1976

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II. The Szilard-Chalmers effect in solid-state systems containing the octa-μ_3-chloro-*octahedro*-hexamolybdenum(II) cluster

by

Kenneth Wayne Lee

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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For the Major Department

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Iowa State University
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TABLE OF CONTENTS

I. CIS-DICHLORODIAMMINEPLATINUM(II). AQUATION EQUILIBRIA AND ISOTOPIC EXCHANGE OF CHLORIDE LIGANDS WITH FREE CHLORIDE AND TETRACHLOROPLATINATE(II)

INTRODUCTION

The subject of this investigation was the reevaluation of the aquation equilibrium quotients of cis-$Pt(NH_3)_2Cl$ and the exchange of chloride in the aqueous three component system, cis-$Pt(NH_3)_2Cl_2$: $PtCl_4^{2-}$: Cl^-. In 1955, Grinberg and Shagisultanova first reported, almost as an afterthought, that at higher concentrations of $PtBr_4^{2-}$, the exchange rate is probably proportional not to the first power of the concentration of $PtBr_4^{2-}$ but to a higher power in the exchange of Br between Br^- and $PtBr_4^{2-}$ (1). Since that report, a number of systems have been characterized involving bromide-containing platinum complexes which required bridging mechanisms for bromide exchange between two of the platinum species (2-6). However, in the chloride complexes of platinum, an anomalous exchange process has been reported only for the case of the anion of Zeise's salt, $Pt(C_2H_4)Cl_3^-$ (7). Furthermore, cis-dichlorodiammineplatinum(II) has assumed special importance because of its recently discovered biological and antitumor activity (8-13). The object of the present work was to provide a more complete characterization of cis-$Pt(NH_3)_2Cl_2$ and to determine if in the ternary exchange system, cis-$Pt(NH_3)_2Cl_2$: $PtCl_4^{2-}$: Cl^-, a process involving a dimeric transition state could be demonstrated.

Due to their relatively slow and therefore easily measurable rates of reaction, the ligand substitution of square-planar platinum complexes have been the subject of a very large number of kinetic studies. From these studies, a coherent model for substitution in platinum complexes has evolved. Application of this model to other low spin d^8 systems has been successful. The development of this model has been traced by several excellent review articles or chapters (14-18). The mechanism generally proposed is of nucleophilic replacement of a ligand by an associative process. As illustrated in Figure 1.1, the nucleophile $\underline{Y}$ attacks along the axis normal to the square. At this point, it should be noted that the solvent, $\underline{S}$, can function in the same manner as $\underline{Y}$, as illustrated in the remaining steps in Figure 1.1. As $\underline{Y}$ moves closer to replace $\underline{X}$, the transition state is believed to approximate a trigonal bipyramid with $\underline{X}$, $\underline{Y}$ and $\underline{L}$, originally *trans* to $\underline{X}$, in the equatorial plane. Finally, $\underline{Y}$ enters the square plane position and $\underline{X}$, now bonded at the labile axial position, is rapidly lost.

To simplify the treatment of the kinetics, the entering group $\underline{Y}$ has usually been held in great excess of $\underline{X}$ during the ligand exchange. At equilibrium, therefore, the reaction was sufficiently close to completion that the reversibility of the substitution was of no consequence. With the concentration of $\underline{Y}$ essentially constant, pseudo first order conditions applied. If the rate of replacement of the solvent ligand $\underline{S}$ was sufficiently high, the aquo-species was held to a negligible concentration. A plot of the pseudo first order rate constant against the concentration of $\underline{Y}$ gave a straight line. The resulting rate expression for the substitution of $\underline{X}$ by $\underline{Y}$ would be:

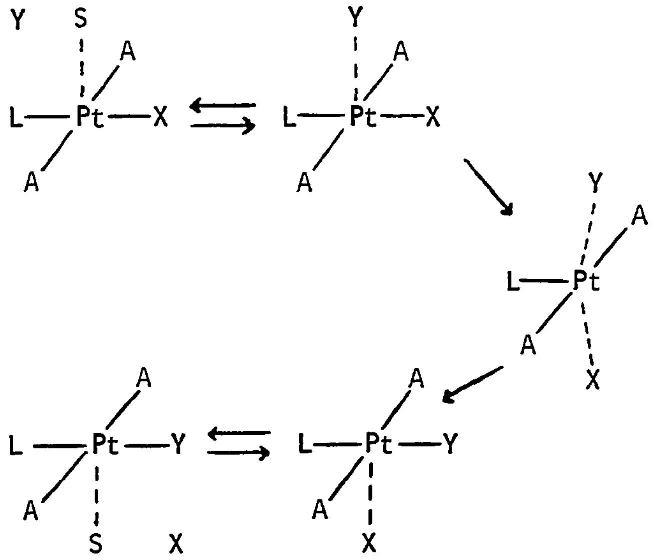


Figure 1.1. Associative mechanism for a platinum(II) complex with a trigonal bipyramidal intermediate

$$\text{Rate} = (k_s + k_y[Y])\,[\text{Pt-X}]. \qquad (1.1)$$

This rate expression is considered to represent normal kinetic behavior for the substitution reactions of Pt(II). The constant, k_s, is the rate constant for the replacement of X by the solvent, which is then rapidly replaced by Y; k_y is the rate constant for the direct replacement of X by Y.

Langford and Gray (18) have summarized the evidence concerning the question of whether substitution reactions of square-planar complexes of platinum(II) involve a trigonal bipyramidal intermediate. The existence of such a transition state and the resultant mechanism accounted for all the available data compiled by those authors.

In agreement with Pearson's concept of hard and soft acids and bases (19), the soft or highly polarizable nucleophiles were the most reactive groups for the replacement of ligands of the soft platinum(II) acid. When compared to the nucleophilic ordering of hard acid organic substrates, the soft acid platinum(II) was quite different. Belluco *et al.* proposed that the ratio of k_y/k_s could serve as a useful measure for the reactivities of a number of nucleophiles (20). The system of *trans*-$[PtCl_2(py)_2]$ (py = pyridine) in methanol at 30°C was chosen for their studies and they defined nucleophilic reactivity, n_{pt}, as $\log (k_y/k_s)$. The expression,

$$\log (k_y/k_s)_i = s_i n_{pt} + \log (k_s)_i, \tag{1.2}$$

where s_i was called the nucleophilic discrimination factor for the ith substrate, represented quite well several other systems involving neutral substrates. The ordering of the nucleophiles by this system illustrated that it is not proton-base strength but rather softness as suggested by Pearson (19) that makes the attacking group more reactive toward platinum(II) substitution.

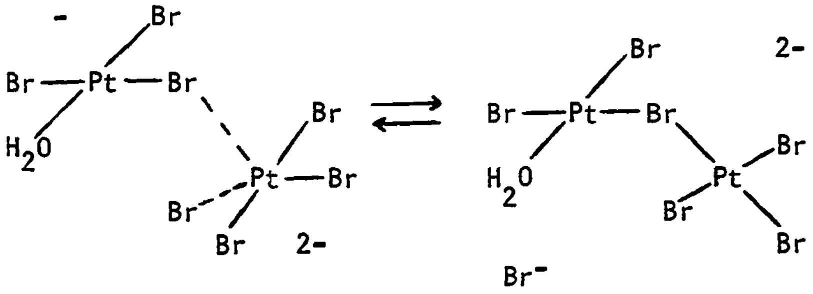
Associated with ligand substitution reactions are the concentration equilibrium quotients for aquation. Several methods have been used to determine the quotients in aqueous solution. Titration of the aquo complexes by Grinberg and Shagisultanova (21) involved using hydroxide as did the procedure by Nikolaeva and Bastukhova (22). Grantham, Elleman and Martin (23) found that the titration data needed to be corrected for the amount of hydrolysis which had occurred during the titration. The aquation of square-planar chloro-ammine complexes of platinum(II) has been studied in this laboratory (23-27) using the titrametric method. In the aquation reaction of $[Pt(dien)Br]^+$ (dien = diethylenetriamine), Martin and Bahn (28) measured the equilibrium quotient by a radiochemical technique. Elding and Leden (29) have used spectrophotometric methods for solutions of $PtCl_4^{2-}$ and have applied the method of corresponding solutions (30) to determine the aquation equilibrium quotients of this platinum complex.

The radiochemical determinations of rates for isotopic exchange reactions facilitate the study of ligand substitution reactions over a much wider concentration range. It is therefore possible to leave the pseudo first order range to which most substitution kinetics have been limited. Anomalies to the normal platinum(II) behavior have been observed in the isotopic exchange which could not be easily handled by conventional kinetic techniques (2-7,31).

As mentioned previously, the history of the anomalous behavior began with the speculations of Grinberg and Shagisultanova (1). It was 12 years after Grinberg's statement on the possible anomalous behavior of $PtBr_4^{2-}:Br^-$ exchange system, that Teggins et al. evaluated this higher order term (2). The $As(C_6H_5)_4^+$ ion was utilized to precipitate both $PtBr_4^{2-}$ and $PtBr_3(H_2O)^-$ in this exchange study. The rate law was found to be:

$$\text{Rate} = k_1[PtBr_4^{2-}] + k_2[PtBr_3(H_2O)^-] + k_d[PtBr_4^{2-}][PtBr_3(H_2O)^-] \quad (1.3)$$

where $k_1 = 2.2 \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 19$ kcals/mole, $k_2 \approx k_1$, and $k_d = 0.22$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 9$ kcals/mole at 25°C and $\mu = 0.1$. The following mechanism was proposed to account for the dimer term:



The dimer term contribution to the exchange rate was thought to have been small in Grinberg's study since high bromide concentrations were used to suppress the aquation of $PtBr_4^{2-}$.

In 1960, Grinberg and Shagisultanova reported another investigation of bromide exchange between $PtBr_4^{2-}$ and both <u>cis</u>- or <u>trans</u>-$Pt(NH_3)_2Br_2$ (32). They found, as did Gano in 1968, that an ion exchange separation of Br^- from $Pt(NH_3)_2Br_2$ was not quantitative, and that precipitation of bromide with $AgNO_3$ was not satisfactory. Precipitation of $PtBr_4^{2-}$ with $Pt(NH_3)_4^{2+}$ was the method utilized to separate the two complexes. At 0.51 mM for both $PtBr_4^{2-}$ and <u>cis</u>-$Pt(NH_3)_2Br_2$ a half time of only 10 minutes was observed at 25°C. The time of half exchange for the <u>trans</u>-$Pt(NH_3)_2Br_2$ complex was even shorter than in the cis-$Pt(NH_3)_2Br_2$ system. Grinberg explained these rapid rates by the trading of ligands between ion pairs of the type: $[Pt(NH_3)_2Br(H_2O)^+][PtBr_3(H_2O)^-]$.

These two systems have now been extensively characterized. Jolley et al. (5) found that an ion exchange separation could be used to separate trans-$Pt(NH_3)_2Br_2$ from $PtBr_4^{2-}$ and Br^- if careful control of the elution rate were maintained. They found that there was direct exchange of the ligands between trans-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ as Grinberg and Shagisultanova had speculated (32). This direct exchange was explained by a mechanism which did not involve free bromide, as had been proposed for the $PtBr_4^{2-}$: Br^- system (2). Vandegrift and Martin (6) demonstrated that direct exchange between cis-$Pt(NH_3)_2Br_2$ and $PtBr_4^{2-}$ occurred without enhanced exchange of the free bromide with either complex. Furthermore, they were able to ascertain that a large portion of this ligand-trading was between one complex and the aquated species of the other.

Another ternary bromide system, $Pt(dien)Br^+$: $PtBr_4^{2-}$: Br^- was studied by Teggins and Martin (3). Two sets of experiments were performed. One involved adding $Pt(dien)Br^+$ and then $^{82}Br^-$ tracers to an aged solution of $PtBr_4^{2-}$, $PtBr_3(H_2O)^-$ and Br^-. The $PtBr_4^{2-}$ and $PtBr_3(H_2O)^-$ were precipitated by the addition of $As(C_6H_5)_4^+$ in order to evaluate the exchange rate and compare this rate to solutions without $Pt(dien)Br^+$. The other situation involved an aged solution of $PtBr_4^{2-}$ and Br^- at isotopic equilibrium with the tagged $^{82}Br^-$

to which was added solutions of Pt(dien)Br^+ and Br^-. Subsequently, anions were replaced by an anion exchange technique, thus allowing the rate of $^{82}Br^-$ entering the cationic species to be determined. In both situations the exchange rate in the separated complex for Br was significantly increased. It was found, however, that the rate of increase was the same for both $PtBr_4^{2-}$ and Pt(dien)Br^+ within experimental error. It was the authors' opinion, based on the data that had been collected, that bromide was not traded between the two complexes as in the case of either the cis-$Pt(NH_3)_2Br_2$ system (6) or the trans-$Pt(NH_3)_2Br_2$ system (5). One complex merely assisted the other through a weak bromide bridge to exchange with the free bromide.

Only one chloride complex of platinum has been shown to exhibit abnormal exchange paths. A rate expression similar to the one found in the $PtBr_4^{2-}$: Br^- system was observed by Lokken and Martin for the $Pt(C_2H_4)Cl_3^-$: Cl^- system in 1963 (7). The ethylene ligand with its unusual bonding involving the donation of electrons from its π bond introduces interesting kinetic properties to the resulting complex. Orgel (33) and Chatt et al. (34) recognized that many of these properties are attributable to withdrawal of electrons from the platinum into the π^* orbital of the ethylene. As a result, ethylene has been shown to be such a very active trans directing group that the trans Cl ligand is virtually labile.

The rate expression found by Lokken and Martin (7) for exchange between the cis chloride on the complex and free Cl^- was determined as:

$$R_{ex} = k_c[Pt(C_2H_4)Cl_3^-] + k_c'[Pt(C_2H_4)Cl_2(H_2O)] + k_d[Pt(C_2H_4)Cl_3^-][Pt(C_2H_4)Cl_2(H_2O)] \quad (1.5)$$

where, at 25°C, $k_c = 2.9 \times 10^{-6}$ sec^{-1}, $\Delta H^{\ddagger} = 21$ kcals/mole; $k_c' = 2.8 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 22$ kcals/mole; $k_d = 8.6 \times 10^{-3}$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 19$ kcals/mole. The term involving k_d appeared similar to the one for $PtBr_4^{2-}$ and required a dimer transition state. However, the second order constant for this chloride system with the much higher activation enthalpy was only four percent as large as the corresponding term in the $PtBr_4^{2-}$ system.

Only the second order rate term was observed in an ethanol solution of $Pt(C_2H_4)Cl_3^-$ (31). Over a range of 10^5, the exchange rate was described by the single term containing k_d in Equation 1.5. Furthermore, k_d was higher by a factor of nine in ethanol than in H_2O. The increase in k_d seemed due to a much higher entropy of activation which overcame a significantly higher $\Delta H^{\ddagger}$. The high values for $\Delta S^{\ddagger}$ implied that despite the similarity in the rate expressions, the dimer mechanisms in this system were much different from the one for the $PtBr_4^{2-}$ system. In Figure 1.2 is shown the suggested mechanism (35) where $R = C_2H_4$ and S = solvent. In step 2a the attack upon $Pt(C_2H_4)Cl_2S$ is proposed to occur along an axial position. Since the trans group to the ethylene is so labile, the dimer is postulated to form the chloride bridge at that position by displacement of solvent as in 2b. In 2c a second bridge might then form by

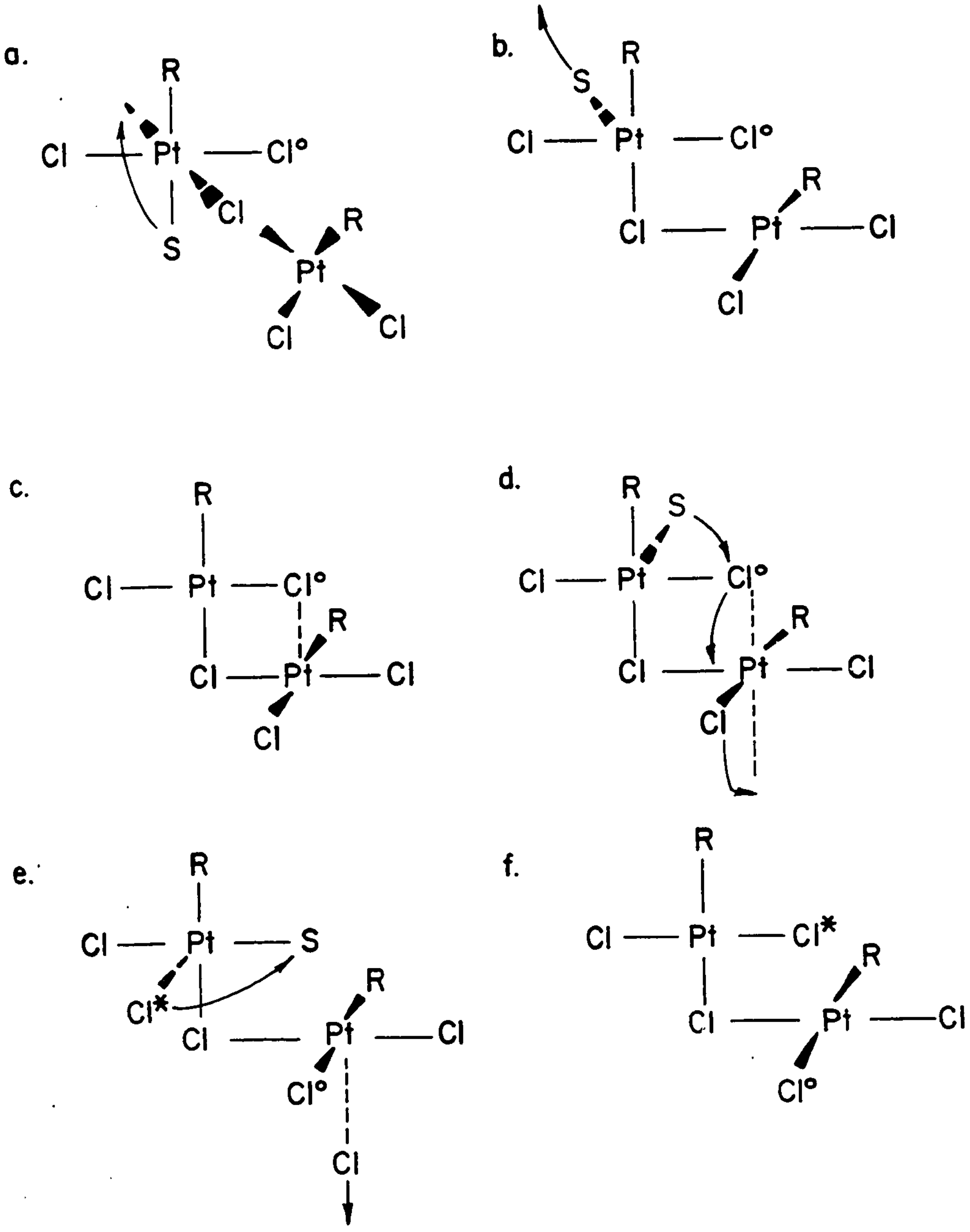


Figure 1.2. Proposed mechanism for the exchange of chloride in $Pt(C_2H_4)Cl_3^-$

donation of a pair of electrons from Cl° to the axial coordination position of the attacking complex. A concerted process, 2d, in which the Cl° is replaced by a solvent molecule on the left platinum, moves Cl° into the <u>trans</u> position opposite ethylene on the right platinum and only a single bridge remains. Exchange takes place as a tagged Cl^- replaces the solvent as shown in 2f, and the untagged Cl°, which is now <u>trans</u> to C_2H_4 equilibrates rapidly with free chloride. The step from 2d to 2e can be considered a competition step with one in which the ethylene on the right platinum moves down to occupy the position opposite Cl°, and the Cl originally opposite it, is lost to the solution thus forming the well-known <u>sym</u>-<u>trans</u>-di-μ-chlorodichlorobis(ethylene) diplatinum(II) species.

