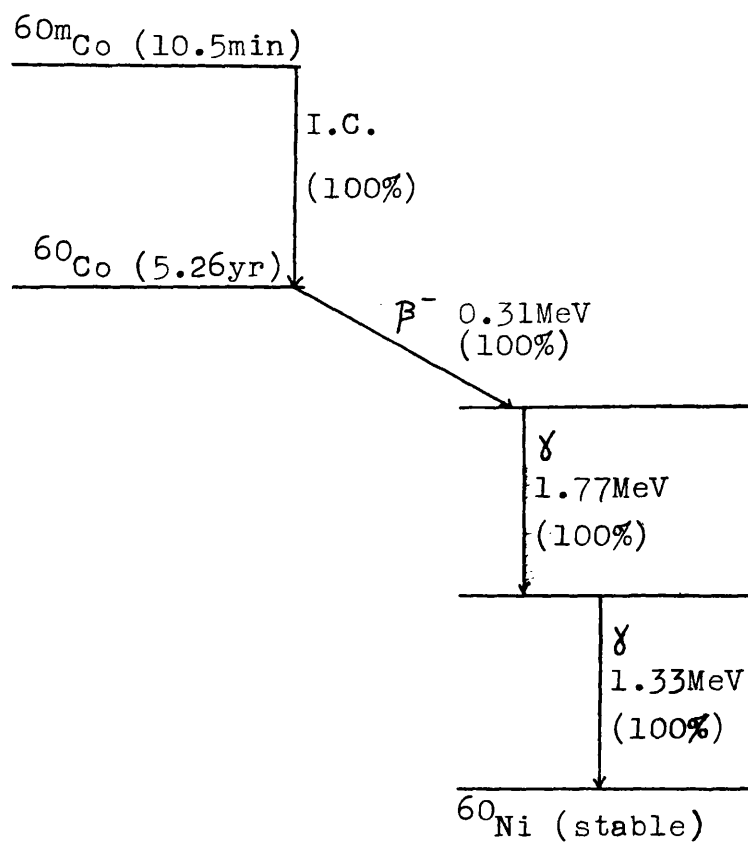
- a) $[M(NH_3)_5Cl]Cl_2$
- b) trans- $[M(NH_3)_4Cl_2]Cl$
- c) trans- $[M(en)_2Cl_2]Cl$

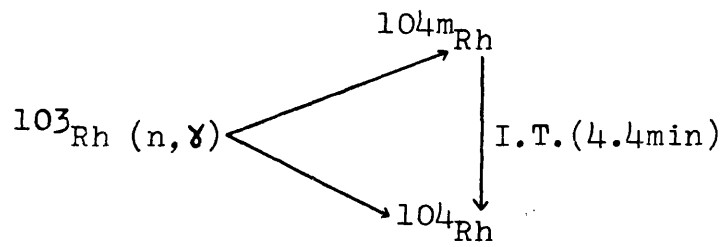
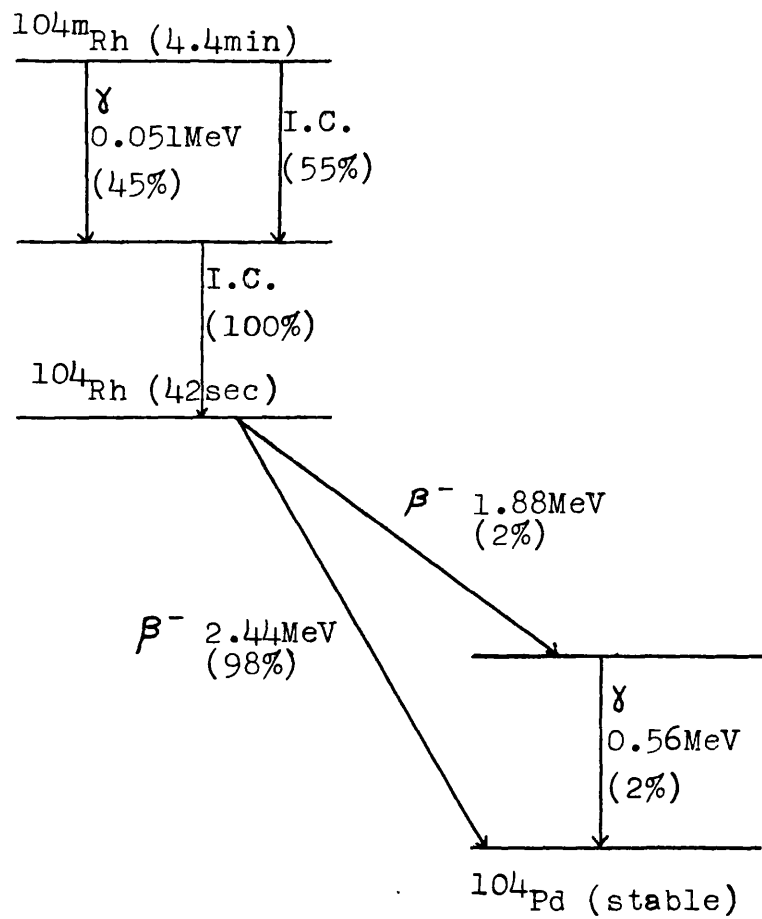
where (en) = ethylenediamine and M is cobalt(III), rhodium(III) or iridium(III). The trans complexes were chosen because they can be prepared more easily and in higher purity than

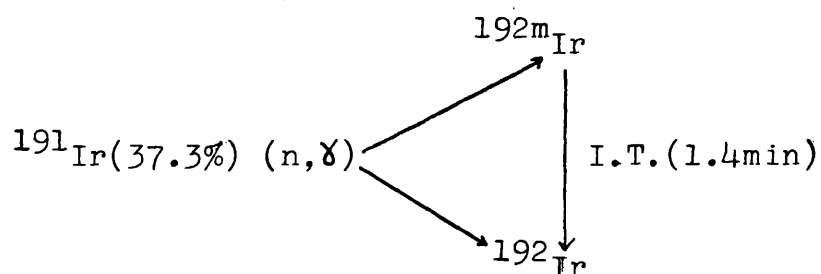
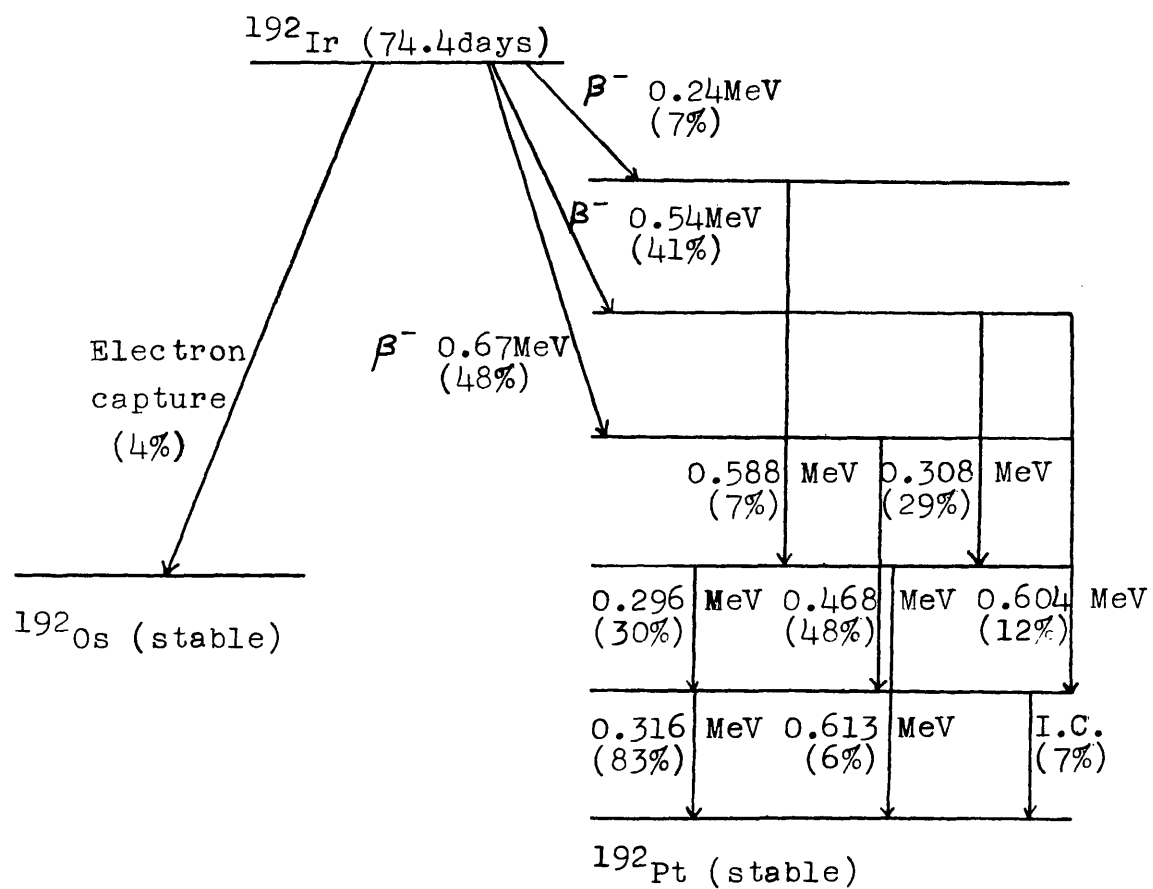
the cis- complexes. Their rate of hydrolysis in aqueous solution is slower, which makes labelling with chlorine-36 easier. Also, the trans- isomers are usually more resistant to gamma radiolysis.

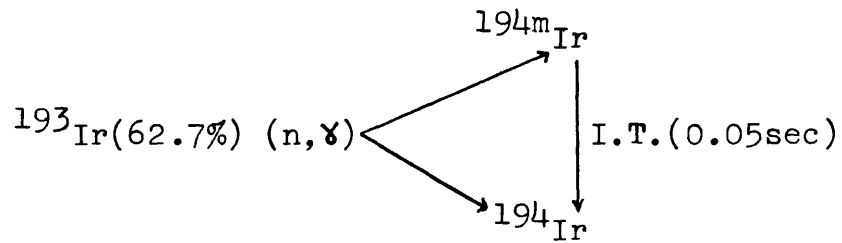
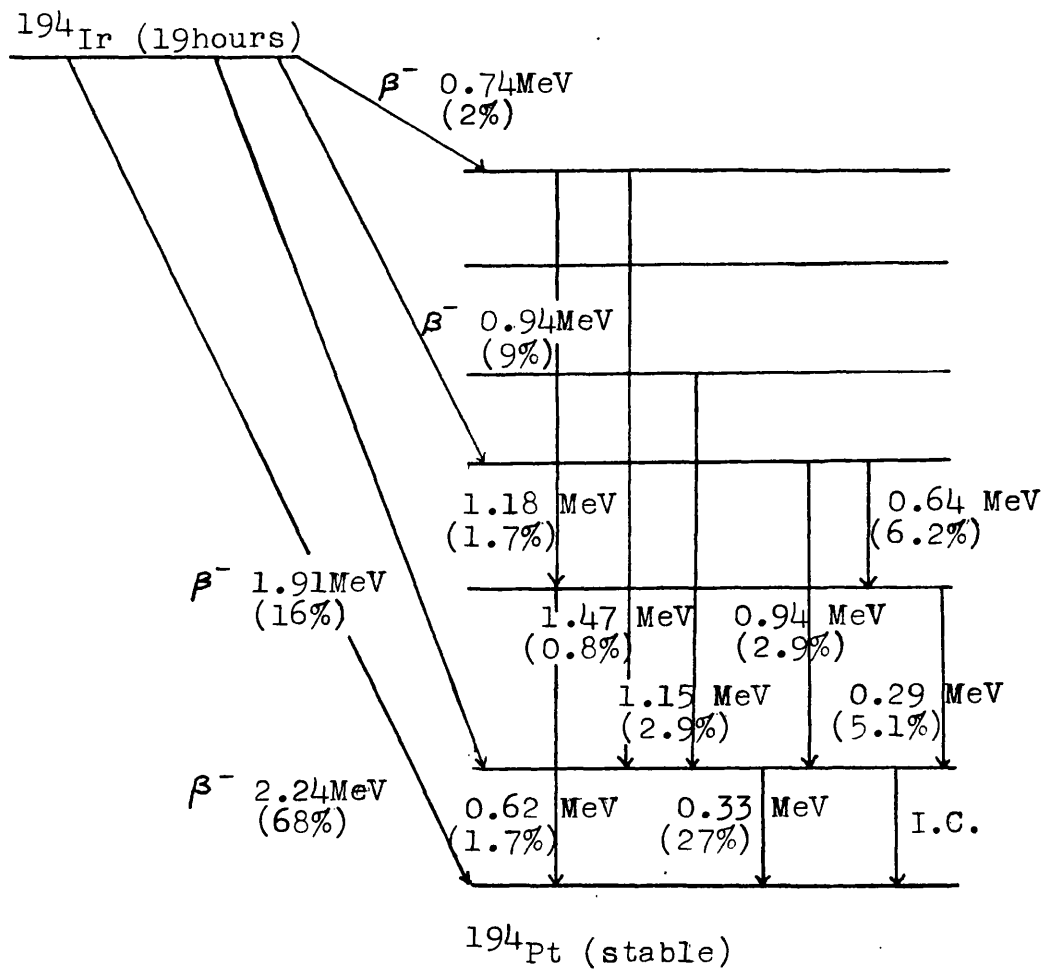
The object of this research is to label the complexed chloride with chlorine-36, and, in some cases, the cobalt atoms with cobalt-60; subject the complexes to neutron bombardment when Szilard-Chalmers recoil of some of the metal atoms will occur; and to study the fate of the labelled chloride or cobalt. Where sufficient activity is produced in the metal atoms by the (n, γ) reaction and the half-lives of the resulting nuclei are suitable, the distribution of recoil products can be studied by conventional electrophoretic techniques. Recoil iridium can be detected as the iridium-192 isotope, half-life = 74.4 days. For higher neutron doses, cobalt-60 recoil products can also be detected but for rhodium the half-lives of the isotopes formed, rhodium-104 and rhodium-104m are short and recoil rhodium atoms cannot be detected.