The rate constants for the exchange via dimerization in the $Pt(C_2H_4)Cl_3^-$ system are much smaller than those encountered in the bromide systems. A bromide ligand can donate electrons into a bridging bond much more readily than chloride. The idea that only a chloride system with the special <u>trans</u>-labilizing properties of a ligand like ethylene could have an observable dimer term in the rate equation needed to be tested.

EXPERIMENTAL

Materials

Platinum

Platinum's chemical behavior has been shown to be affected by what was believed to be an iridium impurity (36). Other possible metals were also suspected as impurities. Platinum used in this study had been previously purified by the chemical method suggested by Jowanovitz *et al.* (36). The basis for this method involved a triple recrystallization of the potassium hexabromoplatinate(IV) with a 97% yield for each recrystallization. Activation analysis (36-38) of the platinum demonstrated that this purification procedure was successful in removing major portions of the platinum metal contaminants.

K_2PtCl_4

The K_2PtCl_4 was prepared from iridium-free platinum by a method similar to the one described by Grantham *et al.* (23). In brief, the actual preparation involved the oxidation of platinum to H_2PtCl_6 with aqua regia. The chloroplatinic acid was then precipitated with K_2CO_3 forming the yellow K_2PtCl_6. The K_2PtCl_6 was reduced in an 80°C aqueous solution to the red K_2PtCl_4 by the slow addition of a saturated aqueous solution of SO_2. A slow evaporation was used to reduce the volume of the K_2PtCl_4 solution and thus recrystallize the sample.

The ultraviolet absorption spectrum provided the most sensitive

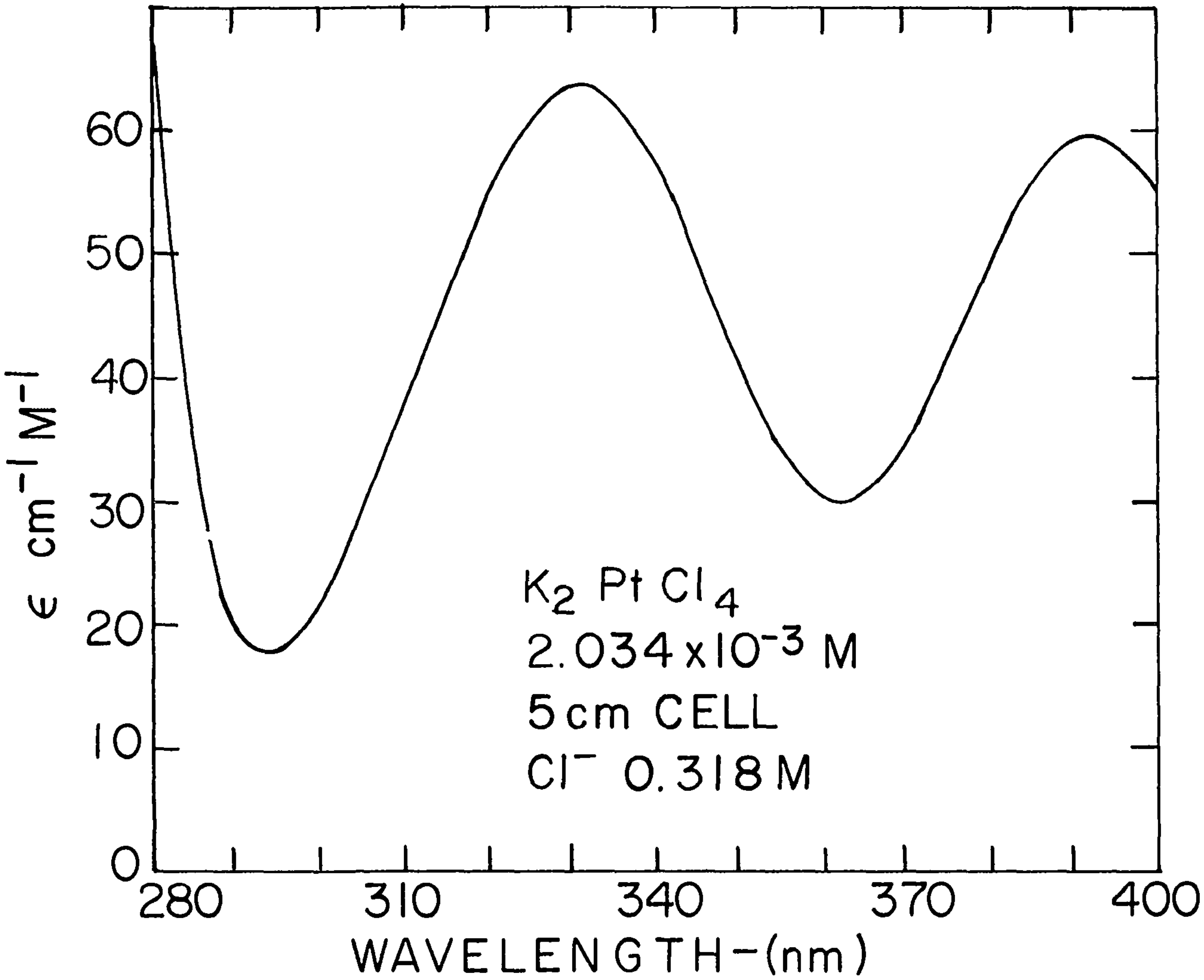


Figure 1.3. Absorption spectrum of K_2PtCl_4 in 0.318 M KCl

criterion for the purity of K_2PtCl_4. The two peaks and two valleys between 250 nm and 400 nm were used to compare the molar extinction coefficients with those reported by Hunter (39). For acceptable purity the total relative percent deviations of the four molar extinction coefficients were less than 1.2%. Figure 1.3 represents a spectrum of K_2PtCl_4 of acceptable purity.

Cis-$Pt(NH_3)_2Cl_2$

Cis-$Pt(NH_3)_2Cl_2$ was prepared by the method of Lebedinskii and Golovaya (40). Briefly, the cis-$Pt(NH_3)_2Cl_2$ was made by adding equal weights of K_2PtCl_4, KCl and ammonium acetate to a minimum amount of water (6 g K_2PtCl_4 in 80 ml). This mixture was heated to a boil for thirty minutes. The authors' method was modified in that the hot filtered solution was cooled only to 35°C for the recrystallization. To obtain acceptable purity, the cis-$Pt(NH_3)_2Cl_2$ needed to be recrystallized only once more in water containing a few drops of HCl. This hot filtered solution was also allowed to cool only to 35°C, at which time the cis-$Pt(NH_3)_2Cl_2$ was filtered off and air dried. The yield was in the range of 10%-20%, based on the amount of K_2PtCl_4 used.

A thermogravimetric analysis gave only the amount of platinum in the compound: 65.01% found, 65.02% calcd. Again, the most sensitive criterion for purity was provided by an ultraviolet absorption spectrum. Figure 1.4 illustrates the spectrum of a sample of cis-$Pt(NH_3)_2Cl_2$ of representative purity. The absorbance

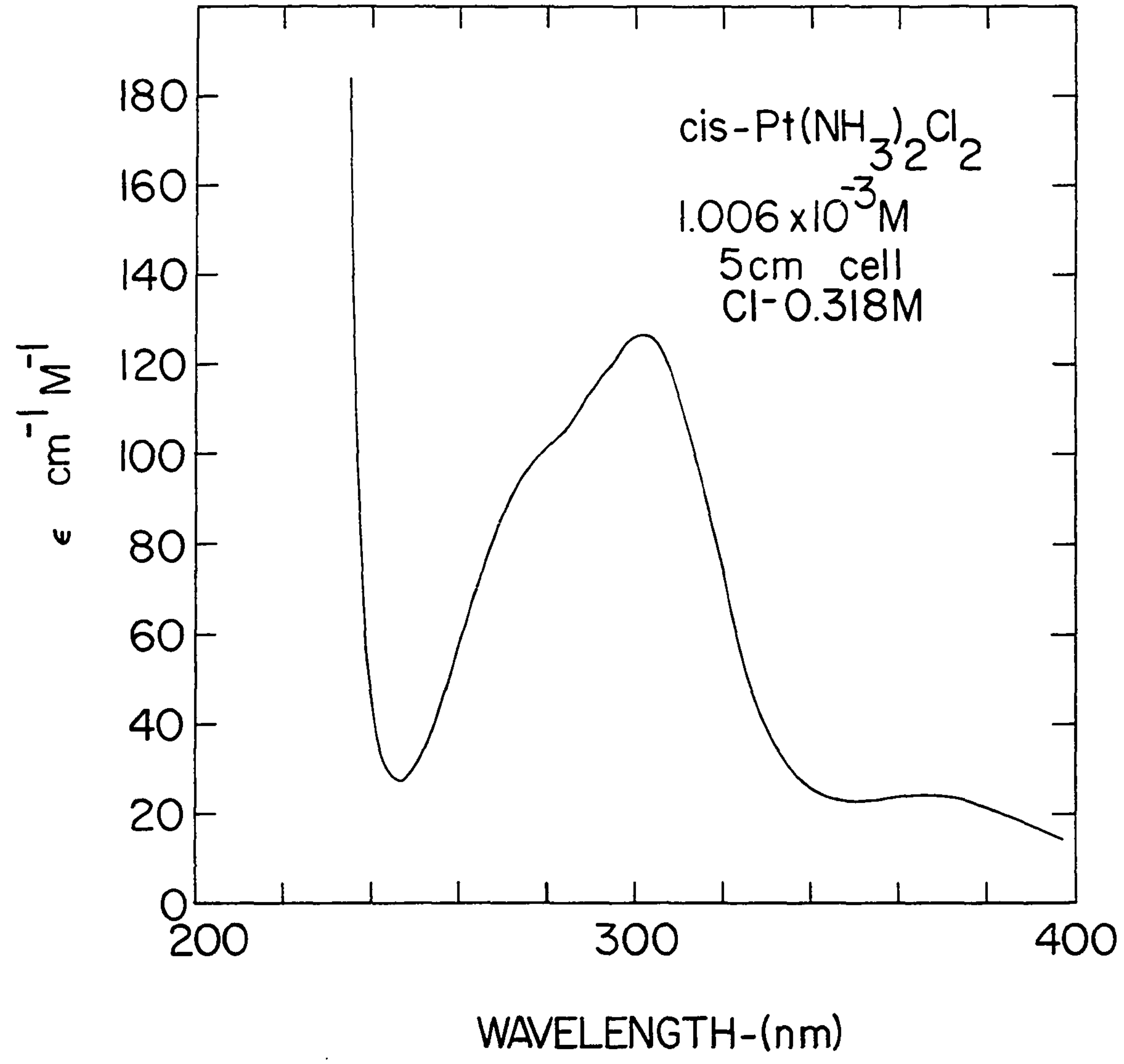


Figure 1.4. Absorption spectrum of cis-Pt(NH$_3$)$_2$Cl$_2$ in 0.318 M KCl

ratio between the peak at 300 nm and the valley at 247 nm needed to be greater than 4.5 for the preparations to be of acceptable purity under the conditions indicated in Figure 1.4.

Dimercury(I) perchlorate

$Hg_2(ClO_4)_2$ was prepared by the method described by Vogel (41). In this synthesis mercury, mercury(II) oxide and perchloric acid were reacted together; any residue left after vigorous stirring for one hour was filtered off. The filtrate was then diluted to the prescribed volume, resulting in an approximately 0.1 N solution.

Sodium hydroxide solution

A carbonate-free solution of sodium hydroxide was prepared by the method published in the forty-fourth edition of the Handbook of Chemistry and Physics (42). The procedure involved filtering a 50% to 50% by weight ratio of NaOH and degassed water through a porous asbestos mat. This operation and the storage of the sodium hydroxide solution was accomplished under a purified nitrogen atmosphere.

Ion exchange resin

Dowex 1-X8, 50-100 mesh anion exchange resin was purchased from Dow Chemical Company in ten pound lots. The resin was converted from the original chloride form to the nitrate form by passing a 5% solution of $NaNO_3$ through the resin bed until chloride was no longer detectable by precipitation with $Hg_2(ClO_4)_2$. The resin was back-washed for at least one hour to remove any foreign matter or broken beads. This procedure also washed away any excess $NaNO_3$ or small amounts of NaCl remaining after the elution step.

Water

All water was initially flash-distilled in the tap distilled water system; the water was then distilled from an alkaline permanganate solution to remove the organic impurities.

Radioactive chloride (^{36}Cl)

Radioactive ^{36}Cl was purchased in the form of 2.68 N HCl from New England Nuclear Corporation, Boston, Massachusetts. The isotope for the kinetics experiments was taken directly from the shipping container without alteration.

Other reagents

All other materials were of analytical reagent grade, meeting the specifications of the American Chemical Society.

Equipment

Ion exchange columns

The columns were identical to those described by Vandegrift (43). The resin bed length, however, averaged 15 cm. When a radioactive tracer technique was used, the column uptake of 20 ml of 0.134 M Cl^- was shown to be better than 99.8%, providing a flow rate equal to or less than one drop per second was used with the sample and the first 100 ml of H_2O eluant.

Filtration equipment

The Hg_2Cl_2 samples were collected on circular filter disks in a chimney filter apparatus described by Adams (44).

Balance

A Sartorius single pan analytical balance, Model 2404, was used for precise weighings. The balance has a 100 gram capacity with a five place digital readout capacity with a precision of ± 0.05 mg.

Constant temperature bath

At both 25°C and 35°C, the temperature of the solutions was controlled to within ± 0.05° in a Sargent constant temperature bath, equipped with a Philadelphia microset thermoregulator, a Sargent Spm 2770 controller and a Sargent-type NSI-12 circulating heater. A refrigeration unit was utilized to cool the water bath at 25°C.

Beta ray counting equipment

The radioactive samples were counted with an end-window Geiger-Müeller counter, serial 3H, of Nuclear-Chicago, Chicago, Illinois. Background activity was decreased by enclosing the samples in a lead shield manufactured by Technical Associates, Glendale, California. The counter was operated in conjunction with a Model 100, Berkeley Instrument Company scaler. The samples were mounted on cardboard and placed in a reproducible manner with an aluminum template on a shelf at a distance of 7 mm from the counter window.

Automatic titrator

Titrations were performed by means of a Radiometer Model SBR2c/ABU1c/TTT1c automatic recording titrator. The apparatus contained a 0.2500 ml capacity buret with an accuracy of ± (1 μl + 0.07%). The water-jacketed titration vessel (used for temperature control) was insulated and covered with black opaque tape. The opaque lid of the titration vessel contained a small stirring paddle, a gas outlet for flushing the system with grade "A" purified nitrogen to remove carbon dioxide, and the two electrodes. The indicator electrode was a Radiometer #G202c glass electrode; a Radiometer saturated calomel electrode, #K401, sufficed for the reference electrode.

Thermogravimetric analyzer

Thermogravimetric analyses were performed on a DuPont 950 differential thermal analyzer used in conjunction with a DuPont 900 differential thermal analyzer recorder from the Instrument Products Division of DuPont, Incorporated, Wilmington, Delaware.

Computation equipment

All computer programs were run on the IBM 360/65-370/158 digital computer. The Cal-Comp Digital Incremental Plotter 470 prepared the plots directly from computer magnetic tape output.

Timers

Precision Scientific Company timers were used which registered intervals to 0.01 minutes.

Procedures

Equilibrium quotients

Cis-$Pt(NH_3)_2Cl_2$ in aqueous solution has been shown to undergo replacement of chloride ligands by H_2O according to the reactions:

$$\underline{\text{cis}}\text{-Pt(NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O} \rightleftarrows \underline{\text{cis}}\text{-Pt(NH}_3)_2(\text{H}_2\text{O})\text{Cl}^+ + \text{Cl}^-,\ K_1, \qquad (1.6)$$

$$\underline{\text{cis}}\text{-Pt(NH}_3)_2(\text{H}_2\text{O})\text{Cl}^+ + \text{H}_2\text{O} \rightleftarrows \underline{\text{cis}}\text{-Pt(NH}_3)_2(\text{H}_2\text{O})_2^{2+} + \text{Cl}^-,\ K_2. (1.7)$$

Each H_2O ligand could be titrated for one acidic proton with an approximate end point of pH 9. Such titrations from a range of concentrations provided the extent of hydration from which the equilibrium quotients could be calculated. The solutions, in which a constant temperature was maintained to ± 0.05°, were aged for periods ranging from 6 to 16 days. The flasks in which the solutions were aged were covered with black opaque tape to exclude light. The ionic strength of 0.318 M was adjusted by the addition of KNO_3.

The solutions were prepared by dissolving enough <u>cis</u>-$Pt(NH_3)_2Cl_2$ to make a solution just below the saturation limit. Aliquots of this solution were then used to prepare the more dilute solutions. The carbonate-free NaOH stock solution was diluted and used under a nitrogen atmosphere. Primary standard grade potassium acid phthalate was dissolved and diluted to a volume from which could be measured a 20.0 ml sample which, when titrated, gave an end point between 60% and 90% of the automatic buret volume. These primary standard solutions were also thermostatically stored.

A typical titration consisted of withdrawing an aliquot (usually 15 ml) from the aged solution and placing it in the water-jacketed titration cell. Grade "A" nitrogen was passed through the sample from four to five minutes with constant mechanical stirring. The titration was completed within sixty seconds. A clean, dry titration vessel was then introduced into the jacketed cell in order to reach the equilibrium temperature before the next reaction. The electrodes, stirring paddle and gas inlet were all washed and dried before each new titration. A typical titration curve is illustrated in Figure 1.5.

A series of titrations was performed on each solution. Initially, the electrodes were standardized at two or three different pH values, using buffered pH solutions. Two or three titrations of the primary standard were then carried out. The aliquot size and volume of the cis-$Pt(NH_3)_2Cl_2$ solution being used dictated the number of titrations completed before another set of primary standard titrations was repeated. One-half of the solution was used, then the series was repeated in order to use up all of the solution. A range of seven to fourteen titrations were performed at each concentration of cis-$Pt(NH_3)_2Cl_2$.

A few of the titrations were run at one-third the normal buret speed. Within experimental error, the end points were the same at both the normal and slower speeds, indicating that essentially no aquation occurred during titration. Solutions containing only 0.318 M KNO_3 were titrated in order to determine the blank volume of the NaOH needed to reach the end point pH of the cis-$Pt(NH_3)_2Cl_2$ solutions. The adjusted titers were determined by subtracting the blank volumes from the total titer volumes.

Exchange in the cis-$Pt(NH_3)_2Cl_2$: Cl^- system

Calculated amounts of cis-$Pt(NH_3)_2Cl_2$, KCl and KNO_3 were weighed with a precision of 0.05 mg and placed in a 200 ml volumetric

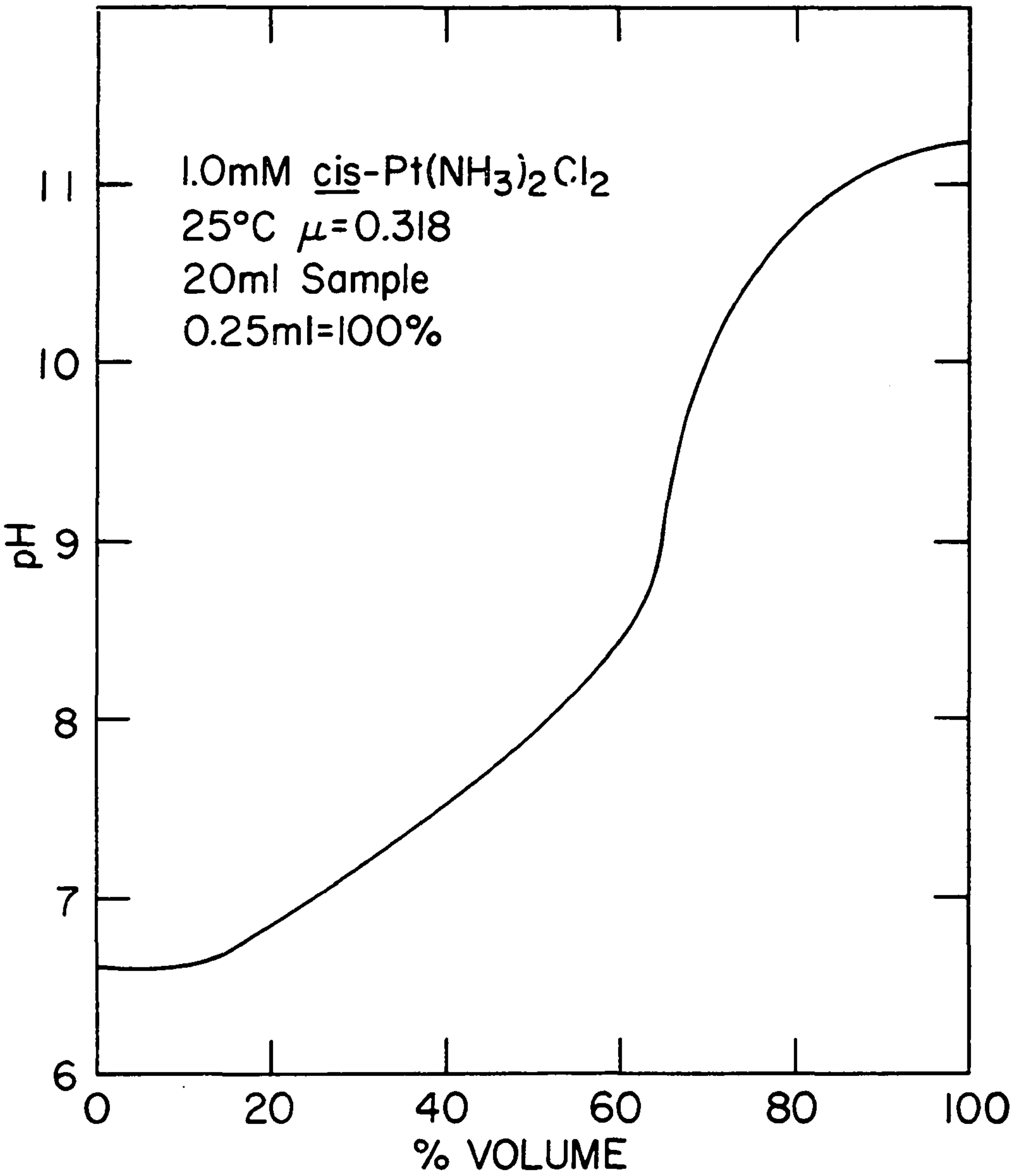


Figure 1.5. A typical titration of <u>cis</u>-$Pt(NH_3)_2Cl_2$ solution

flask. The flask was filled with distilled water and shaken until all of the components were dissolved. After dissolution, the flask was covered with black opaque tape and placed in a constant temperature bath to age for at least three days.

Exchange was initiated by the addition of 25λ of the HCl tracer solution. At measured time intervals, 20 ml aliquots were withdrawn from the exchange solution. The exact time was recorded when the sample volume reached the top of the anion exchange bed. This process took approximately three minutes. The first 100 ml of H_2O eluant were passed through the exchange resin in approximately fifteen minutes, while the final 50 ml of H_2O were allowed to rapidly flow through the column in less than three minutes. All samples were treated in the same manner until the exchange run was completed. Ten milliliters of concentrated aqueous ammonia were added to each of the eluted solutions. Ammonia performed the dual function of stripping the chloride off the platinum complex,

$$\underline{\text{cis}}\text{-Pt(NH}_3)_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{Pt(NH}_3)_4^{2+} + 2\text{Cl}^-, \qquad (1.8)$$

and of maintaining a high pH of the solution so no loss of chloride through evolution of HCl would occur. The solutions were covered with a Fisher Speedy Vap watch glass and placed on a hot plate to evaporate. When the volume reached 50 ml, the beakers were removed from the hot plate and allowed to cool.

Infinity-time samples were taken during the exchange run. This was accomplished by taking three 1.0 ml samples directly from the exchange solution. Distilled water (150 ml) was then added to the infinity-time samples. Since the samples were not separated into different species, the total specific activity of the samples equalled the specific activity of any one component at infinity-time. The concentrated ammonia was added; the solutions were concentrated and were precipitated following the procedure for the individual exchange samples.

$AgNO_3$, which was used in the study of Reishus and Martin (26), was replaced by $Hg_2(ClO_4)_2$. Dimercury(I) perchlorate had the advantages that its chloride precipitates were more uniform in particle size, it was not so sensitive to photodecomposition and it had a higher equivalent weight than AgCl. Precipitation of the samples was effected by acidifying the cooled solutions with dropwise addition of concentrated nitric acid and the addition of excess $Hg_2(ClO_4)_2$. The precipitate was then allowed to settle before the filtering procedure was begun.

The samples were collected on previously weighed filter paper disks and allowed to dry at 60°C for at least one hour after they had been washed three times each with distilled water, ethanol and ether. Three weighed filter disks were carried through the washing and drying procedure in order to obtain tare weights. Changes in the tare weights varied up to 15% of the lowest sample weight, depending on the humidity.

The dried precipitates were carefully weighed in a lightweight aluminum dish to avoid contaminating the single pan analytical balance. The filter disks were mounted on cardboard squares with wide pieces of clear tape in order to prevent contamination and to provide a flat, reproducible surface for counting.

Before any of the exchange runs were counted, a self-absorption curve was determined for Hg_2Cl_2 using ^{36}Cl as the radioactive species. A plot of the self-absorption curve is shown in Figure 1.6. In the range of 1 mg to 5 mg of precipitate per square centimeter (where the exchange samples occurred), the self-absorption curve showed little variation in specific activity for the 0.72 Mev beta ray given off by ^{36}Cl.

The samples on the cardboard were taped to an aluminum template and placed on a shelf under the Geiger-Müeller tube. Counting times ranged from 10 to 30 minutes depending on the amount of activity. The time was varied in order to have the standard deviation of the counting rate less than 5%. The standard deviation of the counting rates was actually much less than 5%, as the activity increased during the exchange experiment. Specific activity for each sample was calculated by dividing the counting rate by the weight of the precipitate.

Exchange in the cis-$Pt(NH_3)_2Cl_2$: tagged $PtCl_4^{2-}$: Cl^- system

For the exchange of cis-$Pt(NH_3)_2Cl_2$ in the presence of tagged $PtCl_4^{2-}$, two solutions of equal volume were prepared. One was prepared by dissolving weighed amounts of KCl, KNO_3 and cis-$Pt(NH_3)_2Cl_2$ in a 100 ml volumetric flask, and the other solution was made by dissolving the same amounts of KCl and KNO_3 and the desired amount of K_2PtCl_4. All flasks were covered with black opaque tape as before

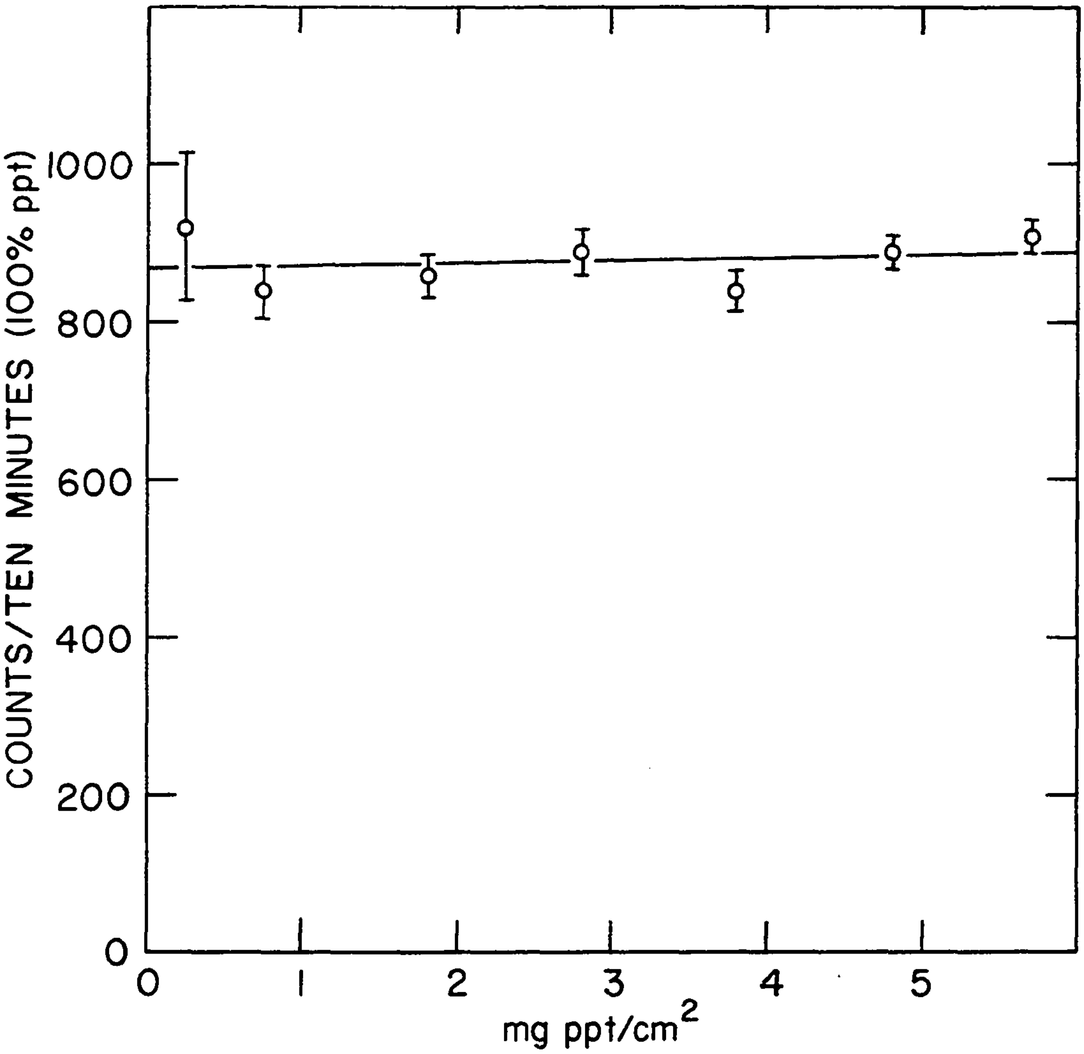


Figure 1.6. Self-absorption curve of Hg_2Cl_2 for the 0.72 Mev beta ray of ^{36}Cl

and to the K_2PtCl_4 solution was added 25λ of the HCl tracer solution. These solutions were allowed to stand for at least 3 days, and in some cases for as long as 30 days in the thermostatically controlled water baths. The exchange was initiated by mixing the two solutions. The remainder of the procedure was identical to that of the *cis*-$Pt(NH_3)_2Cl_2$: Cl^- system.

Exchange in the cis-$Pt(NH_3)_2Cl_2$: untagged $PtCl_4^{2-}$: Cl^- system

The solution for this exchange study was prepared by dissolving the desired amounts of KCl, KNO_3, *cis*-$Pt(NH_3)_2Cl_2$ and K_2PtCl_4 in a 200 ml volumetric flask covered with black tape. The solution was allowed to age in the thermostatically controlled water bath for at least three days. To initiate the exchange, 25λ of the HCl tracer was added to the solution. The remainder of the procedure followed that of the *cis*-$Pt(NH_3)_2Cl_2$: Cl^- system.

TREATMENT OF DATA AND RESULTS

Aquation Equilibria

The titrations of equilibrated solutions of cis-$Pt(NH_3)_2Cl_2$ in water at a constant ionic strength were used to calculate the concentration equilibrium quotients for Equations 1.6 and 1.7. These quotients had previously been determined by Reishus and Martin (26) using a manual titration technique; it was felt that better values could be obtained because of the automatic titration system which had become available.

The end points of titration were determined by the second derivative method. The neutralization points were, in fact, the inflection points of the curve (45). This procedure has been recorded in Table 1.1 for the titration curve illustrated in Figure 1.5. The pH was read from the recorded titration curve every 1% of the buret volume around the inflection point and then a linear interpolation was made between the two readings where the Δ^2pH changed signs. In some cases where the titration volume was small, every 2% volume units were used.

Since the end point occurred above pH of 8.0 in all cases, and since such a small amount of acid was being titrated, it was necessary to subtract from the end point volume of the acid titration the amount of base needed to raise the pH of a blank solution to the end point pH. The blank solution contained only the KNO_3 used to regulate the ionic strength to 0.318 M; furthermore, the blank was determined in triplicate and was always the same volume as the

Table 1.1. Second derivative method for end point determination of the acid-base neutralization illustrated in Figure 1.5; temperature = 25°C; [NaOH] = 2.84 X 10^{-4} mmoles/% vol; 100% = 0.25 ml

Volume (%)	pH	ΔpH	Δ^2pH	End Point
64	8.87			%V = 65 + 6/13
		23		= 65.46
65	9.10		+6	
		29		
66	9.39		-7	
		22		
67	9.61			

titrated volume of complex-containing solution. For example, the blank for the titration used in Table 1.1 was 3.60%, which gave an adjusted titer value of 61.86%. Each titration was treated in an identical fashion.

All titrations of one concentration of platinum complex were used to calculate the arithmetic mean except those which showed erratic electrode response. The standard deviation of the titer mean involved three separate sets of titrations (platinum complex solution, blank and NaOH standardization). The total standard deviation, $\sigma_{\bar{T}}$, for the titer mean was calculated by means of the equation

$$\sigma_{\bar{T}}^2 = \bar{N}_B^2 \left(\sigma_{\bar{V}e}^2 + \sigma_{\bar{V}_B}^2\right) + (\bar{V}e-\bar{V}_B)^2 \, \sigma_{\bar{N}_B}^2 \tag{1.9}$$

where $\bar{N}_B$ = mean normality of NaOH, $\bar{V}e$ = mean total titration volume, $\bar{V}_B$ = mean volume blank and the σ's are the calculated standard deviations of the related means.

The equilibrium quotients, K_1 and K_2, from Equations 1.6 and 1.7, are related to the titer by the following derivation which follows the derivation presented by Sanders and Martin (25) in 1961. For the purpose of clarity and brevity, the following symbols are defined:

a = total complex concentration;

X_e = equilibrium concentration of the monoaquo species;

Y_e = equilibrium concentration of the diaquo species;

T = equilibrium acid concentration = $X_e + 2Y_e$.

The thermodynamic equilibrium constants are defined in terms of activities which can be written in terms of activity coefficients and concentrations. If the activity coefficients are isolated from the concentrations, a new term can be defined as the isolated coefficients term. The concentration equilibrium quotients can be defined as the thermodynamic equilibrium quotients multiplied by this new term. The concentration equilibrium quotients may then be written as:

$$K_1 = \frac{(X_e)(X_e + 2Y_e)}{(a - X_e - Y_e)}\,, \tag{1.10}$$

and

$$K_2 = \frac{(Y_e)(X_e + 2Y_e)}{(X_e)}\,. \tag{1.11}$$

With the introduction and definition of the equilibrium titer, T, the product of K_1 and K_2 may be rearranged to yield a cubic equation in T. Equations 1.10 and 1.11 may be rewritten as:

$$K_1 = \frac{(X_e)(T)}{(a-T + Y_e)}, \tag{1.12}$$

and

$$K_2 = \frac{(Y_e)(T)}{(X_e)}, \tag{1.13}$$

with the product being:

$$K_1K_2 = \frac{(Y_e)(T)^2}{(a-T + Y_e)}, \tag{1.14}$$

which, rearranges to give:

$$(a-T)K_1K_2 = (Y_e)(T^2-K_1K_2). \tag{1.15}$$

Equation 1.13 may be written as:

$$K_2 = \frac{(Y_e)(T)}{(T-2Y_e)}, \tag{1.16}$$

which, upon rearrangement, yields:

$$K_2T = (Y_e)(T + 2K_2). \tag{1.17}$$

The solution of Equation 1.17 for the equilibrium concentration of the diaquo species gives:

$$Y_e = \frac{K_2T}{(T + 2K_2)}. \tag{1.18}$$

Substitution of Y_e from Equation 1.18 into Equation 1.15, followed by rearrangement, yields:

$$T^3 + (T-a)TK_1 + (T-2a)K_1K_2 = 0. \tag{1.19}$$

Equation 1.19 is a function of two variables (a and T) and two parameters (K_1 and K_1K_2). Coley (46) designed a computer program to perform a weighted nonlinear least squares analysis for aquation equilibria of a disubstitutable complex. He used a generalized least squares analysis described by Wentworth (47), who used the pattern set by Deming (48). The least squares adjustment was a minimization of the sum of the weighted squares of the differences between the experimentally determined and the calculated values of T. The only modification to the basic program was the use of weights as only $1/\sigma_{T_i}^2$, where σ_{T_i} was the standard deviation of T as calculated for the a_i concentration of the platinum complex. The original program multiplied $1/\sigma_{T_i}^2$ by N_i, which was the number of titrations used to determine $\bar{T}_i$. Since σ_i was already calculated on the basis of the number of titrations, the multiplication of $1/\sigma_{T_i}^2$ by N_i resulted in an unjustified double weighting of the titer values.

The least squares plots of Equation 1.19, along with experimental points, are shown for both 25°C and 35°C in Figure 1.7. The calculated and observed titer values, at a given concentration of <u>cis</u>-$Pt(NH_3)_2Cl_2$ for both 25°C and 35°C, are tabulated in Tables 1.2 and 1.3, respectively. K_1 and K_2 obtained from the least squares treatment for 25°C and 35°C, together with the indicated $\Delta H°$ values, are included in Table 1.4.