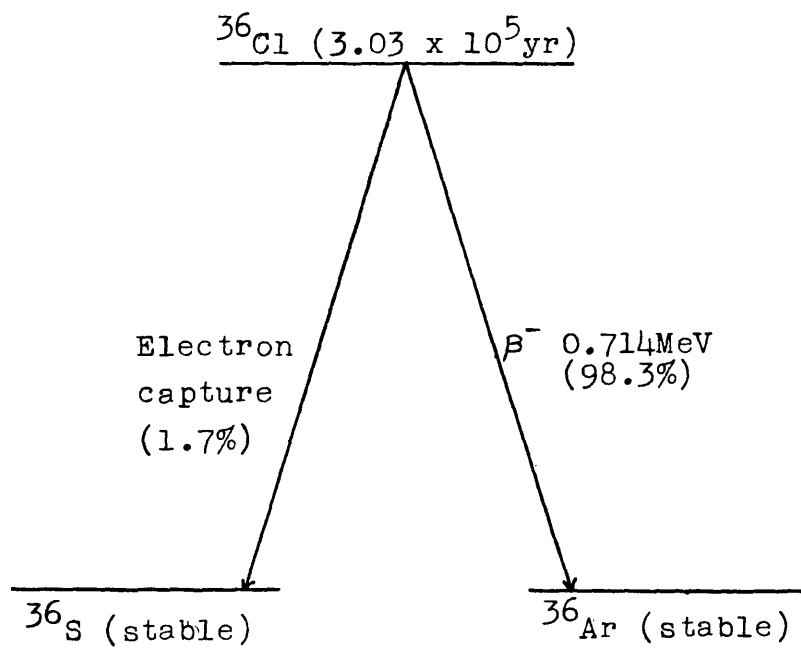
The decay schemes for the isotopes produced in the (n, γ) reaction and that of chlorine-36 are given overleaf.

COBALT-60Thermal neutron reactionDecay scheme

RHODIUM-104Thermal neutron reactionDecay scheme

IRIDIUM-192Thermal neutron reactionDecay scheme

IRIDIUM-194Thermal neutron reactionDecay scheme

CHLORINE-36Decay scheme

CHAPTER V

Experimental

5-1 Methods available for analysis of irradiated complexes

In the past several different techniques have been employed for analysis of product distribution following the (n,γ) reaction. The majority of these have involved dissolution of the solid in water, or some other solvent, prior to analysis. The most widely used technique for transition metal complexes has been paper electrophoresis. In this process the complex ions are separated by migration in an electric field, 63. A strip of filter paper soaked in electrolyte acts as the stationary phase, and the electrolyte solution through which the current flows as the mobile phase. The migration rate of the ions is dependent on two opposing forces; the electrical potential which is the driving force and the resisting forces inherent in the medium. The rate and direction of migration of an ion depend on the size and sign of its charge and on the size of the ion itself. The resisting forces are dependent on the viscosity of the electrolyte, the electrolyte concentration and the extent of adsorption of ions on to the paper strips. These resisting forces are generally small but, together with the dependence of migration rate on ion size, they destroy the linear relationship which would otherwise exist between rate of migration and charge on the ion. Provided voltage, time of electrophoresis, temperature and electrolyte concentration are constant a given ion will

always migrate the same distance, and an ion can generally be identified by its migration distance. This method was first used to study recoil products in 1951, 64. It is suitable for this type of work as even small percentages of radioactive products can be identified, using microgram samples of the solid, by comparing the distance of migration of the unknown ion with that of labelled complex ions prepared for this purpose, 65. Electrophoresis has been used successfully by many workers, for example by Bell and Herr, 42, and Cabral, 43-45, to study recoil products of hexachloroiridates, and by Schmidt, 62, in the investigation of the (n,γ) reaction in ammine complexes of rhodium and iridium. Provided the voltage gradient is small enough, even species of the same charge and very similar size can be separated, as can be seen from the results of Müller, 24, (figure 3-1). More recently, paper chromatography and thin-layer chromatography have been used, 29, in conjunction with paper electrophoresis in the analysis of recoil products in several cobalt(III) complexes. These methods can also be used on a microanalytical scale.

Other solution methods of analysis such as ion exchange, 20, 26, 29, solvent extraction, 20, 26, 32, 48, and precipitation, 41, require larger amounts of irradiated solid for analysis. Also it is not always possible to separate all the recoil products using these methods but they have proved effective in some cases, when only one species is to be estimated. For example, Lazzarini, 32, used solvent extraction to isolate the radioactive parent

ion in his work on the retention ratio of cobalt-60m to cobalt-60g in irradiated cobalt(III) complexes. It must be noted that all these solution techniques suffer from the fact that some of the species observed may be formed by interaction of fragments in the lattice with solvent molecules. The extent of the solvent effect can be estimated by dissolving the solid in various solvents and noting any change in distribution, 29, but it cannot be eliminated.

In this research, where all species are to be detected, paper electrophoresis has been employed. Where only the fate of the chloride ligand is sought, precipitation and ion exchange techniques have been used.

5-2

Preparation of complexes

The following complexes were prepared by methods given in the literature:

<u>Complex</u>	<u>Reference</u>
Chloropentaamminecobalt(III) chloride	66
Transdichlorotetraamminecobalt(III) chloride	67
Transdichlorobisethylenediaminecobalt(III) chloride	68
Chloropentaamminerhodium(III) chloride	69
Transdichlorotetraamminerhodium(III) chloride	69
Transdichlorobisethylenediaminerhodium(III) chloride	69
Transdichlorobisethylenediamineiridium(III) chloride	70

Chloropentaammineiridium(III) chloride andtransdichlorotetraammineiridium(III) chloride

2g of ammonium hexachloroiridate and 25cm³ of .880 ammonia were heated in a stainless steel pressure vessel with a glass liner at 120°C for six hours. After evaporation of excess ammonia, a whitish precipitate of $[\text{Ir}(\text{NH}_3)_3\text{Cl}_3]$ formed which was filtered off. Acidification with 2cm³ of concentrated hydrochloric acid followed by slow evaporation gave yellow crystals. These were filtered off and extracted with 3N hydrochloric acid which dissolved the tetraammine, $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. The residue, $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, was recrystallised from hot water, washed with ethanol and dried at 110°C. The tetraammine was obtained by evaporating the acidic solution to crystallisation, when the product was filtered off and purified in the same way as the pentaammine.

Transdichlorobisethylenediamineiridium(III) chloride

Several methods were used to try to prepare trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$. The preparation of both cis- and trans- complexes was published in 1966 by Kida, 71, but all attempts to repeat the synthesis failed. A preparation using elevated temperature and pressure, similar to that used for the amines was also tried but the yields obtained were very small. However, in 1969 a method of preparation was published by Basolo and Bauer, 70, and this was used successfully.

5-3Analysis of complexes

All the complexes prepared were analysed by Yarsley Testing Laboratories. Nitrogen was determined by the Dumas method and chlorine by the Schöniger method. The results are given in table 5-1.

5-3-1Infra-red spectra

The near infra-red spectra (400cm^{-1} to 4000cm^{-1}) of the complexes were recorded using the Perkin-Elmer 337 Grating Infra-red Spectrophotometer. The complexes were incorporated in potassium bromide discs for the purpose. The spectra obtained were compared with those given in the literature, 70-73. The infra-red spectra were particularly valuable in identification of cis- and trans- isomers. Morris and Busch, 73, showed that in diacidobisethylene-diaminecobalt(III) complexes, the trans- isomer has one strong absorption band at 1600cm^{-1} while for the cis- isomer this band is split into two. This also applies to the rhodium and iridium complexes. All of the ethylenediamine complexes prepared showed only one band at 1600cm^{-1} and were thus confirmed as trans- isomers.

These complexes have now been characterised by far infra-red spectroscopy, using the R.I.I.C. Interferometer type No. F.S.720 at the Physico-Chemical Measurements Unit, U.K.A.E.A., Harwell, 74.

TABLE 5-1Results of nitrogen and chlorine analyses

Complex	Nitrogen		Chlorine	
	Found	Calculated	Found	Calculated
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	28.13	27.96	42.07	42.46
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	25.44	23.98	44.31	45.61
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	20.13	19.61	36.90	37.25
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	21.22	23.79	34.85	36.12
$[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	18.31	20.19	39.16	38.41
$[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$	16.22	17.00	32.97	32.28
$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	17.32	18.24	26.94	27.71
$[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	14.98	15.27	28.32	29.05
$[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$	12.53	13.37	24.74	25.39

5-3-2Molar conductivity measurements

For $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{trans-}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, molar conductivities were measured using a Wayne Kerr Universal Bridge B221. 0.01M potassium chloride solution was used to determine the cell constant. The molar conductance of a complex is dependent on the number of ions the complex dissociates into in solution. The relationship can be summarised as follows:

<u>Number of ions</u> <u>in solution</u>	<u>Molar</u> <u>conductivity</u>
1	Approx.0
2	Approx.100ohm ⁻¹
3	Approx.200-250ohm ⁻¹
4	Approx.350ohm ⁻¹

The molar conductance of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was found to be 265ohm⁻¹, confirming that three ions are formed in solution, while that of $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ was 97ohm⁻¹, corresponding to only two ions in solution.

5-3-3Crystal structure

The detailed crystal structures of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ have been determined by Olovsson, 75. Both have a distorted K_2PtCl_6 structure. The structure of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ has not been published.

Powder photographs of the three pentaammine complexes were measured by the X-ray Crystallography Section of the Solid State Chemistry Group, U.K.A.E.A., Harwell. All three photographs showed the same basic line arrangement. It thus appears that $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ has the same type of structure as the cobalt and rhodium pentaammines.

5-4

Isotopic labelling of complexesLabelling with chlorine-36

All the complexes were labelled with chlorine-36. It was intended to have only the complexed chloride labelled in this way but a proportion of the radioactive isotope was always found as anionic chloride, and for complexes where the rate of isotopic exchange was rapid e.g. in the cobalt complexes, this proportion was fairly high. Because of the varying stability of the complexes with respect to hydrolysis by water and acids, different methods of labelling had to be employed.

Cobalt(III) complexes

The following method was used for $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and trans- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$. 20mg of the complex was dissolved in 15cm³ of water and dilute hydrochloric acid labelled with chlorine-36 (about 10 μ Ci) added. After heating on a steam bath in a closed vessel for one hour and cooling to 0°C, the solution was passed through an anion exchange column of de-acidite FF in the chloride form to exchange active chloride ions for inactive ions. The water was then removed from the solution by vacuum distillation at room temperature. The solid complex, labelled with chlorine-36 in the complex ion, was washed with ethanol and dried in a vacuum desiccator.

Trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ hydrolyses too rapidly for this method to be used. Chlorine-36 was therefore incorporated into the final stages of the preparation of the complex. 40mg of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3$ was dissolved in three drops

of concentrated sulphuric acid and the solution allowed to stand for 24hr. After cooling in ice an equal volume of concentrated hydrochloric acid was added, followed by 0.1cm^3 of 2N hydrochloric acid labelled with chlorine-36 ($10\mu\text{Ci}$). The solution was left for 48hr, when green crystals of trans- $[\text{Co}(\text{NH}_3)_4^{36}\text{Cl}_2]^{36}\text{Cl}$ formed, which were filtered off, washed with dilute hydrochloric acid, ethanol and ether, and vacuum dried. Anionic chlorine-36 could not be removed by ion exchange because of the rapid hydrolysis rate.

Rhodium complexes

All three rhodium complexes were labelled using the following method. 20mg of the complex was dissolved in the minimum volume of water and 0.1cm^3 of dilute hydrochloric acid labelled with chlorine-36 ($10\mu\text{Ci}$) added. The solution was heated on a steam bath in a closed vessel for three hours, cooled and passed through a column of deacidite FF, as for the cobalt complexes. It was then evaporated on a steam bath under reduced pressure using a sodium hydroxide trap to prevent radioactive HCl gas escaping. The concentrated solution was cooled when crystals of the rhodium salt labelled with chlorine-36 in the complex ion separated. These were filtered off, washed with ethanol and ether and dried in a vacuum desiccator.

Iridium complexes

The following procedure was used for all three iridium complexes. 20mg of the complex was dissolved in the minimum volume of water and 0.1cm^3 of 2N hydrochloric acid labelled with chlorine-36 ($10\mu\text{Ci}$) was added. After heating on a steam bath in a closed vessel for six days and cooling,

the solution was passed through a deacidite FF column to remove labelled chloride ions. After evaporation, crystals of the iridium salt labelled in the complex ion separated on cooling and were filtered off, washed with ethanol and ether and dried in a vacuum desiccator.

Labelling with cobalt-60 and iridium-192

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{trans}-[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ were labelled with cobalt-60 by adding a small amount of a solution of $^{60}\text{CoCl}_2$ (about $5\mu\text{Ci}$ of ^{60}Co) to the cobalt(II) chloride used as starting compound in the preparations. Similarly, all three iridium complexes were labelled with iridium-192 by adding labelled iridium compound (about $10\mu\text{Ci}$ of ^{192}Ir) to the starting compound. All five preparations were carried out on a smaller scale than the inactive preparations to obtain as high a specific activity in the products as possible. $\text{Trans}-[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ was not labelled with ^{60}Co as small scale preparation was found to be difficult, because of the number of stages involved, and the resultant specific activity was always too low.

5-5

Irradiation of samples

Samples of the labelled complexes were irradiated with thermal neutrons either in the reactor BEPO at A.E.R.E., Harwell or in the reactor HERALD at A.W.R.E., Aldermaston. The details of the irradiation conditions in the two reactors are given in table 5-2. (Irradiations in the BEPO reactor will be marked with an asterisk in the results section.) In most cases 2mg samples of each complex were

TABLE 5-2Irradiation conditions in the BEPO and HERALD reactors

	BEPO	HERALD
Thermal neutron flux	$1 \times 10^{11} \text{ n.cm}^{-2} \cdot \text{sec}^{-1}$	$2.4 \times 10^{11} \text{ n.cm}^{-2} \cdot \text{sec}^{-1}$
Fast neutron flux	$0.5-1 \times 10^{10} \text{ n.cm}^{-2} \cdot \text{sec}^{-1}$	0
Ambient temperature	$30^{\circ}\text{C}-40^{\circ}\text{C}$	45°C
Gamma dose rate	$1.5 \times 10^5 \text{ R/hr}$	$7 \times 10^4 \text{ R/hr}$

irradiated in small polythene snap-closure capsules which were heat sealed. Up to ten such capsules were placed in a standard aluminium can for introduction into the thermal column of the reactor. To begin with samples were irradiated in the BEPO reactor at a flux of $1 \times 10^{11} \text{ neutrons.cm}^{-2}.\text{sec}^{-1}$ for 10 hours. With the closure of this reactor in December, 1968, subsequent irradiations were done in the HERALD reactor. To compensate for the increase in flux to $2.4 \times 10^{11} \text{ neutrons.cm}^{-2}.\text{sec}^{-1}$ the time of irradiation was reduced to 4 hours 10 mins to give the same value of integrated thermal neutron flux as in the BEPO reactor. Duplicates of the samples irradiated in BEPO were irradiated using HERALD and the results, for the same integrated flux, were in good agreement. Later, all nine complexes labelled with ^{36}Cl were irradiated at flux $2.4 \times 10^{11} \text{ neutrons.cm}^{-2}.\text{sec}^{-1}$ for 41 hours 40 mins, ten times the previous integrated neutron flux. This integrated flux was increased by a further factor of ten, for the cobalt and rhodium complexes, by irradiation at the same flux for one week. The three iridium complexes were irradiated at this flux for 25 mins which corresponds to one tenth of the original integrated thermal neutron flux.

Non-irradiated samples of the complexes were stored at the approximate temperature of the thermal column for a time equal to that of the irradiation and otherwise at room temperature. Following irradiation the iridium complexes were stored for at least ten days, before analysis was begun, to allow iridium-194 activity to decay, thus reducing the amount of radioactivity to be handled.

5-6 Analysis of irradiated complexes5-6-1 Determination of chlorine-36 distribution

Following irradiation, 0.3-0.5mg sample of each complex was dissolved in 15cm³ of water. All irradiated samples were found to be completely soluble. The solution was acidified with 0.5cm³ of 2N nitric acid. 0.5cm³ of 0.1M hydrochloric acid was added as carrier for the chloride ions in the solution. The chloride ions were precipitated as silver chloride by addition of a slight excess of 0.1M silver nitrate solution. The precipitate was collected on a 2cm diameter Whatman No. 1 filter paper, using a Hartley funnel, and washed thoroughly with 0.01M nitric acid. The whole process, from dissolution of the sample to filtration of the precipitate, was carried out rapidly, generally in less than five minutes to reduce errors due to hydrolysis of species present in the irradiated complex to a minimum. These errors will be negligible for the iridium complexes as these are very stable to acid hydrolysis. However, small errors may occur for some of the rhodium complexes and, more especially, for some of the cobalt complexes, because of their more rapid rates of hydrolysis. After washing, the silver chloride precipitate was dried by continued suction. When dry, it was mounted on an aluminium planchet and covered with sellotape. The chlorine-36 activity detected in this sample will be due to chlorine-36 present as chloride ions in the irradiated sample. None of the complexed chlorine will be precipitated.

After removal of the silver chloride precipitate, the filtrate containing complex ions was made alkaline by the addition of an excess of 5% potassium hydroxide solution, causing the precipitation of excess silver ions as a basic complex which was removed by filtration. The alkaline solution was heated on a steam bath for three hours— six hours for the more stable iridium complexes — during which time complex ions were completely broken down by alkaline hydrolysis. Complexed chlorine was released as free chloride ions in the solution. After acidification with dilute nitric acid and addition of 0.5cm^3 of 0.1M hydrochloric acid, chloride ions were precipitated as silver chloride and the precipitate filtered, washed, dried and mounted as before. The chlorine-36 activity detected in this sample was that present as complexed chlorine in the irradiated complex.

0.3-0.5mg of the non-irradiated complex was analysed in exactly the same manner as the irradiated sample to determine the changes brought about by irradiation. Each analysis was repeated a number of times to ensure reproducibility of results.

5-6-2

Counting methods

The activity of each silver chloride precipitate was measured using an end-window Geiger-Müller tube (type MX-123) mounted in an ERD square lead castle. The counts were recorded on a Panax scalar unit. Normally at least 10,000 counts were recorded in order to reduce the statistical error to $\pm 1\%$. The counts per minute recorded were corrected

for background and dead time. Errors due to self-absorption in the sources were eliminated as all were of the same thickness. This was achieved by always adding the same volume of carrier hydrochloric acid which gave rise to the bulk of the precipitate. Samples of silver chloride obtained from irradiated iridium samples could be contaminated with iridium-192. These precipitates were also counted using a well-type scintillation counter. As iridium-192 is a gamma emitter it would be detected by this method, while chlorine-36, a pure beta emitter would not. Thus if no counts were recorded using the scintillation method, the source was free of iridium-192 contamination.

In some cases, particularly for irradiated trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$, great difficulty was found in removing iridium-192 from the silver chloride precipitates by washing. Another method had to be found for effecting the separation of free chloride ions and complexed chloride. Results obtained by electrophoretic methods (given later, table 6-12) suggested that a large proportion of radioactive iridium was present in anionic forms in irradiated samples of trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$, and it seemed likely that these complex anions also formed insoluble silver salts. To overcome the difficulty an ion exchange method was developed. The irradiated complex was dissolved in water and passed through a cation exchange column of Zeocarb-225 resin in the sodium form. Cationic iridium species were retained by the resin while anionic species and chloride ions were eluted with water. The eluant was passed through an anion

exchange column of deacidite FF resin in the nitrate form. Iridium anions were absorbed but as nitrate ions are more strongly held than chloride ions the latter were eluted with water. The free chloride ions in the eluant were precipitated as silver chloride using the method already described and the activity measured. Both the anion and cation exchange columns were eluted with 1:1 concentrated nitric acid:water mixture to remove iridium species. The elution was continued until no more activity remained on the resin. The eluants were combined, made alkaline with potassium hydroxide solution and heated on a steam bath for six hours to break up the complex ions. After acidification, silver chloride was precipitated, collected and its activity measured as described above. Non-irradiated trans- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ was analysed by both the simple precipitation method and the ion exchange method and the same results were obtained in both cases.

5-6-3

Paper electrophoresis

An LKB 3276B paper electrophoresis apparatus was used for all the analyses. The support media were Whatman No.1 paper strips. Each strip was soaked in electrolyte and the excess solution squeezed out. Two strips were placed in the cassette of the apparatus at a time, with equal parts of each end dipping into the electrolyte baths, each containing 900cm^3 of electrolyte. As the electrolyte level was the same in either bath, there was no flow of electrolyte through the paper strips due to hydrostatic

pressure. One bath contained the anode and the other the cathode of the power unit. Approximately 5-10 of the radioactive solution to be analysed was placed at the centre of each strip. A potential difference of 250volts was for a fixed time; two hours for iridium samples and one and a quarter hours for the cobalt samples. The horizontal length of each paper strip was 28cm so that the potential gradient was about 9volts/cm. After electrophoresis, the strips were removed from the apparatus and dried in a horizontal position.

The position of the radioactive material on the paper strip was detected in two different ways. Firstly, the site of the iridium-192 or cobalt-60 activity was determined by a counting method. This was generally done by cutting the dried paper strip into sections 1cm in width and mounting each section on an aluminium planchet to ensure consistent counting geometry. The activity of each section was then measured using an end-window Geiger-Müller tube (type MX123) mounted in a square lead castle. A histogram was plotted using the corrected counts obtained and from this the percentage of each of the recoil species was determined by measuring the area under each peak. The activity of each section could be determined with reasonable accuracy by counting for a suitable length of time. In most cases 10,000 counts were recorded (error $\pm 1\%$) but for some of the smaller peaks only 1,000 counts were recorded (error $\pm 3.2\%$).

The second method used for locating radioactive species

was by autoradiography. The electropherogram was covered with a strip of X-ray film (Industrial G) and left for a suitable exposure time. The whole process was carried out in darkness and, after developing, black spots on the film showed the position of the recoil species. This method was used as a check of the migration distances found by the counting method.

The reproducibility of the electrophoretic method had to be established before it could be used to analyse irradiated samples. In most cases the ions studied were octahedral complexes of iridium, rhodium and cobalt, and therefore significant changes in the size and the shape of the ions were ruled out unless the size of the ligands varied considerably. The concentration of electrolyte used was always the same and therefore the viscosity was constant. The extent of adsorption of ions by the paper strip was investigated using a solution of $[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as sample and 0.01M perchloric acid electrolyte. Electrophoresis was carried out for a set time after which the electrodes were reversed and the current passed in the opposite direction for the same time. At the end of the experiment the activity was found to be still concentrated at one spot showing adsorption effects to be small. However, the spot did not return exactly to the point of application but appeared to have travelled further in the second time interval. This was due to a slight increase in current with time because of slow evaporation of water from the electrolyte solution. This suggests that migration of

a particular ion does not vary linearly with time. For this reason the time of electrophoresis was made exactly the same for a given series of compounds, as extrapolation of results would not be possible. The extent of diffusion processes was also investigated. A spot of labelled iridium complex solution was applied to the paper strip and the apparatus left with no potential difference applied for two hours. The paper was dried and the activity was found to be still centred at the origin although the size of the spot had increased. Thus, diffusion of ions would have little effect on the rate of migration but would decrease the resolution slightly. It was concluded from these results that provided voltage, time and electrolyte concentration were kept constant, the distance of migration of ions would be comparable.

Paper electrophoresis was carried out using various electrolytes. For all complexes, 0.01M potassium perchlorate solution (pH 6.8) and 0.01M perchloric acid (pH 2.2) were used. The perchlorates were chosen because the perchlorate ion is unlikely to form complexes with species present in the irradiated solid. 0.01M ammonium perchlorate solution and 0.01M potassium hydroxide solution were also used for $[^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 4hr 10min in the HERALD reactor.

The non-irradiated labelled complexes, $^{60}\text{Co}^{2+}$, $[^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[^{60}\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, $[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[^{192}\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, and $[^{192}\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ were analysed by paper electrophoresis alongside the irradiated complexes to aid in the identification of recoil species formed.

A sample of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated in the HERALD reactor for 4hr 10min was stored at room temperature for about six times the half-life of iridium-192 i.e. about 15months, until most of the activity in the sample had decayed. Paper electrophoresis was then carried out on this sample using two paper strips and 0.01M perchloric acid electrolyte. The strips were dried and enclosed in cellophane. One strip was re-irradiated at a neutron flux of $2.4 \times 10^{11} \text{ neutrons.cm}^{-2}.\text{sec}^{-1}$ for 4hr 10min to reactivate the iridium atoms absorbed on the paper. The other strip was kept as a control. The irradiated strip was stored for ten days to allow iridium-194 to decay. Both strips were cut into 1cm sections and counted as previously described. By this method, it was hoped to determine the macroscopic distribution of iridium containing species in the irradiated sample as opposed to the distribution of recoil iridium, which was determined by the standard electrophoretic method.

5-6-4

Formation of sulphur-35

Sulphur-35 formed by the (n,p) reaction of chlorine-35 was present in small amounts in the irradiated samples. Its presence was established by measuring the beta absorption curves of some of the irradiated complexes. For all Geiger-Müller counting a 40mg.cm^{-2} aluminium absorber was placed between the source and the counter window to cut out the low energy beta particles of sulphur-35.

5-6-5Infrared spectroscopy

60mg of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was irradiated at thermal neutron flux of $2.4 \times 10^{11} \text{ neutrons.cm}^{-2}.\text{sec}^{-1}$ for 41hr 40min. The near infrared spectrum of the complex was measured as described in section 5-3-1. The far infrared spectra, of the irradiated and non-irradiated complex, from 40cm^{-1} to 400cm^{-1} , were measured using the RIIC Interferometer type No.F.S.720 coupled with a wave analyser at the Physico-Chemical Measurements Unit, U.K.A.E.A., Harwell. The samples were incorporated into wax discs for these measurements. For comparison, the far infrared spectrum of rhodium trichloride was also recorded.

5-7Annealing

$[\text{}^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated in the HERALD reactor for 4hr 10min was annealed at a constant temperature of 100°C and samples were removed after seven hours and 18hours. These were analysed by both the precipitation and electrophoretic methods. The process was repeated using an annealing temperature of 150°C . (The complex decomposes at around 170°C , 76.)

$[\text{}^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated in the HERALD reactor for 4hr 10min was annealed at 150°C and 200°C . Samples were removed after 48hours and were analysed by both precipitation and electrophoretic methods.

5-8Crystal form

$[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared as large crystals by slow evaporation of a solution of the complex. Another sample of $[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared in fine powder form by rapid cooling of a hot saturated solution. Both samples were irradiated in the HERALD reactor for 4hr 10min and were then analysed by paper electrophoresis.