With the wider range of concentrations possible in the present work and with a larger number of titrations made easier by the

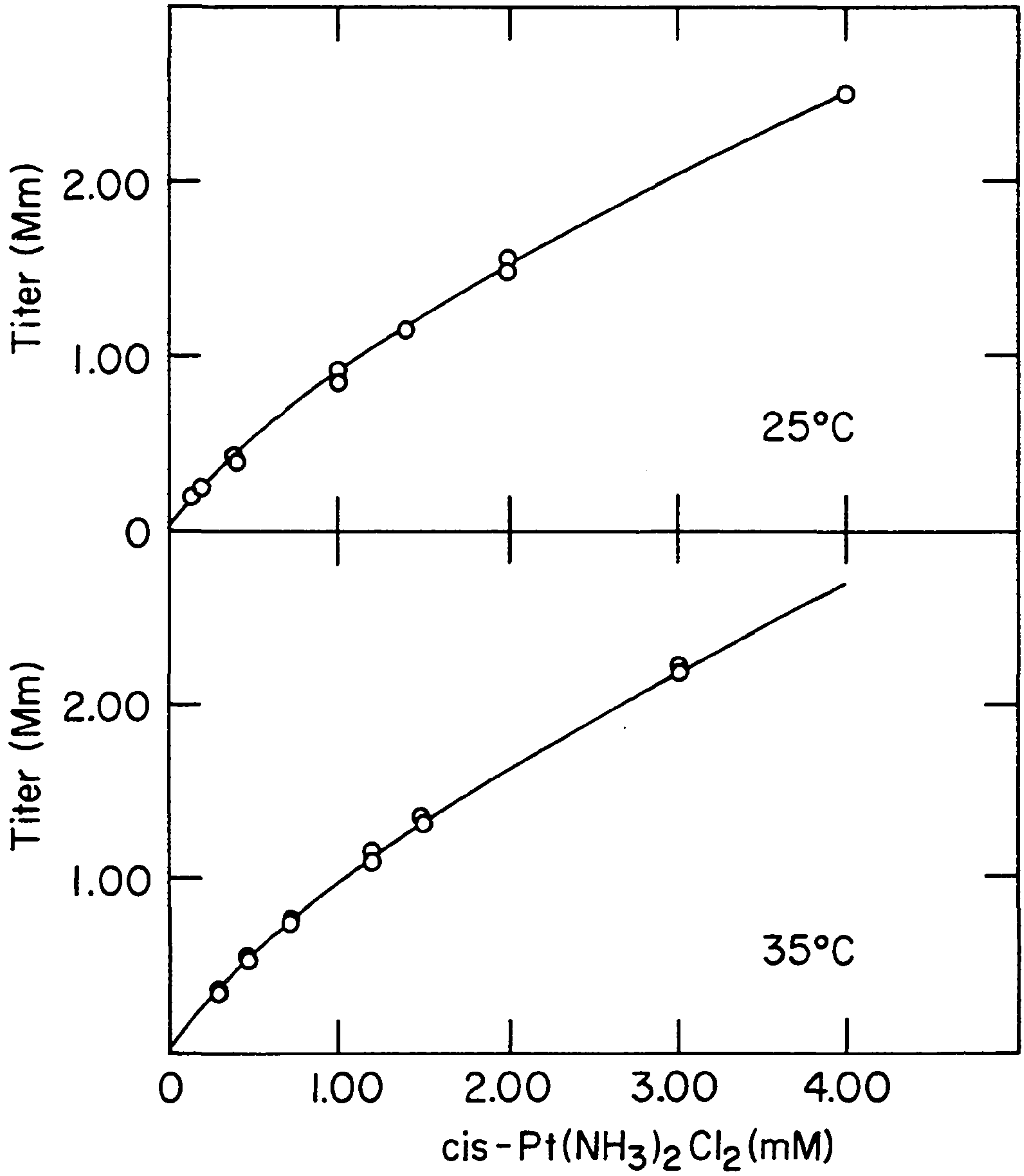


Figure 1.7. Experimental titer values (0) with the least squares adjusted curves at 25°C and 35°C for <u>cis</u>-Pt$(NH_3)_2Cl_2$

Table 1.2. Titration data for *cis*-$Pt(NH_3)_2Cl_2$, at an ionic strength of 0.318 M and 25°C

Number Titrations	Total *c*-$Pt(NH_3)_2Cl_2$ a (mM)	Equilibrium Titer, T (mM)	
		Obsvd.	Calcd.
8	0.1202	0.162 ± .003	.1642
9	.2004	.255 ± .003	.2501
8	.3989	.440 ± .006	.4376
9	.4007	.425 ± .005	.4392
8	.9972	.876 ± .010	.9052
10	1.0018	.930 ± .005	.9084
8	1.3960	1.157 ± .011	1.1716
7	1.9944	1.482 ± .019	1.5291
10	2.0037	1.558 ± .009	1.5343
13	4.0073	2.504 ± .021	2.5123

automatic titrator, the values for K_1 and K_2 were statistically more reliable than those previously determined manually (26). Even so, the present values of K_1 are in fair agreement with the earlier values. However, the present values of K_2 are much smaller. In Figure 1.8, the plots of the concentrations of unaquated, monoaquo and diaquo species versus the initial concentration of *cis*-$Pt(NH_3)_2Cl_2$ for both 25°C and 35°C illustrate the importance of titrating low concentrations of *cis*-$Pt(NH_3)_2Cl_2$ in order to have a significant amount of the diaquo species present to assure a satisfactory

Table 1.3. Titration data for cis-Pt$(NH_3)_2Cl_2$, at an ionic strength of 0.318 M and 35°C

Number Titrations	Total c-Pt$(NH_3)_2Cl_2$ a (mM)	Equilibrium Titer, T (mM) Obsvd.	Calcd.
8	0.2994	0.357 ± .005	.3771
8	.2997	.373 ± .003	.3774
9	.4791	.550 ± .002	.5495
9	.4795	.557 ± .004	.5499
9	.7187	.759 ± .005	.7565
9	.7192	.764 ± .004	.7569
12	1.1978	1.111 ± .005	1.1223
11	1.1986	1.126 ± .006	1.1229
12	1.4972	1.334 ± .005	1.3284
11	1.4980	1.332 ± .006	1.3290
14	2.9944	2.202 ± .009	2.2041
12	2.9970	2.200 ± .010	2.2055

measure of K_2. The lowest concentration of cis-Pt$(NH_3)_2Cl_2$ titrated by Reishus and Martin (26) was 1.5 mM; whereas, it was possible with the automatic titrator to use concentrations as low as 0.12 mM in the present work.

The values of $\Delta H°$ were positive and no more than 10 kcal, which

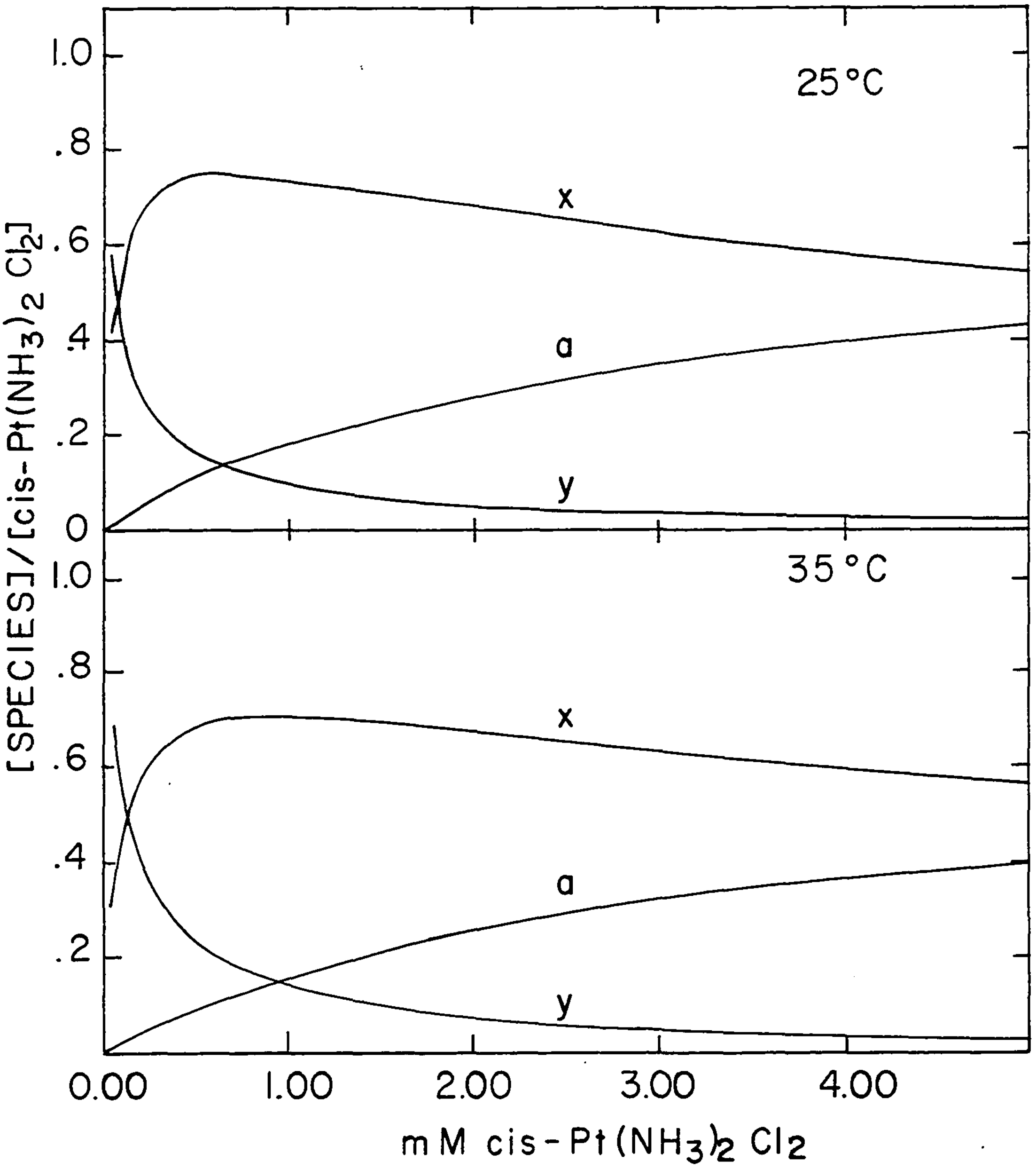


Figure 1.8. Concentrations of species in a solution vs. the initial concentration of cis-Pt$(NH_3)_2Cl$; a = [cis-Pt$(NH_3)_2Cl_2$]; x = [cis-Pt$(NH_3)_2(H_2O)Cl^+$]; y = [cis-Pt$(NH_3)_2(H_2O)_2^{2+}$]

Table 1.4. Aquation equilibrium quotients for *cis*-$Pt(NH_3)_2Cl_2$ at an ionic strength of 0.318 M

	K_1	K_2
25°C	$3.63 \pm 0.22 \times 10^{-3}$ M	$1.11 \pm 0.14 \times 10^{-4}$ M
35°C	$4.37 \pm 0.13 \times 10^{-3}$ M	$1.88 \pm 0.08 \times 10^{-3}$ M
$\Delta H°$	3.4 ± 1.2 kcal	10 ± 2 kcal

is rather typical for aquation reactions of halide ligands in platinum(II) complexes. Both K_1 and K_2 for *cis*-$Pt(NH_3)_2Br_2$ complex (6) were very nearly one-third the values for the chloride complex, which was consistent with the assignment of Pt(II) as a class B metal by Ahrland, Chatt and Davies (49), or a soft acid by Pearson (19).

Chloride Exchange

The chloride ion component comprised the largest fraction of chlorine for all of the exchange experiments. If the chloride concentration is held at sufficiently high levels, chloride is found in solution predominately in the three forms: *cis*-$Pt(NH_3)_2Cl_2$, Cl^- and $PtCl_4^{2-}$. Both complexes undergo aquation of the chloride ligands; the aquation process actually contributes to isotopic exchange. With the lowest chloride concentration employed (67 mM), less than 6% of the *cis*-$Pt(NH_3)_2Cl_2$ and less than 18% of the $PtCl_4^{2-}$ would have undergone aquation at equilibrium. Very great complications were avoided in the treatment by utilization of the approximation that the aquation was negligible. The symbols a, b and c have been used for the total concentration added to solution of cis-$Pt(NH_3)_2Cl_2$, Cl^-, and $PtCl_4^{2-}$ respectively. The exchanging system contained only significant concentrations of the components shown in the scheme in Figure 1.9.

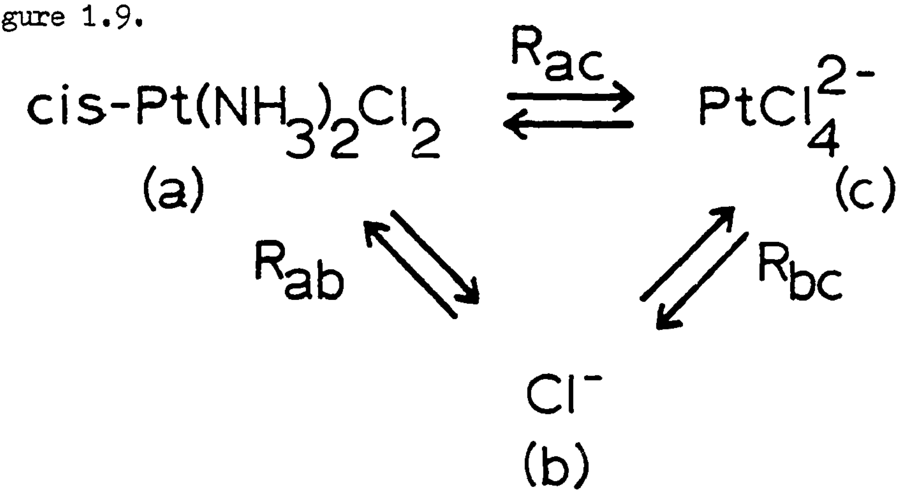


Figure 1.9. Exchange scheme for the three-component system, cis-$Pt(NH_3)_2Cl_2$: $PtCl_4^{2-}$: Cl^-

Isotopic exchange can occur between any pair of components so a description of such exchange required the evaluation of the three indicated rates R_{ab}, R_{bc} and R_{ac} (mols l^{-1} sec^{-1}). Two independent differential equations were needed to describe isotopic exchange in such a three component system:

$$\frac{du_a}{dt} = R_{ab}(S_b-S_a) + R_{ac}(S_c-S_a), \qquad (1.20)$$

$$\frac{du_c}{dt} = R_{bc}(S_b-S_c) + R_{ac}(S_a-S_c). \qquad (1.21)$$

The subscripts refer to the components indicated and u represents a concentration of radioactive ^{36}Cl, normally specified in units of cts m^{-1} l^{-1}. The S quantities represent specific activities of the indicated component (cts m^{-1} mol^{-1}) and are defined by the following:

$$S_a = u_a/2a; \; S_c = u_c/4c; \; S_b = (I-u_a-u_c)/b, \qquad (1.22)$$

where I is the total concentration of ^{36}Cl. The infinity-time values, as mentioned previously, were obtained by the collection and counting of the total chloride of a solution aliquot together with the relation:

$$S_{\infty} = I/(2a + b + 4c). \qquad (1.23)$$

In a two-component exchange system, F_a is considered the fraction of exchange where F_a is calculated using each determined value of u_a:

$$F_a = (u_a-u_{a,o})/(u_{a,\infty}-u_{a,o}). \qquad (1.24)$$

(The subscripts o and ∞ refer to zero and infinity-time). For a three-component system, however, F_a can, in certain circumstances, be greater than one. For a two-component system, the quantity $(1-F_a)$ is an exponential function in time; therefore, a plot of $\ln(1-F_a)$ is linear in time. From such a plot a half-time of exchange, $T_{\frac{1}{2}}$, can be evaluated. For a three-component exchange $(1-F_a)$ is the sum or difference of two exponential functions, and the plot of $\ln(1-F_a)$ cannot be linear over all time. For all conditions listed in Table 1.5, the plots of $\ln(1-F_a)$ could be followed to values of 0.35 - 0.2 for $(1-F_a)$. The plots over this region did not deviate from straight lines by more than the uncertainties in the points. A typical exchange experiment is plotted in Figure 1.10.

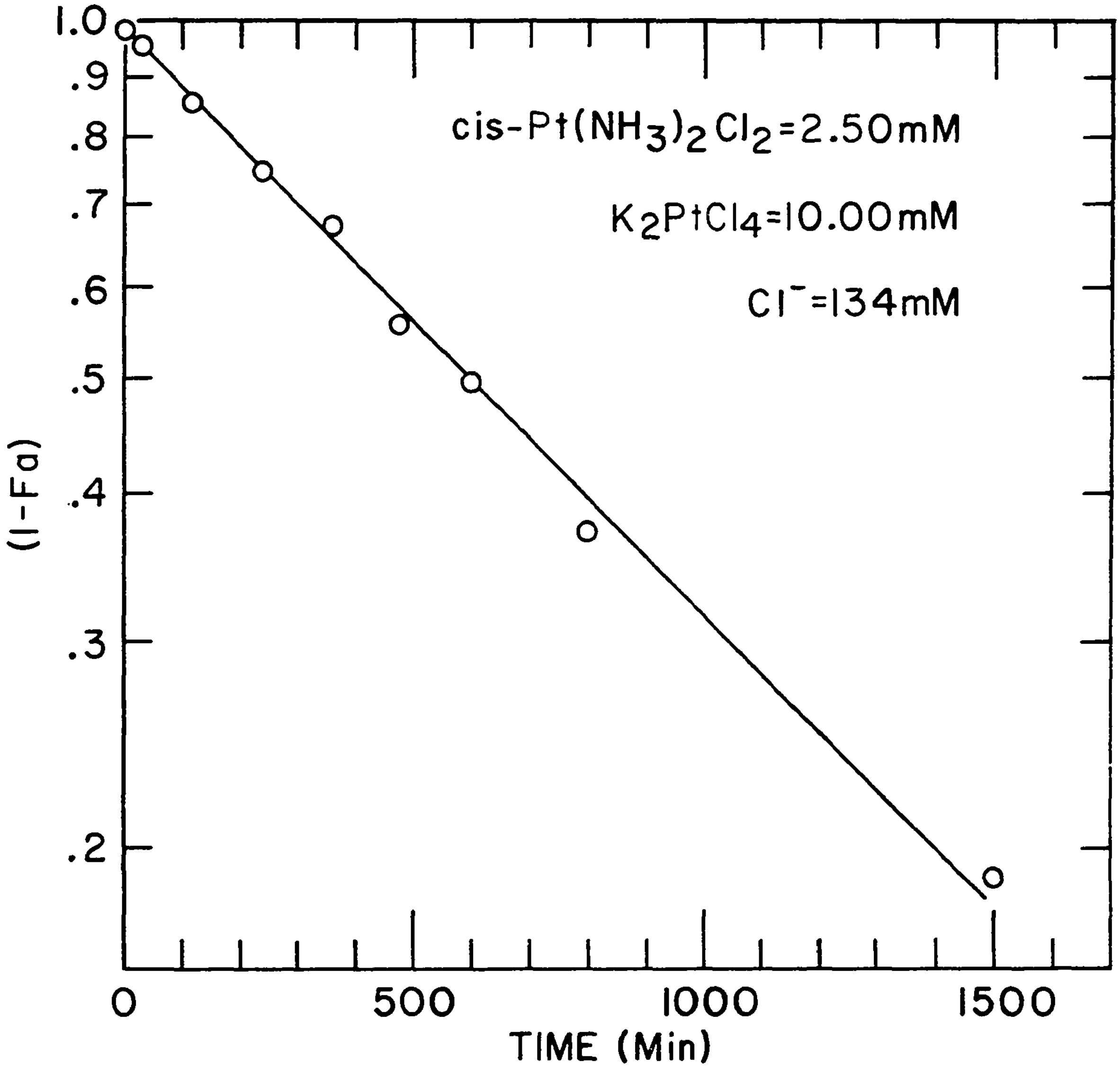


Figure 1.10. Typical exchange experiment with an observed time of half exchange equal to 609 ± 14 minutes

Table 1.5. Isotopic exchange experiments at 25°C and an ionic strength of 0.318 M

Number Experiments	c-Pt$(NH_3)_2Cl_2$ a (mM)	Cl^- b(mM)	$PtCl_4^{2-}$ c(mM)	S_c°	Time of Half-Exchange (minutes) Obsvd.	Calcd.
2	5.00	134	0	-	903 ± 45	936
6	2.50	134	0	-	984 ± 40	970
6	2.50	134	10	$2S_b^\circ$	612 ± 27	637
4	2.50	134	20	$2S_b^\circ$	517 ± 33	491
2	2.50	67	10	$2S_b^\circ$	524 ± 6	528
2	2.50	134	10	0	774 ± 35	727

Observed times of half exchange for each experiment were calculated as (ln 2) divided by the slope of the weighted linear least squares fit to the experimental points. Average values along with their standard deviations for the observed times of half exchange in the experiments under each set of experimental conditions are listed in Table 1.5.