5-9Mixed crystals

In order to determine the importance of the density of hot-zones produced in the solid lattice, mixed crystals of each of the three pentaammine complexes, labelled with chlorine-36, with ammonium chloride were prepared. 5mg of the complex and 1g of ammonium chloride were dissolved in the minimum volume of hot water and the solution cooled when mixed crystals separated. This 0.5% concentration of complex was found to be the highest obtainable in mixed crystal form. At higher concentrations complex and ammonium chloride crystallised separately. The mixed crystals were filtered off, washed with ethanol and ether and dried in a vacuum dessicator. Ammonium chloride was used as the diluent because of its ability to form mixed crystals with the complexes and because of the low cross section of the ammonium group atoms to thermal neutron capture. 150mg samples were irradiated with thermal neutrons in the HERALD reactor for 4hr 10min and then analysed for chlorine-36 distribution by the precipitation method. Addition of carrier hydrochloric acid was not necessary

because of the high proportion of chloride ions in the samples. The irradiated samples were found to be more radioactive than expected. A beta absorption curve showed that the bulk of the activity was due to sulphur-35. The amount of recoil sulphur was high in this case because of the large proportion of chloride in the samples. (In a 150mg sample, around 100mg was made up of chloride.) The beta radiation emitted by sulphur-35 could be cut out using a 40mg.cm^{-2} aluminium absorber. However, when this was done, the count rate of the chlorine-36 was very low. This is not surprising since the presence of a large excess of unlabelled chloride ions in the ammonium chloride had reduced the specific activity of chlorine-36 almost to the limit of confident measurement. Introducing a 40mg.cm^{-2} absorber to cut out sulphur-35 reduced the count rate still further and made accurate determination of the chlorine-36 activity impossible. For this reason this method for studying the influence of hot-zone density was abandoned as impracticable.

CHAPTER VI

Results

6-1 Measurement of changes in chlorine-36 distribution

Table 6-1 gives the count rates for chlorine-36 activity in anionic and complexed forms in non-irradiated and irradiated complexes, measured with an end-window Geiger-Müller tube. Any activity due to sulphur-35 was cut out by a 42mg.cm^{-2} aluminium absorber, placed between the silver chloride source and the Geiger window. Gamma counting of the sources using a NaI crystal produced no count rate above background in any of the cases reported. Any sources which did show gamma activity were discarded and the separation repeated. The percentage of chlorine-36 in anionic and complexed forms was calculated from each pair of count rates. A mean value of two separately obtained results was taken and the resulting percentage distribution of chlorine-36 is given in table 6-2.

6-2

Errors

In the determination of chlorine-36 distribution by the precipitation and ion exchange methods, the errors involved can be divided into two types: a) errors which are inherent in the method of separation used and b) counting errors.

To consider the first type of error; in the precipitation method there will be a small error due to the slight solubility of silver chloride, even under the controlled

TABLE 6-1Corrected count rates of silver chloride sources from

Complex	Non-irradiated		Irradiated 25min.	
	Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	11375 1929	1357 297	- -	- -
$\text{tr}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	394 69	558 106	- -	- -
$\text{tr}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	3930 927	3618 909	- -	- -
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	3257 2686	409 367	- -	- -
$\text{tr}[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	284 283	115 116	- -	- -
$\text{tr}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$	196 860	46 232	- -	- -
$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	6486 3009	577 217	293 378	697 842
$\text{tr}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	179 146	42 29	32 76	338 711
$\text{tr}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$	642 512	70 51	59 64	523 665

complexed and anionic chloride.

Irradiated 4hr.10min.		Irradiated 41hr.40min.		Irradiated 1week	
Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl
865*	144*	120	246	20	492
3943	806	183	370	11	258
72	205	110	151	55	78
29	98	211	305	162	229
1788	1549	98	105	257	242
907	899	735	758	550	519
1461*	210*	1	374	21	398
795	142	0	208	7	238
480	221	430	182	884	443
184	89	137	59	1052	505
796	2740	226	273	120	874
631	1892	469	632	35	247
40	1226	-	-	-	-
144	1952	-	-	-	-
19	712	-	-	-	-
41	1468	-	-	-	-
14	130	-	-	-	-
27	255	-	-	-	-

TABLE 6-2Percentage distribution of chlorine-36 in complexed and

Complex	Non-irradiated		Irradiated 25min.	
	Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	88%	12%	-	-
$\text{tr}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	40%	60%	-	-
$\text{tr}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	50%	50%	-	-
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	89%	11%	-	-
$\text{tr}[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	71%	29%	-	-
$\text{tr}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$	80%	20%	-	-
$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	92%	8%	30%	70%
$\text{tr}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	82%	18%	9%	91%
$\text{tr}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$	90%	10%	10%	90%

anionic forms.

Irradiated 4hr.10min.		Irradiated 41hr.40min.		Irradiated 1week	
Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl	Complexed ^{36}Cl	Anionic ^{36}Cl
85%	15%	33%	67%	4%	96%
25%	75%	41%	59%	41%	59%
52%	48%	49%	51%	51%	49%
86%	14%	0	100%	4%	96%
68%	32%	69%	31%	68%	32%
76%	24%	44%	56%	12%	88%
5%	95%	-	-	-	-
3%	97%	-	-	-	-
10%	90%	-	-	-	-

conditions used. Much larger errors will arise in transferring the precipitate by filtration to form the solid source for counting. Where ion exchange is also involved in the separation, errors due to incomplete elution of each fraction from the column are also present. It is extremely difficult to decide the absolute values of these errors.

The errors in counting rate, due to the random nature of radioactive decay, are more easily estimated. If a series of counting rates are determined for a given radioactive source, the standard deviation, σ , is the square root of the arithmetic mean of the squares of all the deviations in counting rate from the average counting rate. If the average count is x and any particular count is denoted, x_i , then for n determinations on the same sample

$$\sigma^2 = \frac{1}{n} \sum_{i=1}^n (x - x_i)^2$$

When two quantities A and B , of standard deviations σ_a and σ_b are combined arithmetically the standard deviation of the result, σ_{ab} is given by

$$\sigma_{ab}^2 = (\sigma_a f'_A)^2 + (\sigma_b f'_B)^2$$

where f'_A and f'_B are first derivatives of A and B . Using this formula the following expressions for the standard deviations in given quantities are obtained.

Quantity	σ_{ab}
$A \pm B$	$(\sigma_a^2 + \sigma_b^2)^{\frac{1}{2}}$
AB	$(\sigma_a^2 B^2 + \sigma_b^2 A^2)^{\frac{1}{2}}$
A/B	$\frac{A}{B} \left(\frac{\sigma_a^2}{A^2} + \frac{\sigma_b^2}{B^2} \right)^{\frac{1}{2}}$

For 10,000 counts recorded, the standard deviation is ± 100 counts or $\pm 1\%$ of the count rate. Thus for each of the count rates in table 6-1, the error is $\pm 1\%$. Using the expressions given above the errors, due to the standard deviation in count rate, in the percentage distribution of chlorine-36 in table 6-2 were calculated. The standard deviation was around 1.4% of the value recorded, i.e. the error in a result of 90% is $\pm 1.3\%$ and the error in a result of 20% is $\pm 0.3\%$.

The total error in the final results, due to both practical and counting errors, can only be estimated by the difference between two independently obtained results. The largest discrepancy is 3%. Thus it must be concluded that the maximum error in this set of results is $\pm 1.5\%$, since a mean value from the two independent determinations is always taken.

Paper electrophoresis

6-3 Effects of diffusion and adsorption

The results of experiments carried out to determine the extent of diffusion and adsorption using $[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and 0.01M perchloric acid electrolyte are given in tables 6-3 and 6-4. In the diffusion experiment, where no potential difference is applied, the spread of activity is less than 1cm in either direction during a period of two hours. The activity remains centred at the origin showing that diffusion plays no part in ion migration. Adsorption effects are also small as the activity is concentrated at

TABLE 6-3Diffusion effects in paper electrophoresis

Migration distance	Activity
+14 to +1cm	0
+1 to 0cm	4112c.p.m.
0 to -1cm	1520c.p.m.
-1 to -14cm	0

TABLE 6-4Adsorption effects in paper electrophoresis

Migration distance	Activity
+14 to +2cm	0
+2 to +1cm	82c.p.m.
+1 to 0cm	219c.p.m.
0 to -1cm	454c.p.m.
-1 to -2cm	378c.p.m.
-2 to -3cm	117c.p.m.
-3 to -14cm	0

one spot rather than blurred along the strip after applying the same potential difference in opposite directions for equal times. However, the activity is concentrated around -1cm, not at the origin. Therefore the spot has travelled further in the reverse stage of electrophoresis than in the forward stage, showing that there is an increase in current with time.

6-4

Cobalt complexes

The results of paper electrophoresis on irradiated cobalt complexes using 0.01M perchloric acid and 0.01M potassium perchlorate solution as electrolytes, are given in tables 6-5, 6-6, and 6-7. Examples of the histograms obtained are given in figures 6-1, 6-2, and 6-3. For $[^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 4hr.10min. in the HERALD reactor, 0.01M ammonium perchlorate solution and 0.01M potassium hydroxide solution were also used as electrolytes. These results are given in table 6-8.

For the $^{60}\text{Co}^{2+}$ ion the distance of migration in one and a quarter hours is +9 to +10cm in perchloric acid and +4 to +5cm in potassium perchlorate electrolyte.

NOTE: In all tables of electrophoresis results the percentage of the activity in a particular peak is given opposite the migration distance at the centre of the peak.

TABLE 6-5

Results of paper electrophoresis of irradiated

and non-irradiated $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

[illegible]

TABLE 6-6

Results of paper electrophoresis of

irradiated trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Migration distance (cm)	trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$			
	Irradiated 41hr.40min.		Irradiated 1 week	
	HClO ₄	KClO ₄	HClO ₄	KClO ₄
+13 to +12	44%			
+12 to +11				
+8 to +7				
+7 to +6	6%		100%	
+6 to +5		76%		
+5 to +4				100%
+4 to +3				
+3 to +2	50%			
+2 to +1		24%		
+1 to 0			³⁵ S	
-6 to -7			³⁵ S	
-7 to -8				
-8 to -9				
-9 to -10			³⁵ S	
-10 to -11		³⁵ S		³⁵ S
-11 to -12				
-12 to -13	³⁵ S			

TABLE 6-7

Results of paper electrophoresis of irradiated

and non-irradiated trans $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$

Migration distance (cm)	Trans $[\text{}^{60}\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$				Trans $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$			
	Non-irradiated		Irradiated 4hr.10min.		Irradiated 41hr.40min.		Irradiated 1 week	
	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4
+11 to +10								
+10 to +9		21%	59%				61%	
+9 to +8	36%			36%	58%			
+8 to +7								
+7 to +6		79%		64%		49%		
+6 to +5	64%		41%		42%		39%	100%
+5 to +4						51%		
+4 to +3								
+3 to +2								
+2 to +1								
+1 to 0							35 _S	35 _S
0 to -1								
-7 to -8								
-8 to -9							35 _S	
-9 to -10			35 _S					35 _S
-10 to -11								
-11 to -12				35 _S	35 _S	35 _S		

TABLE 6-8

Results of paper electrophoresis of $[\text{}^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ -
using NH_4ClO_4 and KOH electrolytes.

Migration distance (cm)	Non- irradiated		Irradiated 4hr.10min.	
	NH_4ClO_4	KOH	NH_4ClO_4	KOH
+11 to +10	100%	100%	77%	55%
+10 to +9				
+9 to +8				
+8 to +7				
+7 to +6			23%	45%
+1 to 0				
0 to -1				
-9 to -10				
-10 to -11			35S	35S

FIGURE 6-1

Histogram of paper electrophoresis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ -
irradiated 4hr.10min. using 0.01M KClO_4 electrolyte.

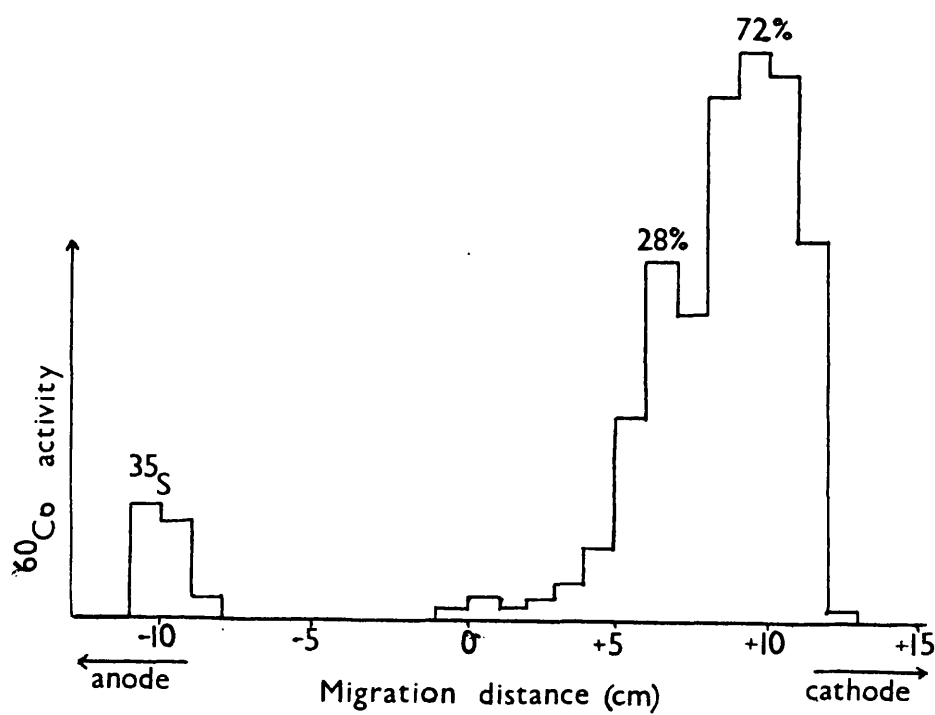


FIGURE 6-2

Histogram of paper electrophoresis of trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ irradiated 41hr.40min. using 0.01M KClO_4 electrolyte.

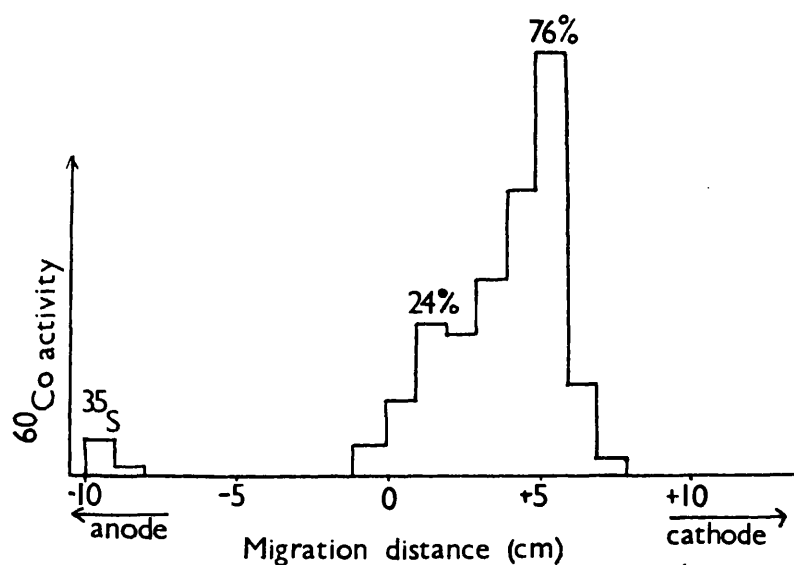
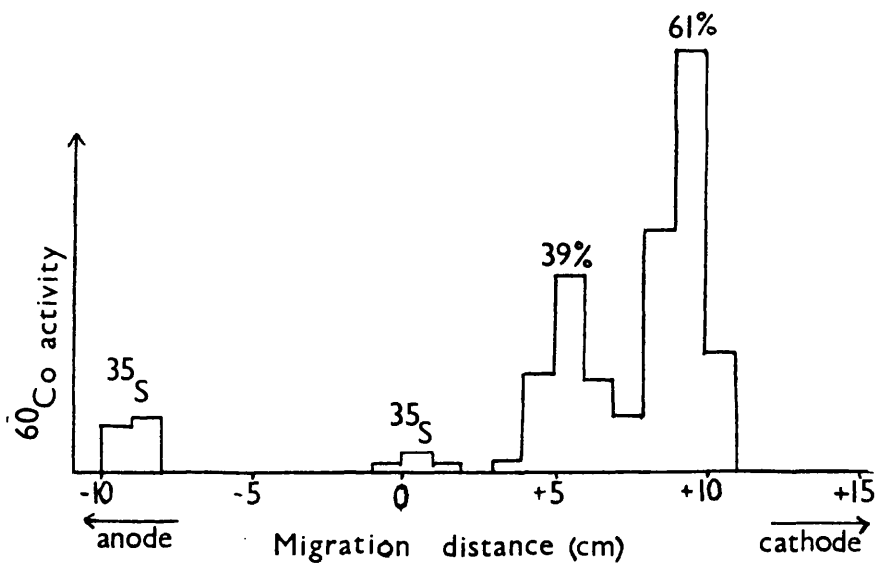


FIGURE 6-3

Histogram of paper electrophoresis of trans $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ irradiated 1 week using 0.01M HClO_4 electrolyte.



6-5Iridium complexes

The results of paper electrophoresis of irradiated iridium complexes are given in tables 6-10, 6-11 and 6-12. Examples of the histograms obtained for these complexes are shown in figures 6-4, 6-5 and 6-6. For the purposes of comparison, the characteristic migration distances of the non-irradiated complex ions labelled with iridium-192 are given in table 6-9.

TABLE 6-9

Migration distances of non-irradiated
iridium complex ions.

Complex	Migration distance (cm)	
	HClO ₄	KClO ₄
$[^{192}\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$	+12 to +11	+13 to +12
$\text{tr}[^{192}\text{Ir}(\text{NH}_3)_4\text{Cl}_2]^+$	+8 to +7	+9 to +8
$\text{tr}[^{192}\text{Ir}(\text{en})_2\text{Cl}_2]^+$	+8 to +7	+9 to +8

TABLE 6-10

Results of paper electrophoresis of
 irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Migration distance (cm)	Irradiated 25min.		Irradiated 4hr.10min.		Irradiated 41hr.40min.	
	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4
+13 to +12				3%		
+12 to +11		3%	18%			
+10 to +9	57%	31%				19%
+9 to +8				13%	7%	
+8 to +7			33%			
+7 to +6				19%	30%	20%
+6 to +5	18%	23%				
+5 to +4			16%		19%	
+1 to 0	23%	36%	29%	55%		56%
0 to -1					39%	
-3 to -4	2%		2%	5%		
-4 to -5		7%				3%
-5 to -6				3%	2%	
-6 to -7			2%			2%
-7 to -8				2%		
-8 to -9					3%	
Total cations	75%	57%	67%	35%	56%	39%
Neutral species	23%	36%	29%	55%	39%	56%
Total anions	2%	7%	4%	10%	5%	5%

TABLE 6-11

Results of paper electrophoresis of
irradiated trans $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Migration distance (cm)	Irradiated 25min.		Irradiated 4hr.10min.		Irradiated 41hr.40min.	
	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4
+11 to +10		10%				
+10 to +9					5%	
+9 to +8						28%
+8 to +7	32%	26%		12%	20%	
+7 to +6			31%			
+6 to +5						26%
+5 to +4	17%		28%	20%	37%	
+1 to 0	43%	53%	36%	46%	26%	38%
-2 to -3			2%			
-3 to -4	4%					
-4 to -5			3%	15%		
-5 to -6		11%			4%	8%
-6 to -7	4%					
-8 to -9				7%	6%	
-11 to -12					2%	
Total cations	49%	36%	59%	32%	62%	54%
Neutral species	43%	53%	36%	46%	26%	38%
Total anions	8%	11%	5%	22%	12%	8%

TABLE 6-12

Results of paper electrophoresis of
 irradiated trans $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$

Migration distance (cm)	Irradiated 25min.		Irradiated 4hr.10min.		Irradiated 41hr.40min.	
	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4
+10 to +9					3%	
+9 to +8		11%		13%		
+7 to +6	15%		20%	4%	12%	6%
+5 to +4		11%	18%	11%		
+4 to +3	17%				20%	
+3 to +2						12%
+2 to +1				24%		
+1 to 0	40%	45%	39%	13%	37%	
0 to -1						39%
-2 to -3	28%		9%	6%		
-3 to -4				7%	13%	
-4 to -5		19%		6%		17%
-5 to -6			10%	7%	10%	
-6 to -7		14%				18%
-8 to -9				4%		
-10 to -11			4%	5%	5%	8%
Total cations	32%	22%	38%	28%	35%	18%
Neutral species	40%	45%	39%	37%	37%	39%
Total anions	28%	33%	23%	35%	28%	43%

FIGURE 6-4

Histogram of paper electrophoresis of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
irradiated 4hr.10min. using 0.01M KClO_4 electrolyte.

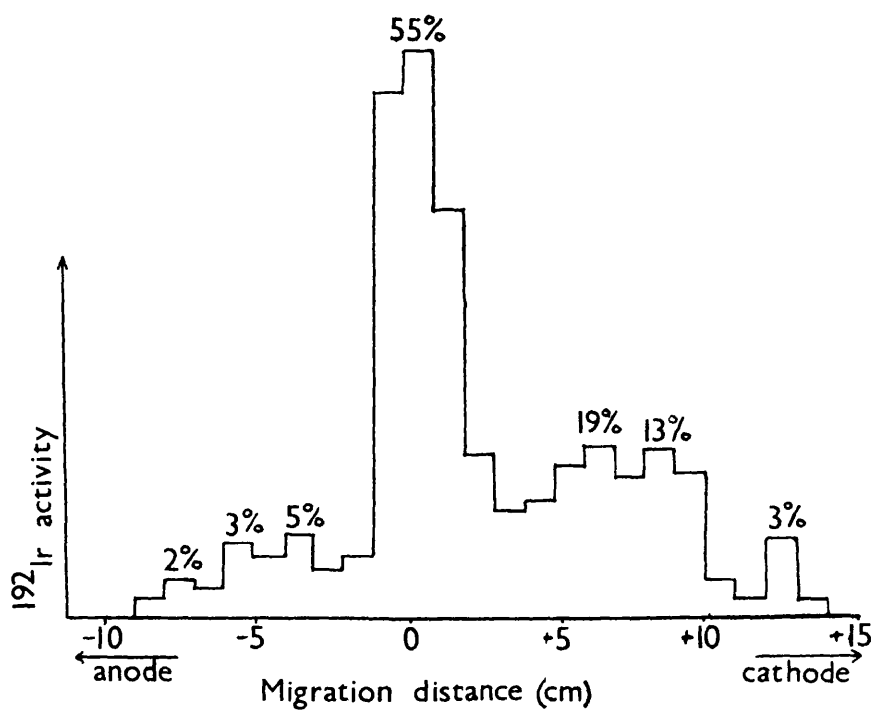


FIGURE 6-5

Histogram of paper electrophoresis of trans $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ irradiated 25min. using 0.01M KClO_4 electrolyte.

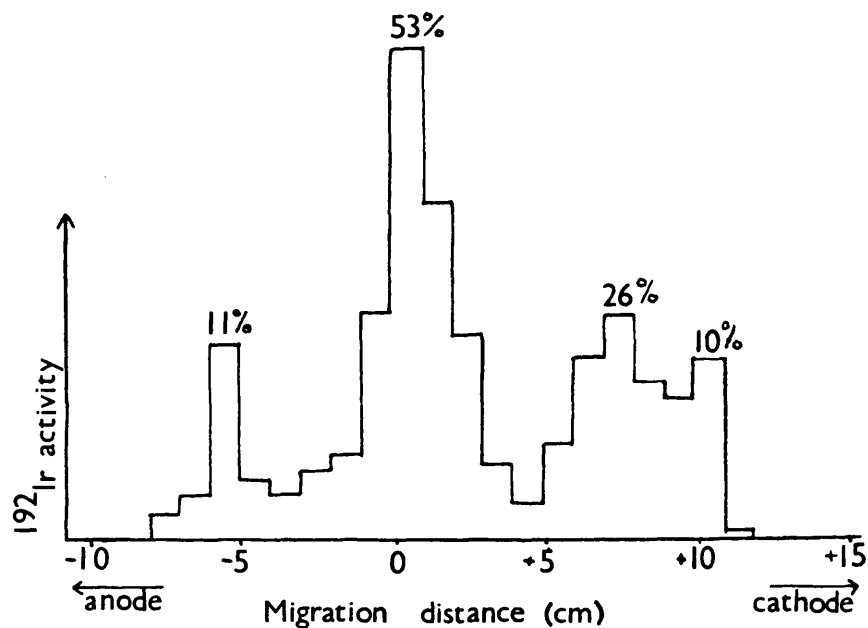
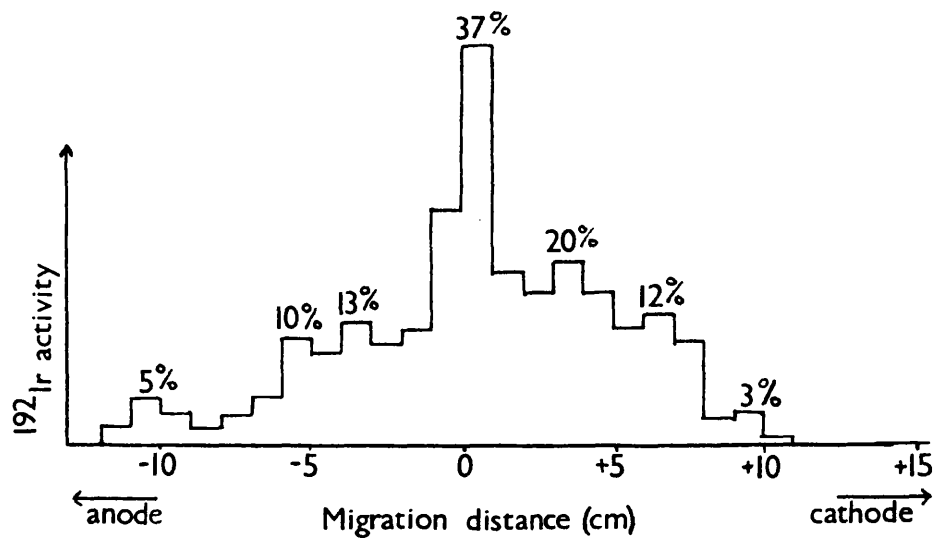


FIGURE 6-6

Histogram of paper electrophoresis of trans $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ irradiated 41hr.40min. using 0.01M HClO_4 electrolyte.



6-6 Errors in results obtained by paper electrophoresis

There will be two separate errors in these results: error in the migration distance recorded and error in the percentage distribution of activity calculated from the area under the histogram peaks.

Migration distance

Since the electrophoresis strips are generally cut into 1cm sections, the position of the centre of the peak is not fixed accurately. It can only be stated that the centre of the peak lies between x cm and $(x+1)$ cm. There are slight variations in the conditions of electrophoresis. For example, the temperature of the electrolyte may be different in separate runs and the voltage may fluctuate slightly. Thus the same ion under nominally the same conditions may have a migration distance just less than x cm in one experiment and just greater than x cm in another. In the first case the recorded migration distance would be $(x-1)$ to x cm and in the second x to $(x+1)$ cm. Thus a maximum error of ± 1 cm must apply to each result obtained.