It is seen from Table 1.5 that the times of half exchange for experiments in which $PtCl_4^{2-}$ was absent were greater than 900 minutes. These times were significantly reduced by the presence of $PtCl_4^{2-}$; therefore, it was concluded that $PtCl_4^{2-}$ does influence the isotopic exchange for cis-Pt$(NH_3)_2Cl_2$. The rates, R_{ab} and R_{bc}, in Figure 1.9 can be resolved into two components:

$$R_{ab} = R^{o}_{ab} + R'_{ab} \tag{1.25}$$

$$R_{bc} = R^{o}_{bc} + R'_{bc}. \tag{1.26}$$

The components with zero superscripts correspond to rate processes in the absence of the other platinum complex. A primed component corresponds to a catalysis of the exchange process by one complex between the other complex and free chloride. The R^{o}_{ab} values were obtained from the exchange experiments without $PtCl_4^{2-}$ present by means of the following equation:

$$R^{o}_{ab} = \frac{2ab(\ln 2)}{(b + 2a)T_{\frac{1}{2}}} . \tag{1.27}$$

If the exchange occurs primarily by the aquation process between cis-$Pt(NH_3)_2Cl_2$ and Cl^-, Equation 1.6, with negligible formation of cis-$Pt(NH_3)_2(H_2O)Cl^-$, R^{o}_{ab} will be described by the equation:

$$R^{o}_{ab} = k_{1,a}[\underline{\text{cis}}\text{-}Pt(NH_3)_2Cl_2]. \tag{1.28}$$

The value of $k_{1,a}$ calculated from the experiments in the absence of $PtCl_4^{2-}$ has been given in Table 1.6. The value of $2.30 \pm 0.11 \times 10^{-5}$ sec^{-1} at 25°C was slightly smaller than the value of 2.5×10^{-5} reported by Reishus and Martin (26); however, the agreement was within a reasonable limit from the uncertainty of the experiments. The aquation rate constant for $PtCl_4^{2-}$ was taken as the value of $k_{1,c}$ determined by Grantham *et al*. (23).

The catalysis of exchange for each complex with free chloride by the other platinum complex was considered to be negligible for an initial treatment of the data, i.e., $R'_{ab} = R'_{bc} = 0$. From Table 1.5, the time of half exchange for cis-$Pt(NH_3)_2Cl_2$ was decreased

Table 1.6. Rate constants for exchange processes in the cis-Pt$(NH_3)_2Cl_2$: Cl^- system

Constant	Value at 25°C
$k_{1,c}$	$2.30 \pm 0.11 \times 10^{-5}$ sec^{-1}
$k_{1,a}$[a]	$3.9 \pm 0.2 \times 10^{-5}$ sec^{-1}
k'_{ac}	$3.0 \pm 0.2 \times 10^{-4}$ sec^{-1}M^{-1}
k''_{ac}	$9.0 \pm 0.6 \times 10^{-5}$ sec^{-1}

[a] From (22).

by both the increase in $PtCl_4^{2-}$ concentration and the decrease in Cl^- concentration. Therefore, following the treatment for the cis-Pt$(NH_3)_2Br_2$ system (6), the exchange rate R_{ac}, was represented by the function:

$$R_{ac} = (k'_{ac} + k''_{ac}[Cl^-]^{-1})[\underline{cis}\text{-}Pt(NH_3)_2Cl_2][PtCl_4^{2-}]. \qquad (1.29)$$

Equations 1.20 and 1.21 were solved by a computer program written by Vandegrift (43), based on the Runge-Kutta method of numerical analysis (50). A subroutine was added to the basic program which allowed various trial values of k'_{ac} and k''_{ac} to be used by the program with the values of $k_{1,c}$ and $k_{1,a}$ indicated in Table 1.6 held fixed. The times of half exchange were evaluated from the numerical solutions. In this way, it was possible to determine by an iterative computation the values for the constants k'_{ac} and k''_{ac} which minimized the quantity

$(T_{\frac{1}{2}\text{ calcd}} - T_{\frac{1}{2}\text{obsd}})^2$, for the three sets of conditions with initially tagged $PtCl_4^{2-}$. The computed values for the times of half exchange are included in Table 1.5, and they agree quite satisfactorily with the observed times within experimental uncertainty. Values for the indicated rate constants are included in Table 1.6. Furthermore, with another modification of the computer program, the values of $S_{a,b,c}$ could be computed as a function of time. The plots of $(1-S_{a,b,c}/S_{\infty})$ are illustrated in Figure 1.11 for both tagged and untagged $PtCl_4^{2-}$ systems. From this illustration the distribution of activity can be followed as a function of time in the three components of the exchange system.

In the experiments for which the $PtCl_4^{2-}$ was not initially tagged, the time of half exchange was somewhat longer than for experiments with comparable concentrations in which the $PtCl_4^{2-}$ was tagged. With the rate constants in Table 1.6 and with the assumption that $R'_{ab} = 0$, the computed value for the time of half exchange was slightly smaller than the observed time of half exchange. The difference between the computed and the observed values was well within reasonable uncertainty. It was therefore concluded that there was negligible catalysis of the exchange between <u>cis</u>-$Pt(NH_3)_2Cl_2$ and Cl^- by $PtCl_4^{2-}$. Rather, the enhancement of the exchange rates involved a trading of chloride ligands between the two different complexes without the formation of a free chloride intermediate.

The rate constant, k'_{ac}, was only 4% as large and k''_{ac} was 17% as large as the corresponding constants for the bromide system

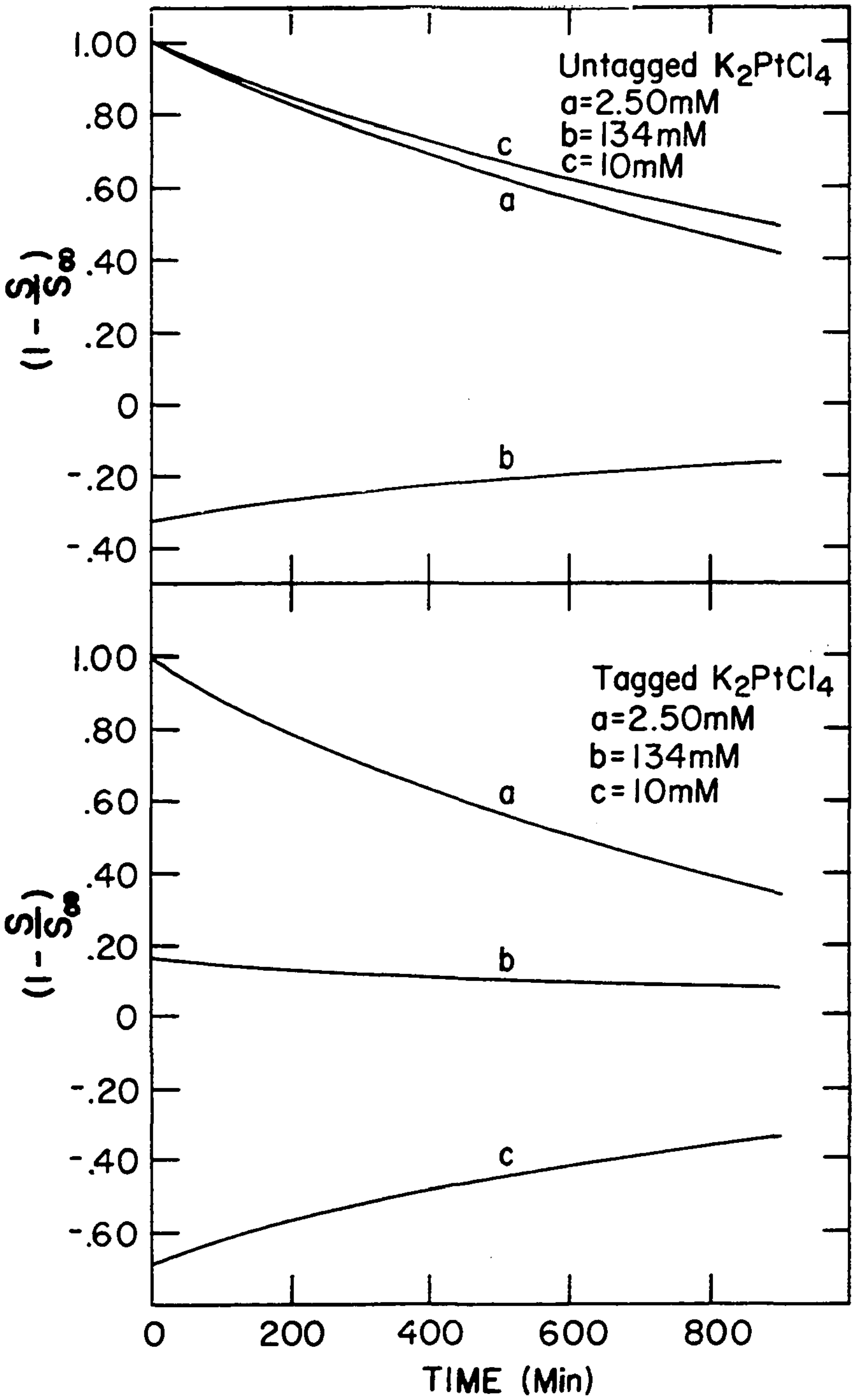


Figure 1.11. Change of specific activity with time for three components of the exchange system; a = <u>cis</u>-$Pt(NH_3)_2Cl_2$; b = Cl^-; c = $PtCl_4^{2-}$

at 25°C. The lower values for the chloride system probably reflect the reduced stability of the chloride bridges, so the formation of the dimeric transition state contributed a higher component to the activation enthalpy. The values of R_{ac} for all experimental conditions were scarcely more than 10% of the aquation contribution to R_{bc}. Therefore, the contribution of the ligand trading to the R_{ac} should not cause an experimentally detectable change in the time of half exchange for $PtCl_4^{2-}$.

The chloride-dependent process, characterized by k''_{ac} was more than twice as fast as the chloride-independent process under any of the experimental conditions. A mechanism which is consistent with the slower chloride-independent rate term is illustrated in Figure 1.12. In step A, one of the chloride ligands of the $PtCl_4^{2-}$ is proposed to attack along the axial position of cis-$Pt(NH_3)_2Cl_2$. A chloride ligand from cis-$Pt(NH_3)_2Cl_2$ also aligns with the axial position of the $PtCl_4^{2-}$ in step B. A concerted movement of the ligands from step B to the positions illustrated in step C is assumed. The two complexes separate in a pattern reverse of steps A and B as shown in steps C and D. Thus, the proposed double-bridged mechanism accomplishes the exchange without free chloride dependence. Similar mechanisms have been proposed for the corresponding bromide systems(5,6).

At least a portion of the chloride-dependent process was presumed to occur by a mechanism similar to the one shown in Figure 1.12 with the exception that one of the nonbridging chloride ligands was replaced by an aquo group. Three possible intermediates which

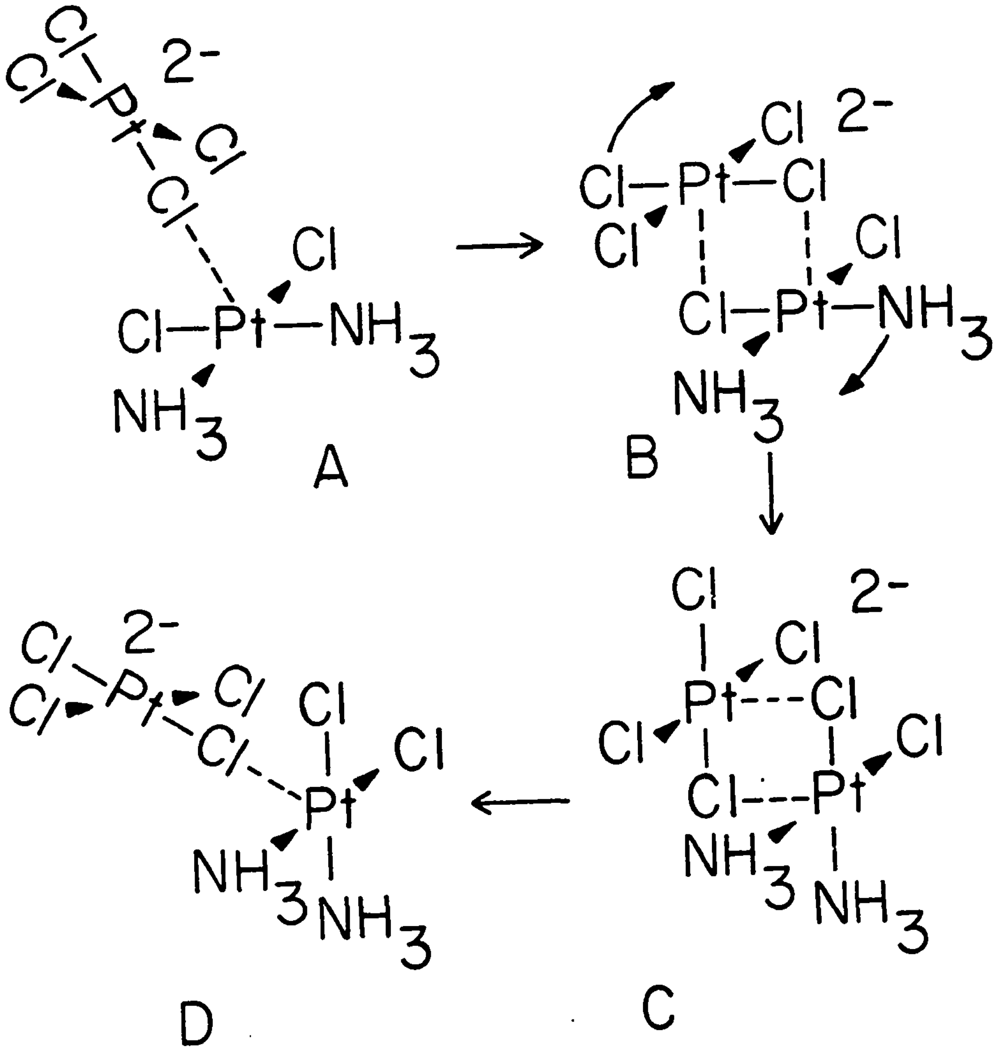


Figure 1.12. Possible mechanism for the chloride-independent isotopic exchange of chloride ligands in the <u>cis</u>-$Pt(NH_3)_2Cl_2$: Cl^- : $PtCl_4^{2-}$ system

were kinetically indistinguishable are illstrated in Figure 1.13 along with the corresponding reactants. The intermediates illustrated in Figure 1.13 correspond to the transition state between steps B and C in Figure 1.12. Either complex could form its corresponding aquo complex and in the case of $Pt(H_2O)Cl_3^-$ the intermediate of exchange had two possible positions for the aquo ligand, as shown at the bottom of Figure 1.13. In the case of <u>cis</u>-$Pt(NH_3)_2Br_2$, a portion of the bromide-dependent process was also found to occur by a process which presumably involved a singly-bridged intermediate, $[Br_3Pt\text{-}Br\text{-}Pt(Br)(NH_3)_2]^-$ (43). A proposed mechanism for the chloride system involving a singly-bridged intermediate is illustrated in Figure 1.14. That the enhanced rate of aquation of $PtBr_4^{2-}$ was less than the isotopic exchange rate indicated that the singly-bridged mechanism in the bromide system could not account for the total bromide-dependent process. It has not been possible to characterize the chloride system as completely as the bromide system; possibly the chloride-dependent process could involve either or both of the processes proposed. The poorer characterization of the chloride system resulted from the relatively lower values in R_{ac} in comparison to R_{ab}. Thus, in none of the experimental conditions was R_{ac}, which must be calculated by differences, as large as R_{ab}. Unique to this system was the use of $S_c^o = 2S_b^o$. Thus, the direct exchange between the two complexes gave larger changes in specific activity when exchange was initiated. Even with this new feature and corresponding complication with the treatment of data, characterization of the system was relatively poor.

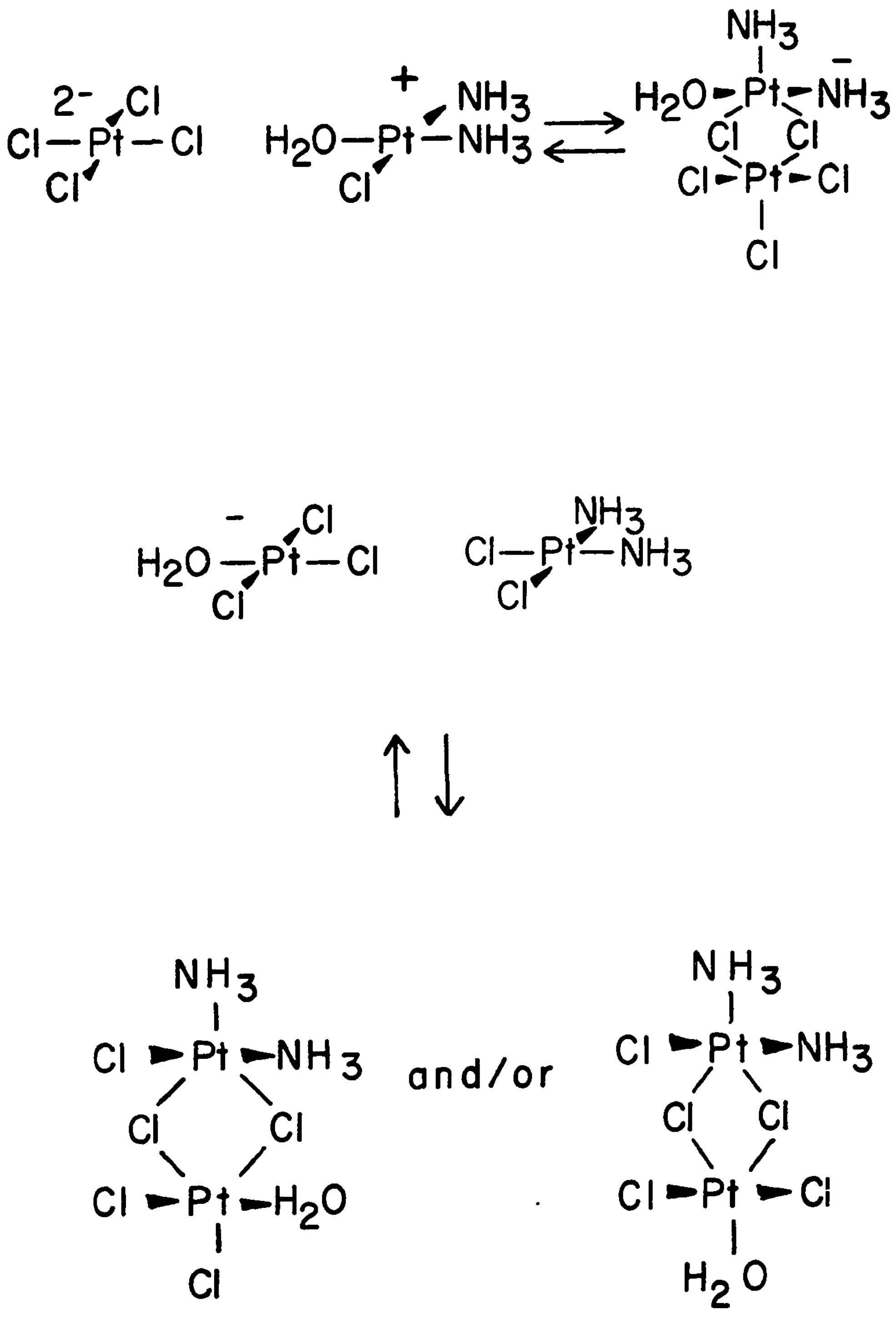


Figure 1.13. Proposed intermediates involving double bridges for the chloride-dependent isotopic exchange process in the *cis*-$Pt(NH_3)_2Cl_2$: Cl^- : $PtCl_4^{2-}$ system

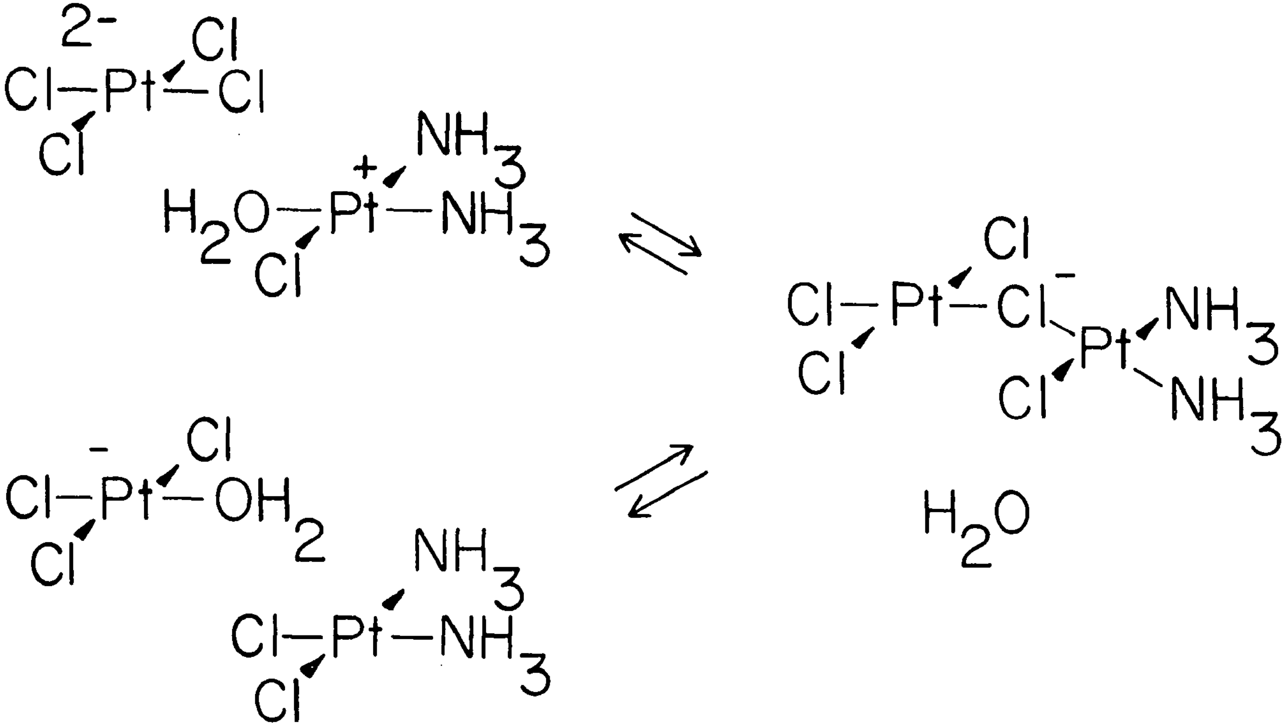


Figure 1.14. Proposed mechanism involving a singly-bridged intermediate for the chloride-dependent isotopic exchange process in the *cis*-$Pt(NH_3)_2Cl_2$: Cl^- : $PtCl_4^{2-}$ system

In part, the better characterization of the bromide systems was due to the higher stability constants for bromide complexes; it was possible to work with lower bromide concentrations than chloride concentrations and therefore to achieve a higher contribution in the halide-dependent process. Although the trading of chloride ligands between the two platinum complexes has been demonstrated, the limitations in the accuracy which it was possible to achieve herein indicated that meaningful activation parameters would not be obtained through temperature-dependent studies; they were not attempted.

SUMMARY

The aquation equilibrium quotient values for K_1 at 25°C and 35°C were within a reasonable experimental uncertainty of those found by Reishus and Martin (26). Statistical treatment of a large amount of data provided by automatic titration equipment yielded more reliable values for K_2 at both 25°C and 35°C. The $\Delta H°$ values found for <u>cis</u>-$Pt(NH_3)_2Cl_2$ were positive and no more than 10 kcal, which was quite typical for aquation reactions of halide ligands in platinum(II) complexes.

Chloride ligand exchange was found between <u>cis</u>-$Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$ with no measurable catalysis of exchange for free chloride. It was further found that although there was exchange between the two complexes themselves, the greater part of the ligand exchange was between the pairs [<u>cis</u>-$Pt(NH_3)_2Cl_2$][$Pt(H_2O)Cl_3^-$] and/or [<u>cis</u>-$Pt(NH_3)_2(H_2O)Cl^+$][$PtCl_4^{2-}$]. The intermediates for the proposed mechanisms were similar to those for mechanisms proposed for other second order rate terms containing two complex concentration terms (2,3,5,6,7,31).

Only one other chloride system has been characterized which also possesses a second order rate term, <u>viz</u>. $Pt(C_2H_4)Cl_3^-$ and Cl^-. However, further comparison of the two chloride systems could not be made due to the labilizing effect of the ethylene group. Perhaps the $Pt(NH_3)Cl_3^-$ complex could be studied for comparison to the Zeise's salt system.

Even though recent clinical tests (13) showed that cis-$Pt(NH_3)_2Cl_2$ was of little value in tumor inhibition in humans, knowledge gained by studies of Pt(II) complexes and other biologically active metal complexes may have an especially practical use in the near future.

II. THE SZILARD-CHALMERS EFFECT IN SOLID-STATE SYSTEMS CONTAINING THE OCTA-μ_3-CHLORO-_OCTAHEDRO_-HEXAMOLYBDENUM(II) CLUSTER

INTRODUCTION

Neutron capture may have chemical consequences for the atom to which the reacting nucleus belongs. In most cases the kinetic energies imparted to yield a "hot atom" are orders of magnitude larger than those encountered in conventional chemistry. Nuclear transformations, therefore, may initiate chemical reactions which require high energies of activation and which are quite unexpected or previously unobserved. These chemical processes have become known as the Szilard-Chalmers effect in honor of L. Szilard and T. A. Chalmers, who first demonstrated the chemical effects of nuclear reactions in 1934 (51). They studied the behavior of radioactive iodine atoms formed in neutron-irradiated liquid ethyl iodide. Some of the radioactive iodine could be extracted into water and the rupture of the carbon-iodine bond was attributed by these authors to the mechanical recoil imparted to the iodine nucleus by the incident neutron. Subsequently, Amaldi et al. (52) demonstrated that the gamma ray emission following thermal neutron capture imparted sufficient recoil energy to the nucleus to break the bonds holding the capturing atom to the remainder of the molecule. During the late 1930's, experimental studies of Szilard-Chalmers reactions began to divide along two general lines. One was the utilization of the effect to prepare radioactive sources of high specific activity, and the other involved the mechanistic interpretations of the process itself. The subject of this investigation has been the Szilard-

Chalmers effect in the $Mo_6Cl_8^{4+}$ moiety. The effects of thermal annealing and amount of water in the target material upon the retention of radioactivity in the parent compound were examined.

The development of "hot-atom" chemistry and its many aspects has been treated in a series of review articles (53-59). Interest in "hot-atom" chemistry has steadily increased in recent years, especially in the area of solid-state systems.

The "hot atoms" occurring in the nuclear transformations are, unfortunately, thermalized so rapidly that the "hot" reactions cannot be followed kinetically by present-day experimental techniques (53). A product analysis (which is performed at a considerable time after the "hot" event) constitutes the principal experimental treatment presently used. Under most conditions, the "hot" atoms are formed in the sample in such low concentrations that they can be traced only by their radioactive properties. All "hot atom" studies, therefore, must be centered on a radioactive nuclide produced by the nuclear event.

The chemical behavior of atoms which have undergone nuclear transformations is at present only partially understood, especially for the solid state. Many investigations involving inert bonding systems have shown that the radioisotope produced by neutron bombardment in dilute solution or in the gas phase rarely remains in the parent compound. However, when pure liquids or solids with inert bonding systems are activated by thermal neutrons, an appreciable fraction of the total activity has frequently been found in the parent compound. This retentive activity presumably arises from secondary reentry processes. Various theories proposed to explain this process will be briefly described.

The binding energy of a thermal neutron absorbed by a nucleus is in the range of 6-8 Mev. This energy is emitted in the form of one or more γ-quanta in one of many possible cascades. A γ-quantum of energy, E_γ, gives a nucleus of mass, M, a recoil energy:

$$E_R = E_\gamma^2/2Mc^2. \tag{2.1}$$

For a 6-8 Mev gamma ray the recoil velocity will be of the order of 10^{14} Å/sec. A distribution of recoil energies has been calculated (60-63); however, the assumptions needed for these calculations have never been fully justified. In general, the average recoil energy is found to be of the order of several hundred ev, and the probability that the recoil energy is below 50 ev is only about 1%. For simple molecules such as CH_3I, where iodine recoils, it is possible to calculate the recoil and the associated vibrational energy (64) for bond breaking. It appears, in agreement with experimental results (64) that, at most, about 1% of the molecules survive the recoil.

Now the question arises as to how the recoil atoms are slowed down. The best mathematical treatment to date is very restrictive in scope. The slowing-down of recoil atoms in a inert medium is roughly analogous to the moderation of neutrons. The neutron slowing-down process is assumed to take place by elastic collisions (65). The average number of collisions necessary to reduce the initial energy, E_0, of a particle of mass, m_1, to some value, E, in collisions with particles of mass, m_2, is:

$$n = (\ln\frac{E_o}{E})/[\frac{(m_1-m_2)^2}{2m_1m_2}\ln\frac{m_1-m_2}{m_1+m_2} + 1]. \qquad (2.2)$$

Even in relatively simple gaseous molecules, the mechanisms are much more complicated (63); however, this simple formula gives good agreement with experimental observations (66) of recoil ranges in noble gases. In solids, however, such calculations are hardly justified, since the recoiling atoms or molecular fragments immediately collide with surrounding molecules or ions which cannot move freely.

The models, which have been proposed in order to describe the (n,γ)-reactions in solids, have appeared in detail in several reviews (54,67,68). In 1940, Libby proposed in his "ligand loss model" (69) (based on experiments with permanganates and phosphates) that a central atom may "eject" one or more ligands. Various new species are formed upon dissolution of the sample with the radioactive atom possibly in different oxidation states.

An "elastic collision" or "billiard ball model" was proposed by Libby (70) in 1947 and extended by Miller, Gryder and Dodson (71) in 1950. The basic feature of this model is that the recoil atom loses its energy predominately in "billiard-ball" collisions with the atoms of the surrounding molecules. These elastic collisions may account for large yields of recoil atoms in the parent compound by causing replacements of the type:

$$^{80}Br + C_2H_5Br \rightarrow C_2H_5{}^{80}Br + Br. \qquad (2.3)$$

However, this model cannot account for the formation of relatively large yields of radioactive products resulting from hydrogen substitution and carbon-carbon bond rupture. If the recoil halogen atom can impart sufficient energy to a hydrogen atom to break the carbon-hydrogen bond in an elastic collision, then the halogen atom should be left with sufficient energy after the collision to enable it to escape from the reaction cage. This theory has been invoked for inorganic solids; however, calculations (72) of the expected effects for various systems have shown no correlation with experimental results.

In a modification of the "elastic collision model" to the "elastic-inelastic collision model," Friedman and Libby (73) now proposed that in the low energy region of about 10 ev, the recoil atom can undergo inelastic collisions which supposedly lead to the formation of products corresponding to hydrogen-substitution and synthesis. This model is unable to account for the distribution of radioactive products resulting from recoil halogens reacting with the liquid hydrocarbon media (74). Reactions leading to parent retention in these systems occur in an energy region below that leading to hydrogen substitution.

Willard's "brush heap" or "random-fragmentation model" (75) was also proposed for organic liquids, but aspects of this model have been brought to bear on reactions in solids. In this model, the recoil atom loses its energy by inelastic collisions with the surrounding molecules and breaks bonds indiscriminately. When the recoil energy has been reduced below bond-breaking energies, the recoil atom may combine either with the radicals in its immediate vicinity, or with radicals it encounters in the course of its diffusion in thermal equilibrium with the medium.

The "hot zone model" proposed by Harbottle and Sutin (76) was based on Seitz and Koehler's treatment of atomic displacement by irradiation (77). In this model, the recoiling atom is assumed to produce atomic displacements in the slowing-down process. Since a displacement requires approximately 50 ev, about six atoms are displaced for a typical recoil energy of 300 ev. The lattice is heated in these processes; in the model it is assumed that the total recoil energy is generated at one point and dissipated by heat conduction. This "hot zone" eventually comprises about 1000 atoms which remain above the melting point of the crystal for about 10^{-11} seconds. Although the disorder of a liquid may not be attained, unusual chemical reactions have reasonable chance of occurring. It was further proposed that such reactions probably do not have time to go to completion but are quenched by the cooling of the "hot zone." Subsequent heating of the irradiated crystals may give these reactions an opportunity to proceed further. Thus there should be a possibility of obtaining information on the primary reactions by thermal-annealing experiments.

Müller has modified the "hot zone model" and has proposed the alternative "little disorder model" (67,78). Müller used crystals of K_2ReBr_6 diluted with K_2SnCl_6 in order to determine the size of the "hot zone" by measuring the Re activity found in complexes of the type $ReBr_{6-n}Cl_n^{2-}$ after neutron irradiation. The "hot zone" was found to be of the order of 5 Å as compared to 10-15 Å in the "hot zone model."

Gardner et al. (79,80) have recently investigated the effects of (n,γ)-recoil of cobalt, rhodium and iridium in ^{36}Cl-labeled $[M(NH_3)_5Cl]Cl_2$ and $[M(trien)Cl_2]Cl$. Based on measurements of liberated ^{36}Cl, they estimated that between 2-5 X 10^5 metal-chlorine bonds were broken per (n,γ)-reaction, and proposed a "super hot model" in which the zone was composed of a large distorted region of the lattice. However, Rössler and Otterbach (81) have criticized these experimental results and have suggested that possibly the findings were due to bulk radiolysis of the samples.

All of the previously discussed models concerned the "hot-atom" events taking place in the initial stages or roughly the first 10^{-11} seconds following the nuclear event. The subsequent annealing reactions have been discussed in terms of various mechanisms derived from solid-state physics (54). These mechanism, however, largely ignore the role of electrons; they cannot account for various effects of crystal defects not directly connected with the reaction zone (82). A model proposed by Maddock and Collins (83) interpreted various annealing phenomena in terms of formation of polynuclear species. Anderson (84) and Nath and Vaish(85) have shown that crystal defects can influence or even control the annealing reactions by release or trapping of charge carriers. Since detailed reviews of these models and mechanisms have been included in the original papers, only a brief discussion of the most recent annealing model proposed by Nath will be included here.

Nath et al. (86) have shown that the phenomenon of exchange in radioactive Co-doped systems and thermal annealing of recoil damage in the solid state are analogous to each other. They therefore concluded in the model that participation of free electrons governs thermal annealing. It was postulated that during thermal treatment of chelates with recoil damage, as well as of radioactive Co^{2+}-doped chelates, electrons are lifted to the conduction band from well-populated electron donors, i.e. from the valence band, and the free electrons are captured by the radioactive Co^{2+} ions to form excited Co^{+} (or Co atoms) which instantaneously interacts with a neighboring inactive chelate molecule to effect isotopic exchange. E. Lazzarini and A.L. Fantola Lazzarini, in several recent studies (87-90), have shown that their experimental work on novel cobalt systems, in general, supports the "Nath model."

The annealing and recoil models discussed above have more or less been based on results obtained from a few related systems. Only in recent years has it been fully realized that a "hot-atom" event in a solid is a complex interplay of many different factors, such as the nuclear reaction, the parent ion or molecules, the crystal structure, possible crystal defects and the conditions under which the processes take place. Fenger (53) has suggested, therefore, that all the observed phenomena on many diverse solid systems cannot be described in terms of general "models" as has previously been attempted.

Two of the many systems in which hydrates and anhydrous compounds have been studied will be compared in terms of the retention in the parent compound. In the systems of permanganates (91,92), dichromates (93), calcium bromate (94) and iridium complexes (95), the hydrates have lower retention than their corresponding anhydrous forms. For the iridium complexes of $Na_2IrCl_6 \cdot XH_2O$ where X = 0,2 and 6, the per cent retentions reported by Cabral and Maddock (95) were 20.8%, 12.0% and 3.5% respectively, after aging the solutions of the irradiated products for 1445 minutes. Harbottle and Sutin (54) suggested that the decrease in retention of the hydrates was due to an *in situ* reduction of the recoil fragment by the lattice water. However, it might also reflect a reduced tendency to anneal in the hydrated material. In two recent studies (96,97), however, the opposite of the previously described trend was true. Dimotakis, *et al*. (96) found that the retentions of $[Co(en)_3]Cl_3$ and $[Co(en)_3]Cl_3 \cdot 3H_2O$, under identical conditions, were 66.8% and 88.5%, respectively. Therefore, the limited data in the literature on retention in hydrated and anhydrous salts do not reveal a consistent pattern of behavior and tends to support the conjecture set forth by Fenger (53) that unrelated solid systems cannot fit general models.

The only molybdenum systems for which Szilard-Chalmers reactions have been reported are MoO_3 (98) and $Mo(CO)_6$ (99-102). Systems involving the same heavy atom such as $[Mo_6Cl_8]Cl_6 \cdot 2H_2O$ and $Mo(CO)_6$ may not have similar recoil or annealing events; but the studies of $Mo(CO)_6$ (99-102) can be used to illustrate some of the techniques involved for following neutron-irradiated molybdenum systems.

Harbottle and Zahn (100) used the different isotopes of molybdenum in $Mo(CO)_6$ in an attempt to determine the effects of different recoil energies on the retention of radioactivity in the $Mo(CO)_6$ parent molecule. The samples of $Mo(CO)_6$ were sealed under a vacuum in quartz tubes for the irradiations. These samples were kept at liquid nitrogen temperature between bombardment and separation. Part of an irradiated sample (without separation from the recoil fragments) was used to determine the entire induced activity. The nonvolatile recoil fragments were then separated from the parent compound by vacuum sublimation of the target compound. Characteristic areas under the peaks of the pulse-height gamma ray spectra, taken with a NaI(Tl) well crystal scintillation counter, were used as a measure of the activities of the different isotopes. The retentions found for $^{90}Mo(CO)_6$ and $^{99}Mo(CO)_6$ under identical conditions were 75.0 ± 2.0% and 73.7 ± 1.0% respectively.

Zahn <u>et al</u>. (101) observed the incorporation of recoil atoms into the parent species in neutron-irradiated $Mo(CO)_6$ following post-irradiation thermal treatment. The experimental techniques were similar to those described for the previous $Mo(CO)_6$ systems. One-pulse thermal annealing showed a continuous increase in retention in $Mo(CO)_6$ up to 100°C, where a plateau region of approximately 72% retention was observed. This plateau continued up to the highest temperature studied of 190°C. The $Cr(CO)_6$ system was also described extensively. The work reported the effects of pre- and post-irradiation gamma treatment and exposure to carbon monoxide atmospheres.

Groening and Harbottle (99) used ^{99}Mo and ^{101}Mo to follow the "isotope effect" in $Mo(CO)_6$. In this isotope study, different retentions were found which had not been reported for ^{99}Mo by Harbottle and Zahn. (100). At 10°C the reported retentions were 70% and 62% for $^{99}Mo(CO)_6$ and $^{101}Mo(CO)_6$, respectively. Furthermore, one-pulse annealing curves showed several plateaus of retention for both ^{99}Mo and ^{101}Mo.

Sublimation was the means by which the parent compound was separated from other radioactive species in the $Mo(CO)_6$ systems. In any separation procedure, various physical or chemical properties of the parent compound may be used to promote separation from other radioactive species. More complete resolution of the chemical fractions will give a clearer picture of the "hot atom" process. In numerous systems, it has been observed that differences in separation procedures will lead to a different retention for a given chemical species. Therefore, a knowledge of the chemistry of a system must be known before a suitable separation can be found. A brief discussion of the physical and chemical properties of molybdenum(II) chloride will be included in this section.

In 1859, the first synthesis of molybdenum dichloride was reported by Blomstrand (103). Numerous routes of preparation have been devised; most involve the reduction of $MoCl_5$. Lindner et al. (104), in one preparatory route, found that molybdenum(II) chloride could be synthesized by passing phosgene over molybdenum metal in a dry atmosphere at 600°C.