Percentage distribution of radioactive products.

The simplest way to estimate the errors involved in calculation of product distribution was to run the electrophoresis of the same sample several times and note the variation in results. This was done for a number of samples. Results were found to be reproducible to within $\pm 5\%$. This constitutes a fairly large error for more abundant species and for species of low abundance the error is extremely large. However, it must be remembered that these are maximum errors, and the actual errors are likely to be much smaller.

6-7 Re-irradiation of electropherogram of irradiated
 $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after decay of induced ^{192}Ir activity

The control electropherogram, which was not subjected to re-irradiation, showed only a negligible count rate compared to the re-irradiated paper strip. Re-irradiation produced iridium-192 on the electropherogram and the amount of activity produced depended directly on the amount of iridium present. Therefore the activity measured after re-irradiation shows the distribution of iridium in the whole solid (not simply recoil iridium) produced by the first irradiation of the solid. 0.01M perchloric acid was used as electrolyte. The results are given in table 6-13.

TABLE 6-13

Macroscopic distribution of iridium in $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ -
irradiated 4hr.10min. in the HERALD reactor, as determined
by re-irradiation of an electropherogram.

Migration distance (cm)	Percentage ^{192}Ir activity
+14 to +12	0
+12 to +11	2%
+11 to +10	0
+10 to +8	98%
+8 to -14	0

6-8 Infrared spectroscopy of irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

The near infrared spectra of the irradiated complex showed no significant differences from that of non-irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. However, far infrared spectroscopy showed that some change had occurred on a macroscopic scale in the structure of the complex as a band was observed in the spectrum of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 41hr.40min., which was not present for the non-irradiated complex. The far infrared spectrum, from 40cm^{-1} to 400cm^{-1} , of non-irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is shown in figure 6-8. That of the irradiated complex is given in figure 6-7. The far infrared spectrum of rhodium trichloride has also been recorded and, though it is not well resolved, is given in figure 6-9 for purposes of comparison.

6-9 Effect of crystal form

In table 6-14 the electrophoresis results obtained for $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 4hr.10min. in the HERALD reactor in two forms, as large crystals and as a powder are compared.

6-10 Annealing

Annealed samples were analysed by both precipitation and electrophoretic techniques. The results for chlorine-36 distribution are given in table 6-15 and those of electrophoresis in table 6-16 and table 6-17.

FIGURE 6-7

Far infrared spectrum of irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

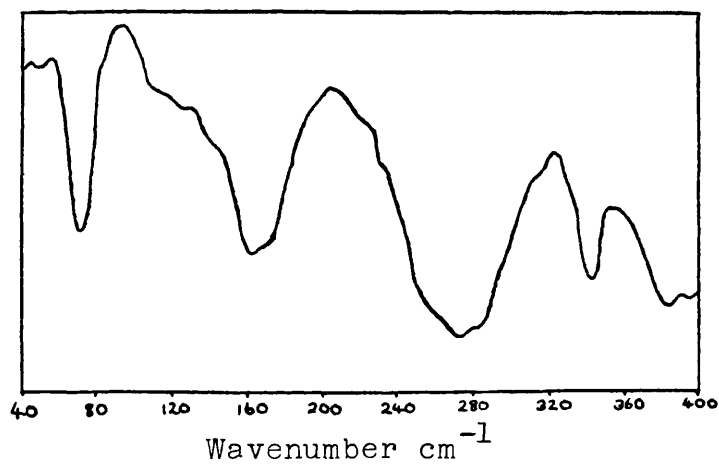


FIGURE 6-8

Far infrared spectrum of non-irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

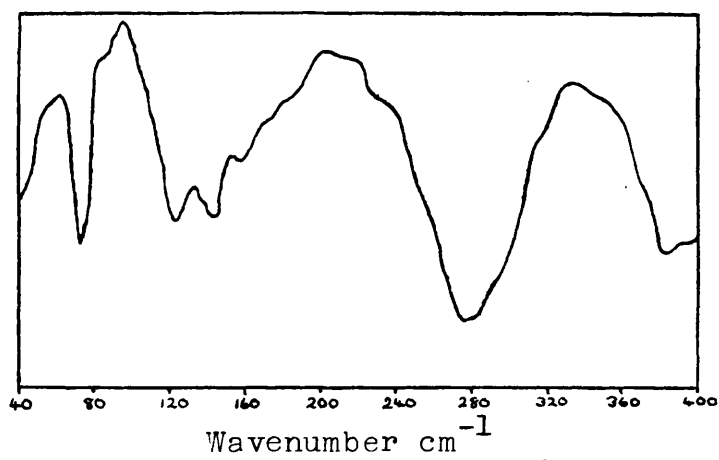


FIGURE 6-9

Far infrared spectrum of RhCl_3

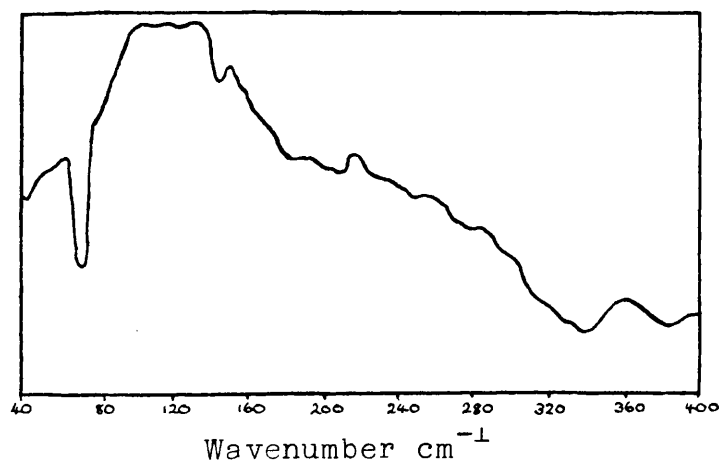


TABLE 6-14

Results of paper electrophoreses to compare iridium-192 distribution in $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated in crystalline and powder forms.

Migration distance (cm)	HClO_4		KClO_4	
	Crystals	Powder	Crystals	Powder
+13 to +12			5%	
+12 to +11		4%		1%
+11 to +10	19%			
+10 to +9			5%	
+9 to +8	22%			9%
+8 to +7		25%		
+7 to +6			20%	
+6 to +5	23%			18%
+5 to +4		34%		
+1 to 0	31%	28%	67%	66%
-3 to -4		6%		4%
-4 to -5	4%		2%	
-5 to -6				
-6 to -7		3%		2%
-7 to -8	1%		1%	
Total cations	64%	63%	30%	28%
Neutral species	31%	28%	67%	66%
Total anions	5%	9%	3%	6%

TABLE 6-15

Chlorine-36 distribution in annealed $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 and $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 4hr.10min.

Complex	Annealing temperature	Annealing time	Percentage distribution	
			Complexed ^{36}Cl	Anionic ^{36}Cl
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Unannealed	-	85%	15%
"	100°C	7hr.	88%	12%
"	100°C	18hr.	87%	13%
"	150°C	7hr.	84%	16%
"	150°C	18hr.	86%	14%
$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Unannealed	-	5%	95%
"	150°C	48hr.	10%	90%
"	200°C	48hr.	8%	92%

TABLE 6-16Results of paper electrophoresis of irradiated $[\text{}^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after thermal annealing.

Migration distance (cm)	Unannealed		Annealed 100°C for 18hr		Annealed 150°C for 18hr	
	HClO ₄	KClO ₄	HClO ₄	KClO ₄	HClO ₄	KClO ₄
+13 to +12						
+12 to +11						
+11 to +10	100%	72%				73%
+10 to +9			100%	75%	100%	
+9 to +8						
+8 to +7						
+7 to +6		28%				27%
+6 to +5				25%		
+5 to +4						
+4 to -14						

TABLE 6-17

Results of paper electrophoresis of irradiated

 $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after thermal annealing.

Migration distance (cm)	Unannealed		Annealed 150°C for 48hr		Annealed 200°C for 48hr	
	HClO_4	KClO_4	HClO_4	KClO_4	HClO_4	KClO_4
+13 to +12		3%	14%	7%	19%	
+12 to +11	18%					
+11 to +10			15%			10%
+10 to +9				18%	11%	
+9 to +8		13%	17%			
+8 to +7	33%				12%	
+7 to +6		19%				25%
+6 to +5			23%			
+5 to +4	16%			28%	18%	
+1 to 0	29%	55%	29%	42%		59%
0 to -1					38%	
-3 to -4	2%	5%			2%	6%
-4 to -5				2%		
-5 to -6		3%				
-6 to -7	2%		2%	3%		
-7 to -8						
Total cations	67%	35%	69%	53%	60%	35%
Neutral species	29%	55%	29%	42%	38%	59%
Total anions	4%	10%	2%	5%	2%	6%

CHAPTER VII

Discussion

In discussing the significance of the results given in Chapter VI, it must be remembered that, apart from the work on infrared spectroscopy, all the methods used to study the irradiated complexes involved their initial dissolution in water. Therefore the products identified by these methods were those formed by interaction of water with the species, present in the solid irradiated complexes. The form of the species in the solid lattice can in some cases be implied from the behaviour of the products under various solution conditions, e.g. varying pH.

7-1 Changes in chlorine-36 distribution

The results obtained using the precipitation and ion exchange techniques are given in table 6-2. Any reduction in the percentage of complexed chlorine-36 in the irradiated complex as compared with the non-irradiated complex indicates that a proportionate number of metal to ligand chlorine bonds have been broken and do not reform.

Considering first the cobalt complexes, for an irradiation time of 4hr.10min., $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ show no permanent rupture of Co-Cl bonds. After 4hr.40min. irradiation, $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ is unchanged, but for $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ rupture of Co-Cl bonds has taken place. It appears that the distribution of chlorine-36 has reached an equilibrium arrangement with

33% in the complexed form and 67% in the anionic form, though this is probably coincidence. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ breaks down to an even greater extent after one weeks irradiation with only 4% of the chlorine-36 remaining in complexed form. $\text{Trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ is still unchanged after one weeks irradiation. $\text{Trans}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ must be given special mention since it undergoes hydrolysis even in the short time of chloride ion precipitation and great difficulty was found in obtaining consistent results. However, it seems that, apart from the results at the shortest irradiation time, which may be erroneous owing to hydrolysis, this complex also suffers no permanent Co-Cl bond rupture.

A similar trend is observed for the rhodium complexes. $\text{Trans}[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ shows no Rh-Cl bond rupture even after one weeks irradiation. $\text{Trans}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$ is unaffected after 4hr.10min., begins to break down after 4hr.40min. and shows even more Rh-Cl bond rupture after one week. $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is also unaffected after 4hr.10min. but is almost completely broken down after the two longer irradiation times.

All three iridium complexes show almost complete bond rupture after 4hr.10min. irradiation and when the irradiation time was reduced to 25min., $\text{trans}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ and $\text{trans}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ were still almost totally disrupted, while $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was only partially broken down, i.e. 30% of the chlorine-36 remained in complexed form.

Certain general trends are observed in these results.

The order of stability to metal-ligand chlorine bond rupture appears to be cobalt>rhodium>iridium. Also, for cobalt and rhodium the order of stability of the complexes is $\text{trans}[\text{M}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} > \text{trans}[\text{M}(\text{en})_2\text{Cl}_2]\text{Cl} > [\text{M}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. For iridium the trend seems to be reversed with $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ being more resistant to breakdown than the other two complexes. The stability of most of these complexes to metal-ligand chlorine bond rupture seems to be the reverse of that observed in most reactions e.g. acid hydrolysis, thermal decomposition.

7-2

Paper electrophoresis

It has already been established that, provided the voltage, time and electrolyte concentration used in the paper electrophoresis experiments are constant, the migration distance of a given ion will be constant, but can only be measured to within the experimental error of $\pm 1\text{cm}$. Because the resolution obtained is quite low, it must be noted that an ion found to have the same migration distance as a known, isotopically labelled ion cannot be positively identified as the same ion, only as an ion of similar charge and size. The best guide to the nature of the ions present is their behaviour in electrolytes of different pH. Taking these factors into consideration, an attempt will be made, in the following sections, to give at least a general assessment of the ions found in irradiated cobalt and iridium complexes.

7-2-1

Electrophoresis of cobalt complexes

The electrophoretic study of irradiated cobalt complexes can be divided into two sections. First, irradiation of $[^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{trans}[^{60}\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ for 4hr.10min., when no significant recoil cobalt-60 is formed and the activity measured is that of the cobalt-60 labelling introduced prior to irradiation. The effect which is studied here is the macroscopic effect throughout the crystal lattice. Secondly, unlabelled cobalt complexes were irradiated for 41hr.40min. and one week, and the distribution of activity due to recoil cobalt-60 atoms was measured.