Sheldon (105-108) characterized many of the chemical aspects of the molybdenum cluster. Using the acid hydrate of molybdenum(II) halide, an entire series of anionic compounds were prepared. Sheldon arrived at the hexanuclear formulation on the basis of conductivity and cryoscopic measurements. The anhydrous series of $(Mo_6X_8)Y_4$ where X = Cl, Br, I; and Y = Cl Br, I, OH followed. Using tracer techniques with radioactive chloride, Sheldon demonstrated that the outer halogens of $(Mo_6Cl_8)Cl_6^{2-}$ exchange rapidly, but exchange of the internal halogens was not observed. It was noted that $(Mo_6Cl_8)Cl_4$, octa-μ_3-chloro-tetrachloro-octahedro-hexamolybdenum(II) (OHMO), decomposes above 300°C in air and 800°C in vacuo. Furthermore, $(Mo_6Cl_8)Cl_4$ was found to be amorphous immediately after preparation but gradually acquired X-ray powder patterns in moist air as the dihydrate, $(Mo_6Cl_8)Cl_4 \cdot 2H_2O$ (OHMOD), formed.

Of significance was the solution chemistry described by Sheldon (105,106). When the crystalline acid, $(H_3O)[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$, dihydronium octa-$\mu_3$-chloro-hexachloro-octahedro-hexamolybdate(II) hexahydrate (DOHMO), was dissolved in water, the initially clear solution rapidly gave precipitates. Therefore, excess hydrochloric acid must be maintained for stable solution. The solubilities of the acid form and many of its salts were found to be much higher in ethanol than in aqueous solutions.

Many incorrect molecular formulae were adopted in the earlier studies of the polynuclear complexes of molybdenum(II). However, the correct composition of the crystalline acid form of molybdenum(II) chloride has been known for some time (109). The $Mo_6Cl_8^{4+}$ moiety was characterized in studies of several related crystalline compounds of molybdenum(II) chloride by Brosset (110,111). The inner $(Mo_6Cl_8)^{4+}$ cluster consists of a nearly regular octahedron of molybdenum atoms with the Mo-Mo distance of 2.63 Å. This compares with the distance of 2.72 Å found in molybdenum metal (112). A chlorine atom is symmetrically located above each of the eight triangular faces of the metal octahedron forming three molybdenum-chlorine bonds of 2.56 Å. The remaining chlorine atoms in the $(Mo_6Cl_8)Cl_6^{2-}$ of the acid form are located directly out from each molybdenum along the C_4 axes at a distance of 2.43 Å.

Sheldon (105), in discussing the bonding in the hexachloroanions of $(Mo_6Cl_8)^{4+}$, described a tetragonal pyramid of chlorine atoms about each Mo atom. The bonding was described in terms of hybrid orbitals on the Mo atoms. The z axis of each Mo is directed toward the center of the cluster and the x and y axes are directed toward bridging chlorides. The bonding hybrids, $d(x^2 - y^2)sp^3$, were used for both internal and external halogen bonding. The d(xz,yz) orbitals were filled with the remaining molybdenum nonbonding electrons. Gillespie (113) described a structure which utilized all of the metal electrons for bonding. Crossman et al. (114) and Cotton and Haas (115) proposed molecular orbital treatments for the bonding in

$(Mo_6Cl_8)^{4+}$. In the approach of Cotton and Haas (115), some of the available orbitals were reserved for specific bonding. Metal orbitals used to bond with the internal halogens were $d(x^2 - y^2)$, s, p(x,y). The metal p(z) orbital was used for bonding to atoms located externally to the metal cluster on the C_4 axis. The resulting molecular orbital energy level diagram accounted for the diamagnetism, the metal-metal bond order and the relative chemical reactivity of internal and external halogens in the cluster.

EXPERIMENTAL

Materials

$(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ (DOHMO)

The synthesis of the acid form of molybdenum(II) chloride, $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ followed that described by Dorman (116). Molybdenum metal was obtained from the Rembar Corporation and had a reported purity of 99.9%. Aluminum round of 99.999% nominal purity was obtained from laboratory stock. Analysis of Mo and Cl were performed on both OHMO and OHMOD. Anal. Calc. for $[(Mo_6Cl_8)Cl_4]\cdot 2H_2O$: Mo, 55.51%; Cl, 41.02%; H_2O, 3.47%; Cl/Mo, 2.00; H_2O/Mo, 2/6. Found: Mo, 55.8 ± 0.2%; Cl, 41.5 ± 0.4%; H_2O (by difference), 2.7%; Cl/Mo, 2.01; H_2O/Mo, 1.55/6. Calc. for $(Mo_6Cl_8)Cl_4$: Mo, 57.50%; Cl, 42.50%; Cl/Mo, 2.00; Found: Mo, 57.0 ± 0.2%; Cl, 42.2 ± 0.2%; H_2O (by difference), 0.8%; Cl/Mo, 2.00; H_2O/Mo, 0.45/6. The analysis resulted in the correct ratio of chlorine to molybdenum in both compounds; however, the water present indicated that the dihydrate (OHMOD) was slightly deficient and the supposedly anhydrous material actually contained a small amount of water. Furthermore, under similar conditions of analysis, Schäfer and Plautz (117) found a ratio of H_2O to Mo of 1.76 to 6 which also indicated less water than expected in OHMOD. Though the amount of water was slightly different than the theoretical values, the chemical names of the compounds used in the rest of this text refer to the analyzed compounds.

Gels

Sephadex G-10 gel was obtained from Pharmacia Fine Chemicals, Incorporated, Piscatawny, New Jersey. The gel was allowed to swell in 1.5 N HCl for 30 minutes before using. Bio-Gel P2, 200-400 mesh, was purchased from Bio-Rad Laboratories, Richmond, California. This gel was soaked in 1.5 N HCl for one or more hours before using.

Water

All water came from the flash-distilled water system.

Other reagents

All other materials were of reagent grade.

Equipment

Gel columns

The glass columns for the separations measured 1 cm (inside diameter) and 15 cm in length. A course frit to support the bed was located just above a stopcock and above the bed portion was a small reservoir. Bed length varied with the amount of gel used; however, most of the columns contained 2 g of dry gel, which gave a bed length of 4 cm when wet.

Gamma ray counting equipment

An RIDL 400 channel analyzer, Model 34-12B, was utilized to record the spectrum of counts versus energy. A NaI crystal doped with thallium was coupled to a photomultiplier tube in order to count the incident gamma rays by scintillation. A two and a half ton lead brick shield with a 3/4 inch steel frame and inside aluminum cover provided a housing to reduce background radiation. The channels between 0 and 100 (2.5 Kev per channel) were summed in order to indirectly measure the amount of molybdenum present by counting the large gamma ray peak in the ^{99m}Tc spectrum.

Fractionator

An automatic fraction collector including a drop-counting mechanism manufactured by Research Specialities Company, Richmond, California, was utilized for separating samples during elution curve determinations. Numbered 8 mm test tubes provided easy cataloging of the elution curves. A plexiglass attachment which fit over the aluminum cover of the NaI(Tl) crystal of the scintillation counter was necessary for reproducible positioning of the test tubes over the detector.

Vacuum pump

A "Duo Seal" vacuum pump manufactured by W.M. Welch Company, Chicago, Illinois, was used for both the utility vacuum line work and the sealing of Vycor tubes under a vacuum.

Temperature bath

Temperatures were held constant during annealing experiments in a Tecam sand bath produced by Authur H. Thomas Company, Philadelphia, Pennsylvania. The heater in the sandbath was controlled by a Philadelphia microset thermoregulator in conjunction with a Precision Scientific Company controller. With this apparatus, temperatures were controlled at 120.0 ± 0.5°C, 200.0 ± 0.7°C and 320.0 ± 1.2°C.

Temperatures and temperature variations were recorded on a Sargent Model MR potentiometric recorder which followed the potential produced by a chromel-alumel thermocouple.

Procedures

Neutron irradiation

The majority of the samples were irradiated as a solid. In these cases only containment of the powder during irradiation was necessary. Polyethylene vials with a two milliliter capacity sufficed for these samples. From 0.01 to 0.60 gram samples were weighed into the vials fitted with snap-closure lids. After closing, the excess plastic was trimmed off the vial and the cap was heat-sealed to the vial. Five vials were tested for leaks by heating in boiling water for five minutes, then rapidly dipping the vials below the surface of ice water. Only the vial which had not been heat-sealed allowed water to enter around the cap during the cooling process.

During the handling of the vials, polyethylene gloves were worn in order to decrease the amount of sodium deposited on the surface of the materials being irradiated. Each vial, after being heat-sealed, was then sealed in a polyethylene envelope. The envelope could then be easily removed after irradiation in order to eliminate the activity due to the sodium deposited during packing.

Liquid samples undergoing short irradiations of less than fifteen minutes were also sealed in the polyethylene vials. The sample volumes were limited to one milliliter in the two milliliter vials in order to provide head space for gaseous products formed during irradiations. Furthermore, the vials containing liquids were encapsulated in larger polyethylene containers which were also heat-sealed. During all of the short, liquid irradiations, only one small vial leaked and this leakage was contained by its polyethylene envelope.

For long irradiations of liquid samples or for irradiation of solids which would later be treated under severe conditions, Vycor tubes were used. The tubes were narrowed and thinned about six centimeters from the rounded bottom in order to facilitate breaking after irradiation. In the case of liquids, the samples were frozen with liquid nitrogen in the one centimeter diameter Vycor tubes. After the sample had been loaded into the tube, the ten centimeter stem above the neck was attached to a vacuum pump. The tubes were sealed with a torch while under vacuum, and in order to test the vacuum, a small spot was heated on the sealed tube until the Vycor was pulled in slightly due to the vacuum or blown out due to the expanding hot air. All tubes not having a vacuum were repacked.

The Ames Laboratory Research Reactor facilities provided both thermal neutron irradiations and prolonged ionizing irradiations. At the reactor, the samples, sealed as described above, were enclosed in a pill-shaped "bunny" which was sent close to the reactor core by the use of pneumatic tubes. The R6 and R8 tubes were utilized by this experimenter. The R6 tube had easy access, permanent lead shielding and a flux of 8 X 10^{12} neutrons per second, whereas the R8 facility had the capability of cooling the samples immediately after irradiation in a Dewar filled with Dry Ice. R8 had a flux of 10^{13} neutrons per second but was not permanently shielded. Unless otherwise stated, all irradiations were limited to ten minutes.

All "bunnies" were opened in a containment box in order to limit the contaminated area. Transfers of radioactive powder or opening of irradiated vials were also performed in the containment box. All solid and liquid wastes of possible radioactive nature were carefully stored and were discarded according to prescribed health physics procedures.

Gel separations

A small amount of ammonium molybdate was added to the molybdenum cluster dissolved in 1.5 N HCl in order to test separation conditions. Initial separation experiments were followed by a molybdenum spot test (118). Ten milliliters of phenylhydrazine were dissolved in twenty milliliters of glacial acetic acid. A drop of the effluent from the column being tested and a drop of the phenylhydrazine solution were placed on a filter paper. A pink to red color indicated the presence of molybdate in the effluent.

The final procedure involved the preparation of a slurry of 2 g of Sephadex G-10 in 1.5 N HCl, which was then left to stand for approximately thirty minutes. Even though longer periods of standing caused slight gel decomposition, no loss of separation efficiency was noted. After standing, the gel was packed in the previously described column.

If the cluster was in the DOHMO form, a solution of the compound could be obtained by simply dissolving the irradiated solid in 1.5 N HCl; however, if the cluster had undergone dehydration, it was necessary to add two milliliters of ethanol to the 1.5 N HCl solution and heat to approximately 80°C for one minute in order to dissolve the solid. The resulting solution of 10 ml to 25 ml was added to the column with the prepared gel bed. A partial vacuum from a water aspirator was necessary to obtain a flow rate of one drop per second. After the sample volume had reached the top of the gel bed, 150 ml of 1.5 N HCl was passed through the column into a 250 ml suction flask. The column was placed on another suction flask and the molybdenum(II) chloride was removed from the column quantitatively by decomposing the cluster. An 80°C solution of 1 g NaOH, 5 ml of 30% H_2O_2 and 60 ml of water was slurried with the gel in the column apparatus. The solution was added in three portions and pulled through the gel with aspiration after each portion was slurried. Using irradiated cluster samples, no detectable activity was left on the column after this procedure was completed. No attempt was made to reuse the gel.

The solutions in the suction flasks were reduced in volume to approximately 10 ml by boiling. Tests on the distillate from this solution showed no detectable activity. The flasks were allowed to cool and the solutions were quantitatively transferred to 50 ml volumetric flasks. Either fifteen or twenty milliliters of the solutions to be counted were pipetted into a plastic vial.

One final procedure following the column separations was the spectrophotometric determination of MoO_4^{2-} (119). For this, a weighed amount of ammonium molybdate, dissolved in 1.5 N HCl, was added to the column. 10.0 ml volumes of the effluent were continuously collected in 25.0 ml volumetric flasks. The acid was neutralized with a concentrated solution of NaOH and the resulting solution was buffered at pH = 7.0 with a phosphate solution. The absorbance of each fraction was measured at 227 nm. From the standard curve illustrated in Figure 2.1, the amount of MoO_4^{2-} in each sample was determined.

The column separation using Sephadex G-10 appeared to have the necessary characteristics of a good separation procedure. The procedure was rapid compared to the half life of ^{99}Mo; only small amounts (0.01 g) of radioactive material were needed. The column completely retained the cluster while molybdate was quantitatively eluted in a convenient band.

Recrystallizations

The most reliable procedure to determine the retention in any compound is the recrystallization of that compound to constant specific activity. However, this procedure has the drawbacks of requiring large samples, increasing the radiation dose received by the experimenter and increasing markedly the time after irradiation before separation is effected. The amount of sample needed to obtain three recrystallizations was at least 0.2 g of the molybdenum

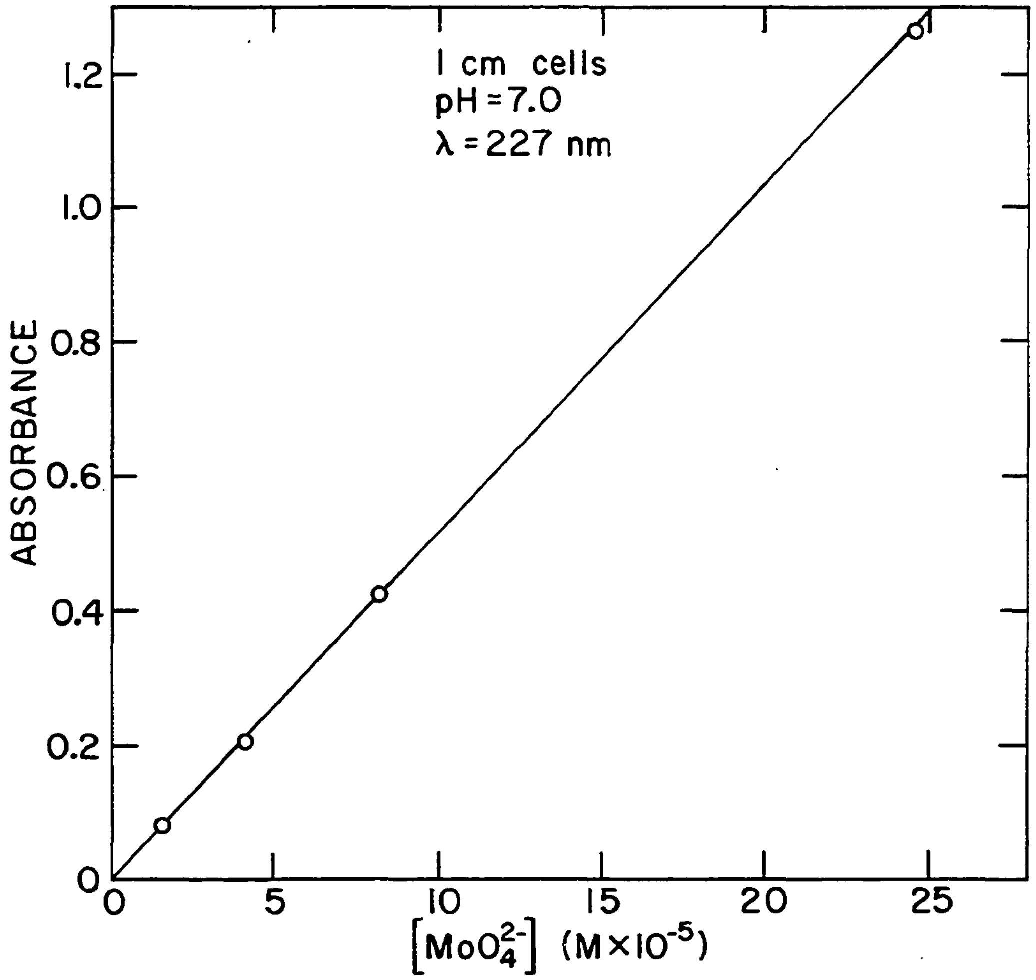


Figure 2.1. Absorbance versus concentration of molybdate in a neutral solution

cluster. The recrystallization procedure was repeated five times on the first sample in order to determine how many steps were necessary to obtain a constant specific activity. Three were found to suffice.

The crystallization procedure involved dissolving the cluster compound as previously described and filtering the solution through Whatman #50 filter paper. The solution was diluted with 1.5 N HCl to 25 ml. From this stock solution was determined the total specific activity of the cluster by taking 1.0 ml which was placed in a 25.0 ml volumetric flask and diluted to volume with 1.5 N HCl for spectrophotometric analysis. Another one milliliter sample for counting was placed in a counting vial and enough 1.5 N HCl solution was added to bring the solution volume to 15.0 ml. For the first crystallization, the stock solution was rinsed into an evaporating dish where the solution was allowed to evaporate until the first crystals started to form. The dish was immediately placed in an ice bath and allowed to cool for approximately one hour. The crystals were removed from the solution by a suction filtering apparatus. Cold, concentrated HCl was sparingly dropped on the crystals for rinsing purposes. The rinsed crystals were dissolved with 1.5 N HCl, and diluted to 25 ml. 1.0 ml aliquots for analysis and for counting were taken from this solution. The second and third recrystallizations were identical to the first except that 3.0 ml and 5.0 ml aliquots were taken for analysis, respectively.

The absorbance of each solution was recorded and the amount of cluster was determined from the standard curve illustrated in

Figure 2.2. The specific activity for each sample was calculated by dividing the grams of DOHMO into the net activity. Retention of the parent compound was determined by dividing the specific activity of the untreated sample into the specific activity of the recrystallized samples. In calculating the retention in a recrystallization experiment, the second and third specific activity values were averaged.

Determination of activity

The activity counted was that of the ^{99m}Tc decaying to its ground state ^{99}Tc with an energy peak for the gamma ray of 142 Kev. The decay scheme (120) applicable to this system was

$$^{99}\mathrm{Mo} \xrightarrow[66\ \mathrm{hr}]{} {}^{99m}\mathrm{Tc} \xrightarrow[6\ \mathrm{hr}]{} {}^{99}\mathrm{Tc}. \qquad (2.4)$$

In Figure 2.3 is illustrated the relative parent and daughter activities versus time, taking into account the percent of the decay which will actually result in activity in the energy range being counted (0 to 250 Kev). As seen in the illustration, approximately forty hours must be allowed after completion of separation before counting the samples in order that the ratio of the daughter ^{99m}Tc activity be approximately a constant fraction of the parent ^{99}Mo activity.