To consider first the results obtained for $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ given in table 6-5, after the shortest irradiation time, (10hr in BEPO, 4hr.10min. in HERALD), two peaks appear in neutral electrolyte and only one in acid electrolyte. Non-irradiated $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ has a migration distance of between +9 and +11cm in both electrolytes. The results can be explained as follows. Two cobalt-60 species are present in the irradiated solid. In neutral electrolyte one of these gives an ion with a charge of +1 and the other an ion of charge +2 and migration distance similar to that of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. In acid solution both species form +2 ions which are not resolved by electrophoresis. Since there is no appreciable Co-Cl bond rupture for this irradiation time both species must contain at least one Co-Cl bond. Co^{2+} is therefore not formed. Various formulae are possible but it is most likely that the species in about 70% abundance is

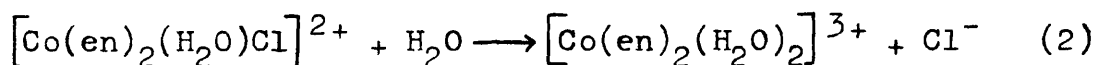
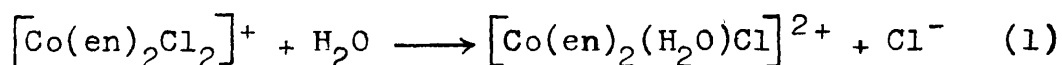
the parent ion. The other ion, in neutral solution could be $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{Cl}]^+$ or $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ where one Co-N bond is broken. Both could be formed from the reactive fragment $[\text{Co}(\text{NH}_3)_4\text{Cl}]^{2+}$ which could exist in the solid. In acid electrolyte $[\text{Co}(\text{NH}_3)_4\text{Cl}]^{2+}$ would be converted rapidly, by acid hydrolysis to $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ which would be indistinguishable from $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by the method used. This explanation requires that about 30% of the irradiated solid is in the form $[\text{Co}(\text{NH}_3)_4\text{Cl}]^{2+}$ since it is the macroscopic effect which is being measured. The results obtained with 0.01M NH_4ClO_4 electrolyte, (table 6-8), show only 23% of this +1 ion but within experimental error the difference is slight and the results confirm that the change in distribution from acid electrolyte is a pH effect. In 0.01M KOH electrolyte (table 6-8) a +1 ion and a neutral species are formed. This would suggest interaction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}]^{2+}$ with OH⁻ ion at different rates to give first $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{Cl}]^+$ and then completely breakdown to $\text{Co}(\text{OH})_3$ which will be a neutral species.

For the longer irradiations, recoil cobalt activity was measured and Co-Cl bonds had been broken. Two peaks were observed with neutral electrolyte and only one with acid. None of the radiocobalt is as the parent complex ion in either case and about 50% of the activity appears to be due to $^{60}\text{Co}^{2+}$ for the one week irradiation.

For trans $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, (table 6-6), only the recoil cobalt-60, formed in the two longer irradiations, was studied. It is difficult to assign formulae to the ions

observed. They may range in charge from +3 to +1 and must have the general formula $[\text{CoX}_n\text{Y}_{6-n}]^{+(n-3)}$, where X is NH_3 or H_2O and Y is Cl^- or OH^- . The peak at +2cm may be a binuclear species with NH_2^- or OH^- as bridging ligands. Only one species is observed for the one week irradiation which is apparently singly charged. Study of this complex is limited by the fact that the parent ion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ has not been prepared labelled with cobalt-60, and its behaviour in the different electrolytes has not been determined.

The results of paper electrophoresis of non-irradiated $\text{trans}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (table 6-7) show two species in both electrolytes, one centred around +6cm and the other +9cm. The mode of hydrolysis of the complex is as follows, 77;



Reaction (1) proceeds about 100 times faster than reaction (2). The species at +6cm must be $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ while the other at +9cm will be $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$. No third species corresponding to $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ was observed, presumably because, in the time of electrophoresis, reaction (2) does not proceed to any measurable extent. The rate of hydrolysis (reaction (1)) is greater in acid solution and this explains why the proportion of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is small in acid electrolyte. For $[\text{}^{60}\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ irradiated 4hr.10min., the same two species are present in both electrolytes. However, in both cases the percentage of $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}]^{2+}$

is higher than in the non-irradiated complex. This indicates that the irradiated solid is more susceptible to hydrolysis. Reactive species, such as radicals or ligand deficient species, must have been formed by neutron irradiation.

For recoil cobalt-60 distribution after the two longer irradiations, two species are present in both cases. In acid media, one is at +5 to +6cm (40%) and the other at +9cm (60%). In neutral electrolyte one appears at +4 to +5cm (50%) and one at +6 to +7cm (50%). These are not resolved for the one week irradiated sample. Allowing for errors in the calculation of percentage abundance, it appears that one peak is due to $^{60}\text{Co}^{2+}$ i.e. that at +9cm in acid and at +4 to +5cm in neutral electrolyte, while the other peak between +5 and +7cm is the original ion or one of similar charge and size.

7-2-2 Electrophoresis of iridium complexes

For irradiated iridium complexes, it is the distribution of recoil iridium species which is examined by paper electrophoresis. Certain general trends are observed in the lower sections of tables 6-10, 6-11 and 6-12. For $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $\text{trans}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ the percentage abundance of neutral species is always greater in neutral electrolyte than in acid but for $\text{trans}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ the percentage is approximately the same in both electrolytes. It is possible that for the amines the neutral species is, at least in part, composed of basic species such as hydrated

iridium oxides, whose nature is altered in acid solution. For all complexes, a higher percentage of iridium-192 activity was found in cationic form in HClO_4 solution than in KClO_4 solution. For the amines the difference corresponds to the different proportion of neutral species in the two media, while for $\text{trans}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ the proportion of anionic iridium-192 activity is higher in KClO_4 solution than in HClO_4 solution. For the amines the amount of anionic iridium-192 is generally small, $\leq 12\%$, but for $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ it is comparable with the percentage of cationic activity.

For $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ the cationic activity decreases with increasing irradiation time, with a corresponding increase in the percentage of neutral species. For $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ the trend is reversed with cationic activity increasing and neutral activity decreasing. $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ shows fairly constant results for all irradiation times.

Identification of recoil species

It is virtually impossible to identify all the recoil species which are formed with any certainty using the apparatus available. Any identification which is made will depend on the effect of pH and irradiation time on a particular species and must, at least in part, explain the general trends which have been outlined above. It must be remembered that the migration distance of an ion is only fixed within $\pm 1\text{cm}$. From the migration distances of the labelled complex ions (table 6-9), species which appear between $+10$ and $+14\text{cm}$ are likely to be doubly charged ions

similar to $[\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$ while those between $+6\text{cm}$ and $+10\text{cm}$ are likely to be singly charged. There is also a possibility that polymeric species may be formed. The bridging ligands are most likely to be NH^{2-} , NH_2^- or OH^- , or ethylenediamine in the case of $\text{trans}[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$. These bridged species would be much larger than octahedral, mononuclear ions and therefore, their migration distances would be much smaller, probably $+4$ to $+6\text{cm}$. It is possible that iridium(IV) species could be formed by oxidation in the reaction zone of the recoil atom, but any reduced atoms i.e. iridium(II) would be immediately oxidised on dissolution.

For the ammine complexes the various ions present can be represented by the general formula $[\text{IrX}_n\text{Y}_{6-n}]^{+(n-3)}$, where X is a neutral ligand, NH_3 or H_2O and Y is a ligand of single negative charge, Cl^- or OH^- . Most of these species would be formed by reaction of ligand deficient species in the solid when dissolved in water. Bridged complexes are also possible. For $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ the range of possible ligands is greater since ethylenediamine ligands may be broken down in the reaction zone to give such species as NH_3 , CN^- , CH_3NH_2 and deprotonated ethylenediamine. The presence of CN^- ions could explain the large percentage of stable anionic species formed. The range of possible recoil products will be larger for $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ than for the amines and it is not surprising that, even with the rather insensitive apparatus used, as many as twelve iridium-192 recoil species have been detected.

The retention values for recoil iridium are generally

low, especially in the case of the pentaammine. In the other two complexes the apparent retention is higher but this may, at least in part, be due to other $+1$ ions which, under the conditions used, have the same migration distances as $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{Ir}(\text{en})_2\text{Cl}_2]^+$.

For the amines in neutral electrolyte the neutral species is almost certainly made up in part of basic species such as hydrated oxides e.g. IrO_2 . In acid these species, or their precursors in the solid, form cationic, possibly polymeric, ions. The existence of polymeric iridium ions has been established, 78. The remainder of the neutral species are probably complexes of the type $[\text{IrX}_3\text{Y}_3]$. No basic neutral species appear in irradiated $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$ since there is no change in the proportion of these in the different electrolytes. Any attempts at more specific identification of recoil species on the basis of these results would be purely conjecture.

7-2-3

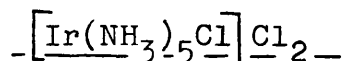
Distribution of sulphur-35

Sulphur-35, formed by the (n,p) reaction of chlorine-35, was detected on all the electropherograms of irradiated cobalt complexes, tables 6-5, 6-6 and 6-7. Undoubtedly radiosulphur was also present in irradiated iridium complexes but the activity of the sulphur-35 was masked by the much higher activity of recoil iridium-192.

In the irradiated cobalt complexes, sulphur-35 was always observed as an anionic species and sometimes, after longer periods of irradiation, as a neutral species. It is

probable that the anionic form is either sulphate, sulphite, sulphide or a mixture of these. The neutral form could be zerovalent sulphur. This identification of recoil sulphur is based on the results obtained for the distribution of sulphur-35 in neutron-irradiated alkali chlorides, 79, where four products, SO_4^{2-} , SO_3^{2-} , S^{2-} and S were identified in the dissolved solid.

7-3 The macroscopic distribution of iridium in irradiated



A sample of $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ which had been irradiated for 4hr.10min. was stored for around six half-lives to let iridium-192 activity decay. Electrophoresis was carried out on the sample using 0.01M perchloric acid electrolyte and the electropherogram was then re-irradiated in order to determine the macroscopic distribution of iridium as a result of neutron-irradiation. Table 6-13 shows that in irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 2% of the total iridium has a migration distance of +11 to +12cm and the remaining 98% a migration distance of +8 to +10cm. By comparison of these results with those obtained for the non-irradiated complexes, labelled with iridium-192 which are given in table 6-9, it appears that 2% of the iridium is present as a +2 cation, which is probably $[\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$ and the remaining 98% is in some other form which seems to be intermediate in migration distance between $[\text{Ir}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $\text{trans}[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]^+$ and is probably singly charged. The results show conclusively that neutron-irradiation of

$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ causes disruption of the complex ions throughout the crystal lattice and not simply in localised regions.

7-4 Infrared spectra of irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

The near infrared spectrum of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ which had been irradiated for 41hr.40min. shows no differences from that of the non-irradiated complex. It can be concluded that the irradiated complex contains a large proportion of ammine complex ions since, basically, the near infrared vibrations are those of the NH_3 ligands. To determine the effect of neutron irradiation on the metal ligand frequencies, it is necessary to study the far infrared spectra from 40cm^{-1} to 400cm^{-1} given in figures 6-7 and 6-8. In general, bands observed at higher wavenumbers than 200cm^{-1} can be assigned to metal-ligand vibrations and those at lower wavenumbers to lattice vibrations. For pure $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (figure 6-8) the band which appears at around 280cm^{-1} has been assigned to two vibrations, $\nu\text{Rh-Cl}$ and δNRhN , whose separate bands overlap to produce one broad band, 74. In the spectrum of the irradiated complex (figure 6-7) this broad band is again observed but in addition a second band appears at 343cm^{-1} . The spectrum of rhodium trichloride (figure 6-9) though not very clear, does seem to have a peak at around 340cm^{-1} but this is very tenuous evidence for assignment of the new band in the irradiated complex.

The results obtained on the macroscopic effect in

$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated for 41hr.40min. by determination of chlorine-36 distribution show that virtually all Rh-Cl co-ordinate bonds are broken. The far infrared spectrum confirms that there is macroscopic disruption in the complex since a completely new band is observed. It is possible that this band is due to vibrations similar to those in rhodium trichloride but this could not be confirmed.

7-5 The influence of crystal form on recoil product distribution.

With reference to table 6-14, the proportions of recoil iridium in cationic, neutral and anionic forms in $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated in the form of large crystals are the same, within experimental error, as those for the same complex irradiated in powder form. More detailed study of the proportions of separate recoil species reveals a significant difference in only one case. Using perchloric acid electrolyte, 19% of a +2 cation is observed in the large crystal form but only 4% in the powder form. The percentage of the species around +5cm is considerably greater in the powder than in the large crystals. No similar difference in distribution is observed when neutral electrolyte is used.

There are two main differences between crystal and powder forms. First, the powder form, having been precipitated rapidly from solution will have a greater density of defects in the lattice than the large crystals and secondly, the surface area, at which interaction with the atmosphere

can occur, will be much greater for the powder form. It would be expected that the retention would be greater in the large crystals as there are less defects present to compete with molecular fragments for the recoil species. This does appear to be the case as shown by the results obtained in neutral electrolyte. In acidic media some other $+2$ species must be formed, making the apparent retention in the crystal form very high (19%). Interaction of the recoil species at the surface of the lattice with the atmosphere would be expected to produce oxides of iridium, which would appear as neutral species on analysis. Therefore if these reactions are occurring to any appreciable extent the percentage of neutral species would be greater for the powdered sample, where the surface area is large. In fact the same percentage of neutral recoil species is observed for both samples. Surface interactions must be negligible. Iridium oxides are probably formed by interaction of reactive species in the solid with water on dissolution. In conclusion, the variation in surface area does not appear to influence recoil product distribution but defect density does affect recoil atom reactions. These conclusions are in agreement with those reached by Maddock et al, 49.

7-6

Annealing

Comparison of the results in table 6-15 shows that the distribution of chlorine-36 in the irradiated samples is unchanged under the conditions of thermal annealing which

have been employed. Therefore thermal treatment following irradiation appears not to alter the macroscopic structure of the solid lattice. This conclusion is supported by the paper electrophoresis results obtained with annealed irradiated $[\text{}^{60}\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, given in table 6-16, which are very similar to those obtained for the unannealed sample. The cobalt-60 activity detected is that which was introduced, as an isotopic label, prior to irradiation and so again it is the macroscopic effect which is being studied and found to remain unchanged.

For irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ it is the recoil iridium-192 whose distribution is being analysed by paper electrophoresis. Comparison of the results in table 6-17 shows that some change does occur on thermal annealing. After annealing at 150°C for two days the percentage of neutral species observed in KClO_4 electrolyte was reduced while there was a corresponding increase in the percentage of cations and, in particular, a new species of 28% abundance and migration distance $+4$ to $+5\text{cm}$ appears. Since this ion is not observed in HClO_4 electrolyte, it must be unstable in acid solution and could be a polymeric species which in acid breaks up to give monomers of higher migration rate. It has already been stated that a proportion of the neutral species is made up of oxides of iridium probably with iridium in the tetravalent state, Ir(IV) . The results suggest that the precursors of the oxides were, to some degree, altered in nature by heating to 150°C . This could be caused by reduction of Ir(IV) species in the

solid to Ir(III) as a result of reaction with reducing defects in the disturbed lattice i.e. F-centres. These Ir(III) species would tend to produce cationic species similar to the parent ion on dissolution and not oxides which are predominantly formed from Ir(IV) species. At 200°C the percentage of neutral species is increased in both electrolytes. This suggests a reverse process to that envisaged above; i.e. oxidation of Ir(III) to Ir(IV) by reaction with oxidising defects such as V-centres. The Ir(IV) species would then form oxides on dissolution.

The above is a purely hypothetical explanation of the results and implies that reducing reactions predominate below 150°C and oxidising reactions above 150°C. This could be due to the higher mobility of F-centres than the larger oxidising V-centres.

In considering the implications of the results obtained in this research, the work can be divided into two sections. Firstly, the fate of the recoil atoms produced by the (n,γ) reaction will be discussed. And secondly, the macroscopic effect produced in the solid complexes by neutron-irradiation will be outlined and possible mechanisms for its production will be discussed.

7-7

Recoil atom reactions

The results of paper electrophoretic separation of recoil cobalt-60 and iridium-192 have been discussed in section 7-2. The best model to explain the distribution of products formed seems to be the hot-zone model.^{13,14} In the molten reaction zone the recoil atom could lose one or more of its ligands and undergo oxidation and reduction reactions. With the rapid cooling of the zone, reactive species, e.g. ligand deficient ions, reduced species, radicals and defects, would be trapped in the crystal lattice. These would then react on dissolution in water to give the wide range of products observed. The number of products observed for cobalt complexes is less than for iridium complexes and this must be due to the greater stability of the iridium complex ions formed in the lattice or in solution. The cobalt complexes formed will probably all revert to one or two complex ions which are the most stable in solution. The billiard ball and random fragmentation models would not allow for the stabilisation of these reactive species since in these models the energy of the

recoil atom is lost gradually; finally being used up in normal thermal reactions, when any reactive species would be removed.

The retention values obtained are generally small but higher values are found for the dichlorobisethylenediamine complexes and this could be due to the greater screening power of the bidentate ligands as suggested by Süe and Kayas, 30. The results obtained for $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ agree reasonably well with those of Schmidt, 62, who also found the largest proportion of activity in neutral form and a very small value for the retention, see figure 3-3. However, Schmidt did not observe any anionic species, but this could be attributable to the different thermal neutron flux and reactor conditions used.

7-8

Macroscopic effect

Various techniques have been used in this research to estimate the size of the macroscopic effect throughout the solid lattice; changes in the distribution of chlorine-36 and cobalt-60 labelling, the change in form of

$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ as determined by re-irradiation of an electropherogram and the far infrared spectrum of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ after irradiation. In all cases the results show that disruption on a macroscopic scale occurs for most of the complexes, provided the time of irradiation is long enough. This disruption requires that at least one metal to ligand bond is broken in most of the complex ions present. Bond energies for these complexes are generally of the order of 5eV. In addition to this energy needed to break the

metal to ligand bond, further energy is required to remove an atom from its lattice position to an interstitial position. It has been calculated on the basis of solid state physics that the total energy to remove an atom to an interstitial site in the crystal is around 25eV, 15. It is obvious from this that a large amount of energy must be supplied to the solid in order to create the amount of disruption which is observed.

7-8-1

Recoil energy effects

The most obvious source of energy is that of the recoil atoms produced by the (n,γ) reaction. A precise evaluation of the recoil energy requires detailed knowledge of the prompt capture gamma ray spectra which are given in the literature, 80, and of the angular correlation of the capture gamma rays. The calculation is complex and tedious. However, an estimate of the magnitude of the recoil energy can be obtained by making certain approximations. If it is assumed that all the energy is emitted as a single gamma ray and that this energy is equal to the neutron binding energy, then the recoil energy, R, is given by

$$R = \frac{537E_\gamma^2}{M} \text{ eV}$$

where E_γ is the neutron binding energy in MeV and M is the mass of the recoiling atom in a.m.u. The recoil energy determined from this equation will be higher than the actual value, since in fact several gamma rays will be emitted in different directions, thus reducing the resultant recoil in

a particular direction. However, recoil energies obtained from this simple equation for various capturing atoms will show any appreciable differences in the order of magnitude of the recoil energy in the various systems. The values obtained for the recoil energy of the atoms, studied in this research, are given in table 7-1. Neutron capture reactions of nitrogen, carbon and hydrogen are negligible because of the low cross sections of these atoms for thermal neutron capture.

The total energy of recoil released in a given amount of solid complex is equal to the recoil energy per atom multiplied by the number of atoms which undergo neutron capture. The number of recoil atoms, N^* , is given by

$$N^* = N \cdot \sigma \cdot \phi \cdot t$$

where N is the number of target atoms, σ is the cross section for thermal neutron capture, ϕ is the thermal neutron flux and t is the time of irradiation. The number of recoil atoms per million target atoms for each irradiation time are given in table 7-2.

Taking each complex in turn and considering all atoms in that complex which suffer recoil, the total recoil energy liberated in one million target molecules can be calculated for each irradiation time. These results are given in table 7-3. They show for the iridium complexes, irradiated for 25min. the total recoil energy dissipated in one million molecules is less than 50eV. However, for $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ and $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$, almost total Ir-Cl ligand bond rupture

TABLE 7-1Approximate recoil energies of atomsrelevant to this research.

Recoil atom	E (MeV)	M (a.m.u.)	R (eV)
^{60}Co	7.544	59.93	510
^{104}Rh	7.078	103.91	259
^{192}Ir	6.053	191.96	102.5
^{194}Ir	6.333	193.97	111
^{36}Cl	8.662	35.97	1317
^{38}Cl	7.738	37.97	847
^{35}S	0.745*	34.97	8.5

* Energy of proton emission following
(n,p) reaction of chlorine-35.

TABLE 7-2Number of recoil atoms produced per million target atoms.

Target atom	Cross section (barns)	Recoil atoms per 10^6 target atoms			
		25min.	4hr.10min.	41hr.40min.	1 week
^{60}Co	36	-	0.130	1.30	13.0
^{104}Rh	149	-	0.536	5.36	53.6
^{192}Ir	370	0.1332	1.332	13.32	-
^{194}Ir	80	0.0288	0.288	2.88	-
^{36}Cl	23	0.0083	0.083	0.83	8.3
^{38}Cl	0.138	0	0.0005	0.005	0.05
^{35}S	0.226	0	0.0008	0.008	0.08

TABLE 7-3Recoil energy dissipated in one million target molecules

Complex	Recoil energy per 10^6 target molecules			
	25min.	4hr.10min.	41hr.40min.	1 week
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	-	395.5eV	3,955eV	39,550eV
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$	-	468eV	4,680eV	46,800eV
$[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ $[\text{Ir}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$	49.8eV	498eV	4,980eV	-

occurs and therefore in one million molecules, two million bonds have been broken. This would require 50MeV of energy, one million times that available from the recoil atoms. For $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ irradiated one week, the recoil energy is much higher, around 40KeV but as all Co-Cl bonds are broken the energy required is 25MeV, again several orders of magnitude greater than the recoil energy. It is obvious that the energy of recoil alone cannot explain the vast amount of disruption which occurs and it is necessary to look to other sources of energy, to explain these macroscopic changes.

Some authors, 81, have suggested that, in the hot-zone model put forward by Harbottle and Sutin, the size of the hot-zone may be several times greater than that predicted originally and may encompass 5,000 atoms rather than 1,000 atoms, as previously estimated. However, it is impossible to adapt this hypothesis to the results obtained here, as the size of the zone would have to extend to millions of atoms in some cases and there is insufficient recoil energy available to produce any substantial temperature increase in such a large volume of the crystal.

Explanation of the results based solely on the theory of hot reactions in the lattice can be discounted for an entirely different reason. The techniques of far infrared spectroscopy and re-irradiation of an electropherogram indicate that on the macroscopic scale only one new product is formed and in certain ways it is similar to the parent complex. For irradiated $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ only one

new peak was observed in the far infrared spectrum and the near infrared showed that the complex was still basically composed of ammine complexes. For irradiated $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ the new complex appears in solution as a single cationic species and is probably a singly charged ion. This preferential production of one new form is in direct contrast to the distribution of products of the recoil atom which presumably have been formed by high energy or 'hot' reactions in the molten zone. Thus the effect of neutron-irradiation on the solid complexes is two-fold: it produces high energy reaction zones around the site of recoil in which a conglomeration of highly reactive species are produced, and secondly, it produces in the remainder of the crystal lattice some form of disruption which is relatively uniform in its nature and must be produced by much lower energy reactions, probably in the epithermal range.

It has already been noted that the order of stability of the complexes to bond rupture on neutron-irradiation appears to be the reverse of that in normal chemical reactions. The only viable explanation which can be suggested to explain this observation is as follows. Large scale disruption must occur for all the complexes. An energy barrier will have to be passed before the fragments of the disrupted molecules can form metastable species in the lattice. This barrier will be higher for the less chemically stable complexes, e.g. cobalt complexes, as the new metastable species will be correspondingly less stable and readily revert to the parent complex. For iridium

complexes the energy barrier will be smaller and a large proportion of the metastable species will be formed. As the time of irradiation is increased, the extent of disorder in the crystal, due to defect production by gamma radio-lysis, will increase. This will tend to lower the energy barrier to the formation of metastable species, since these can now be trapped in defect sites. Therefore more of the disrupted cobalt complexes will reach the metastable state and after a suitable length of time the energy barrier will be low enough for permanent disruption of the complexes to be observed. Using this hypothesis, every complex would have a characteristic critical irradiation dose above which metastable species would be formed in the solid lattice and extensive disruption would be observed on analysis.

The problem now is to determine the source of energy and the mechanism by which this macroscopic disruption initially occurs. Besides the energy of the recoil atoms, there are two other main sources of energy a) the excitation energy of these atoms induced by internal conversion of low energy gamma rays and the subsequent Auger charging effects and b) the energy associated with the gamma radiation which accompanies neutron-irradiation, and can also cause ionisation and excitation of atoms in the solid lattice.

7-8-2

Auger charging effects

Gamma rays of low energy, whether emitted as part of the capture gamma cascade or in the natural mode of decay of the radioactive atoms produced, can become internally

converted. Instead of being emitted as photons, the energy of the excited nucleus is dissipated by the ejection of an electron from one of the shells of the atom. This vacancy produced in the electron shells of the atom, by emission of an internal conversion electron, produces extensive rearrangement in the atom. If an L electron falls into the K shell, the difference in the K and L binding energies is given out either as an X-ray or by emission of another electron. The whole readjustment may involve emission of several such electrons, known as Auger electrons in a cascade. As a result the atom is in a highly excited state and has a large excess positive charge. Molecular dissociation is almost certain to result.

The Auger effect will occur only for atoms which suffer recoil and become radioactive. Excitation, as a result of internal conversion of capture gamma rays, will only effectively add to the energy of recoil and may increase the extent and lifetime of the hot-zone. After the hot-zone has cooled, Auger charging due to the normal gamma decay processes will continue. As can be seen from the decay schemes of the radioisotopes involved (pages 45-48) all three groups of complexes will suffer internal conversion of gamma rays emitted from the radioactive isotopes of the metal atoms, and to approximately equal extents. However, if this continual Auger charging were responsible for the macroscopic effect observed, the extent of the effect would be expected to increase if the complexes were stored for any length of time. In fact this was not

observed. The same results were obtained for the extent of macroscopic disruption regardless of the time interval which had elapsed between irradiation and analysis. This fact also rules out any measurable disruption of the solid complexes due to the effects of the accompanying beta decay processes which would also be time dependent.

7-8-3

Gamma radiolysis

As has already been discussed, the gamma radiation which accompanies thermal neutron irradiation can cause excitation and ionisation in solid complexes. Defects are likely to be produced in the lattice. Electrons released by ionisation will be trapped in interstitial positions and colour centres will be produced. Valency changes are also probable for the transition metal ions.

From all these possible effects induced by gamma radiation, it would seem quite likely that gamma radiolysis could be responsible for the macroscopic disruption of the complex ions in the solid, since its effects would be distributed quite evenly throughout the lattice. However, experiments carried out by other workers, 82, have shown that if $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ labelled with chlorine-36 in the complex ion is irradiated in a cobalt-60 gamma source of 1000 curies for 10 hours no appreciable change in the distribution of chlorine-36 results. These gamma irradiation conditions are of the same magnitude as those experienced by the samples in the thermal column of the nuclear reactor (see table 5-2). It would, therefore, seem that the degree

of disruption caused cannot be solely attributed to the effects of gamma radiolysis.

It therefore appears that, in order for macroscopic disruption to occur in the crystal lattice, both recoil effects and gamma radiation effects are necessary. It is possible that reactions which are set up in the hot-zone of the crystal may well be propagated throughout the lattice as lower energy reactions by interaction with defect centres produced by gamma radiolysis. Electronic processes are the most likely to occur and would possibly result in large scale reduction of the metal ions in the complex and subsequent loss or rearrangement of ligands. This mechanism is suggested very tentatively and cannot be substantiated without further research into this problem.

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