The time of counting was usually five minutes which was sufficient to provide a counting rate error of less than 0.5%. Duplicate five minute counts were taken on each sample to insure no instrument malfunction occurred during the recording of the data. The counts in channels 0 to 99 were summed (0 to 250 Kev) for the total activity of a sample. The 400 channel scintillation counter automatically corrects for dead-time (the time in which the electronic curcuit

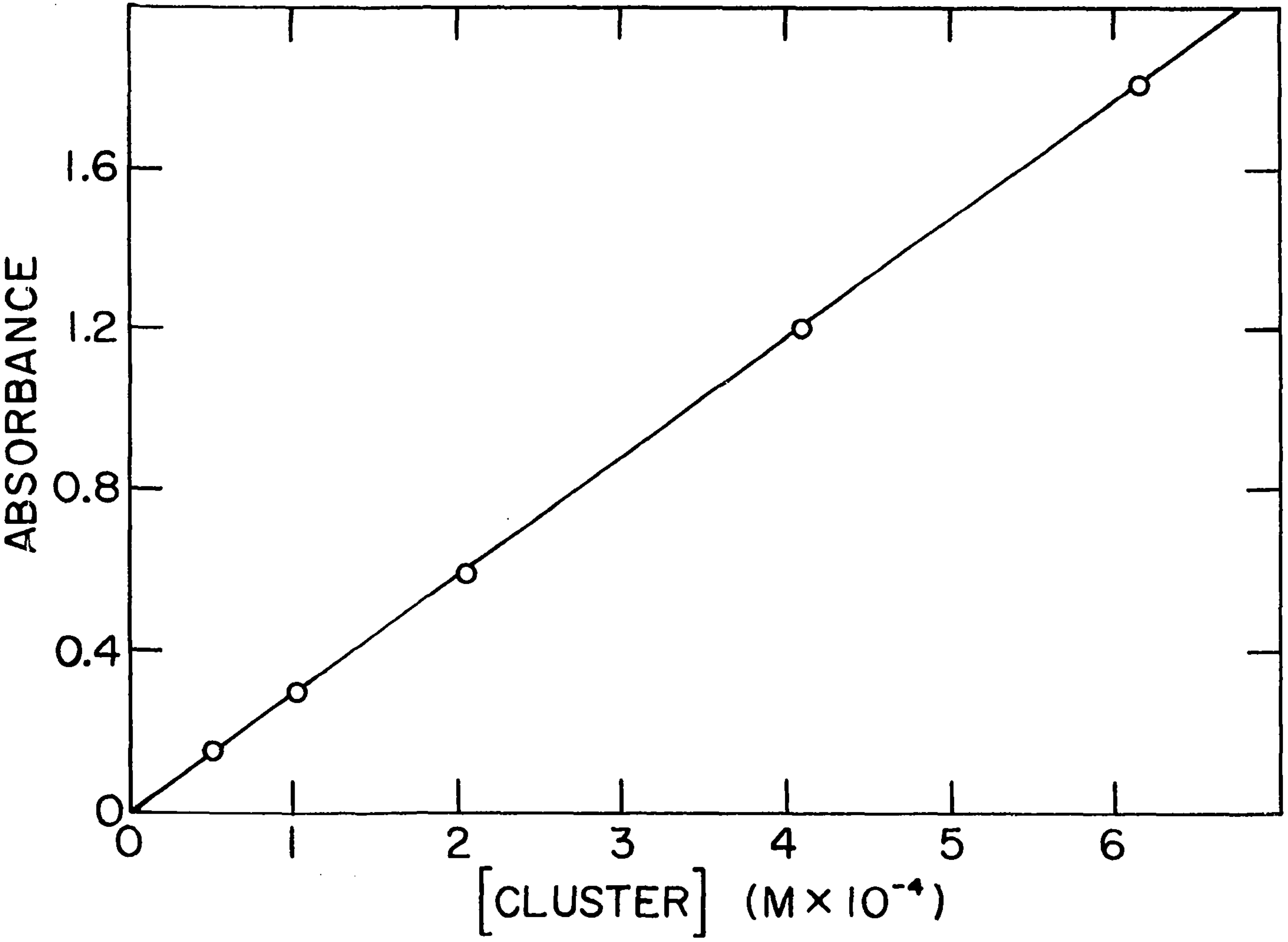


Figure 2.2 Absorbance versus concentration of $Mo_6Cl_8^{4+}$ in a 1.5 N HCl solution (1 cm cells and λ = 310 nm)

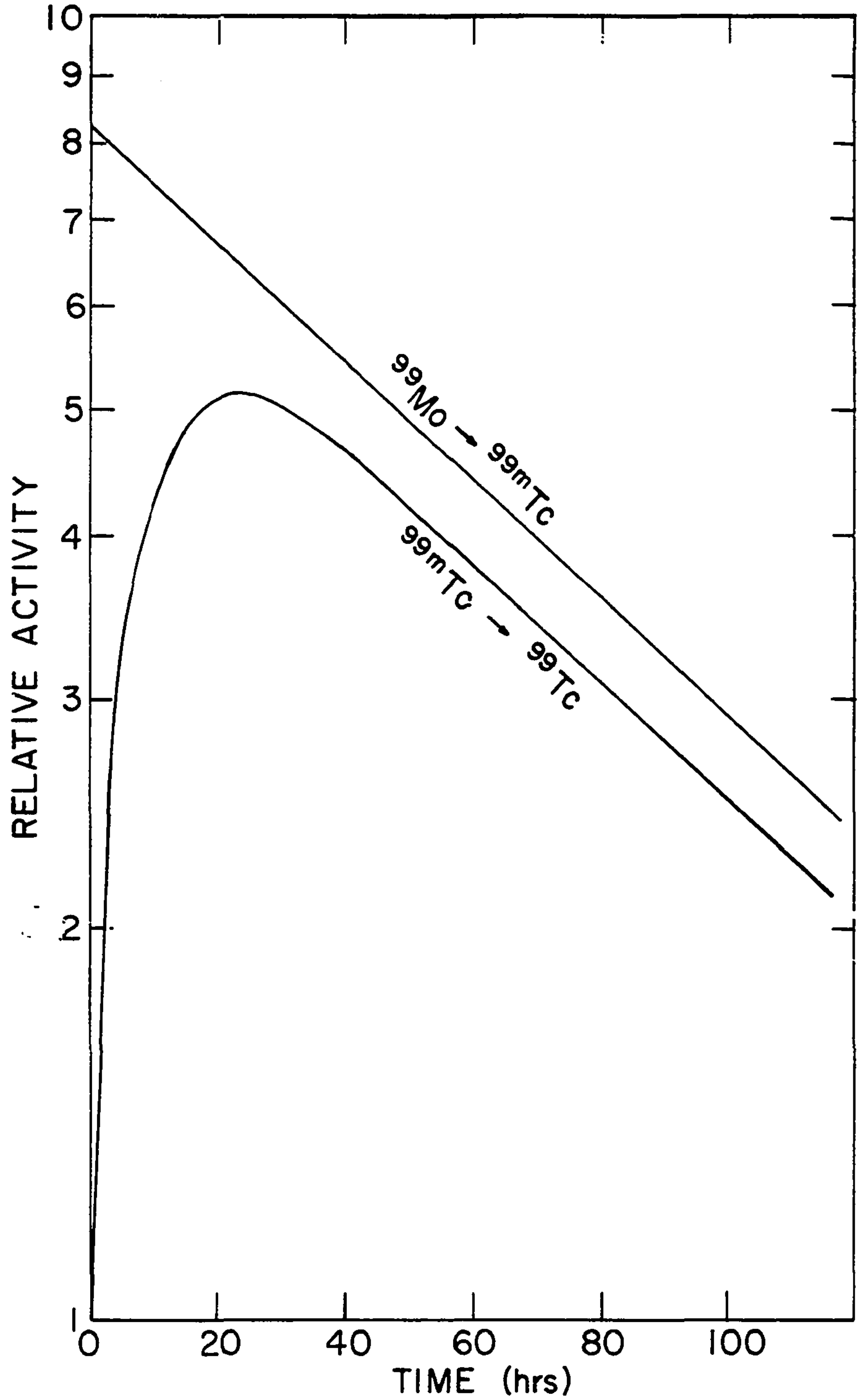


Figure 2.3. Build up of daughter, ^{99m}Tc, activity (0.140 Mev gamma ray decay only) versus time in a sample of pure parent, ^{99}Mo, isolated at zero time

will not respond to another scintillation while storing such an event. The actual activity of the sample was determined by subtracting out background activity from the total activity, correcting then for decay by choosing the zero time as that recorded for the first sample counted in the specific activity experiment.

Annealing

Annealing experiments above room temperature were examined by using the sand bath described earlier. The selected temperatures were 120.0 ± 0.5°C, 200.0 ± 0.7°C and 320.0 ± 1.2°C. The upper limit to the range studied was the highest temperature prescribed by the manufacturer of the sand bath.

The samples were removed from the polyethylene vials and placed in small centrifuge test tubes for heating. The procedure took less than five minutes from unpacking the sample in the dry ice to placing the decontaminated test tubes into the aluminum holder positioned at the top of the sand bath. The samples irradiated in Vycor were simply decontaminated on the outside and placed in a long test tube at the two lower temperatures for immersion in the sand. At 320°C the possibility of the Vycor sample violently rupturing was greater; therefore, in order to safeguard the bath from contamination the Vycor tube was sealed in a stainless steel pipe capped at both ends. Samples at 320°C, involving irradiated material removed from the plastic vials, were placed under a vacuum in order to prevent decomposition. The irradiations for gamma ray annealing were performed in the spent fuel rod pool of the reactor facility. After neutron irradiation and the decaying out of short half life isotopes, the samples were repacked in polyethylene "bunnies" and placed in several plastic bags. The samples were then taped inside a large can attached to a long metal shaft. The apparatus was lowered into the pool and positioned just above several spent fuel rod clusters. The metal shaft was mechanically rotated during the entire irradiation period in order to provide an even gamma ray exposure through all the samples.

The samples which underwent gamma ray annealing were exposed to 22.5 Mrad of the ionizing radiation. The gamma ray flux was measured by using a liquid Fricke solution. The two flux measurements made are listed in Table 2.1.

Table 2.1. Calibration data from the gamma ray facility

Date	Time	Flux (Mrad/hr)
7-11-75	4:00 p.m.	0.438
7-15-75	11:00 a.m.	0.427

Since the decay scheme is known for reactor fuel elements, the average gamma ray energy was calculated to be 0.64 Mev from a standard computer program (Curie, Dose and Thunderhead (NAA-SR-8884)), available from the Health Physics department of the reactor.

RESULTS AND DISCUSSION

Separations

It was initially necessary to prove the effectiveness of the column separation procedure. Furthermore, the possibility of exchange in solution between the cluster and other radioactive species had to be investigated.

Molybdate was intuitively assumed to be the predominant species from fragments of neutron irradiation of the cluster which could exist in an aqueous 1.5 N HCl solution exposed to atmospheric oxygen. The quantitative elution curve of molybdate, as obtained by the procedure described in the Experimental section, is illustrated in Figure 2.4. The highest molybdate concentration occurred at approximately 50 ml of the effluent. From this elution curve, 150 ml of HCl eluant were deemed sufficient to obtain separation of molybdate from the Sephadex column.

A labeled molybdate solution obtained from neutron irradiated ammonium molybdate dissolved in 1.5 N HCl was used to quantify the column separation. Using 150 ml of 1.5 N HCl, at least 99.84% of the radioactive molybdate was removed from the Sephadex G-10 column.
The efficiency of cluster uptake was determined spectrophotometrically. Even though the gel's decomposition products absorbed in the spectral region of interest, the highest possible amount of eluted cluster was less than 0.7% of a 0.05 g sample.

Possible exchange of molybdenum atoms in solution was tested.

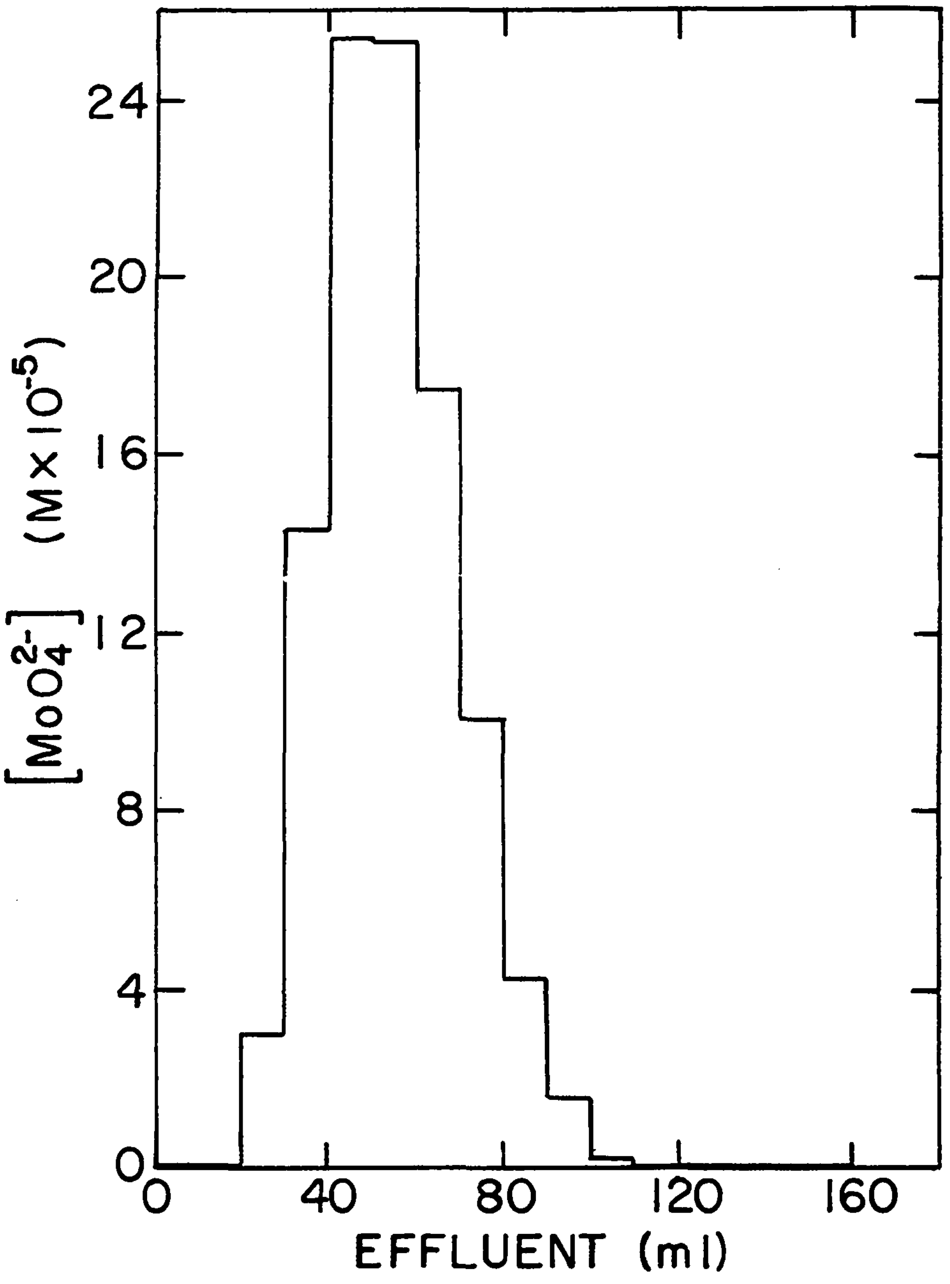


Figure 2.4. Quantitative elution curve of molybdate from Sephadex G-10 column with 1.5 N HCl as the eluant

A 1.5 N HCl solution of the labeled molybdate and DOHMO was allowed to stand for an hour after mixing before the column separation was begun. As in the labeled molybdate solution experiment, no activity remained on the column, indicating that exchange had not occurred. Later tests utilized the radioactive molybdenum resulting from neutron irradiation of the cluster. No variation in the activity remaining on the column was noted when the time between dissolving and separation was varied.

Molybdate was intuitively proposed for initial test purposes as the only radioactive species eluting off the Sephadex column; however, this needed to be confirmed. An irradiated DOHMO sample was dissolved and placed on the Sephadex column. 1.5 N HCl was added as the eluant, and the effluent was collected by the automatic fraction collector. In Figure 2.5 is illustrated the activity versus effluent volume. The activity peaked at approximately 50 ml of effluent as expected from the quantitative elution curve of molybdate in Figure 2.4. However, a significant amount of activity came through the column within the void volume of the gel. This result indicated the existence of a radioactive fraction which had little or no affinity for the Sephadex gel. A fluctuation in the relative heights of the two peaks was noted during repetitive elution curve determinations on separate samples.

In other experiments with irradiated DOHMO, the dissolved materials were refluxed for one hour in order to determine the stability of the radioactive species. Figure 2.6 illustrates the effect of refluxing on the activity in the elution curve. Some of the component

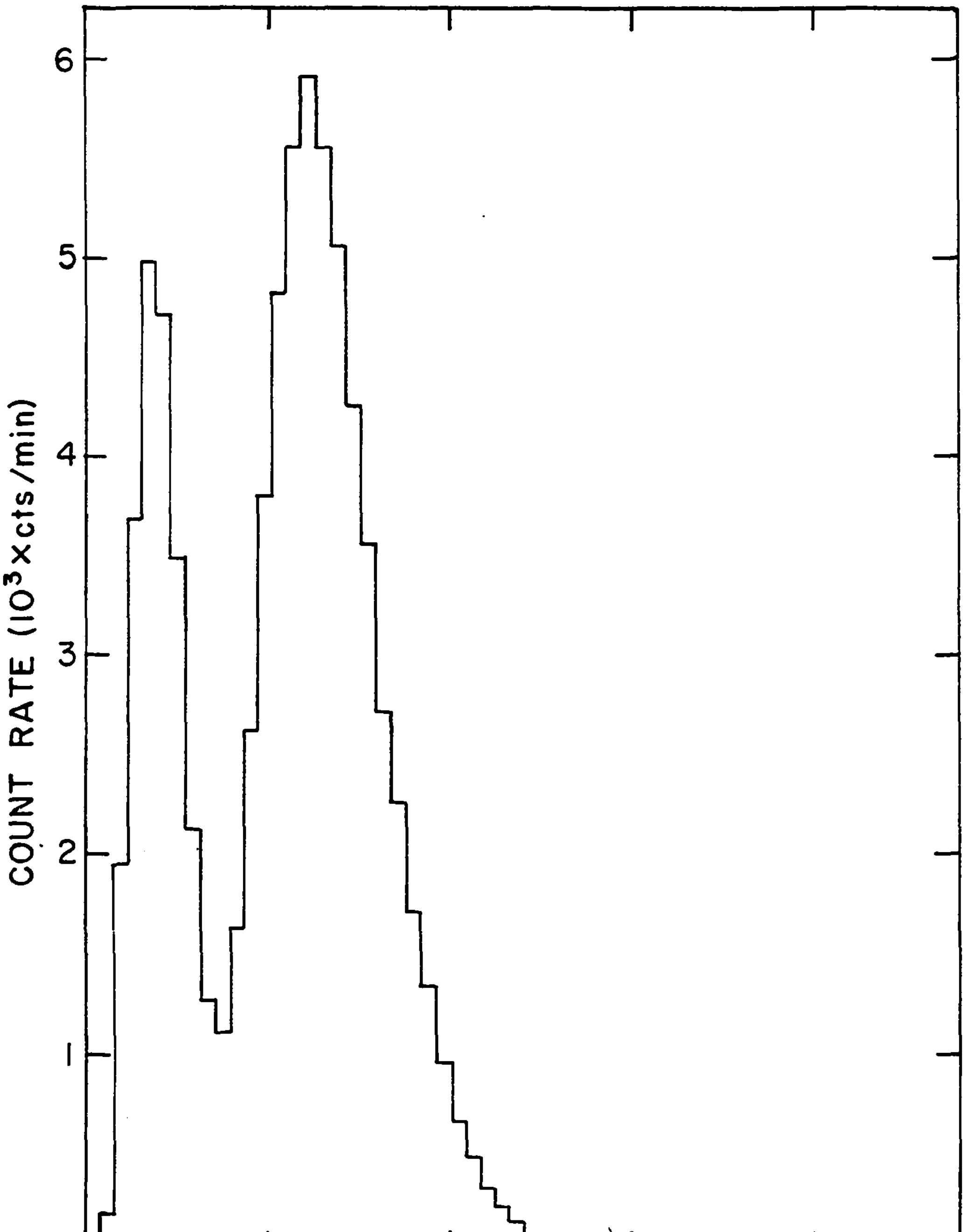


Figure 2.5. Elution curve of activity from an irradiated sample of DOHMO being separated on a Sephadex G-10 column with 1.5 N HCl as the eluant

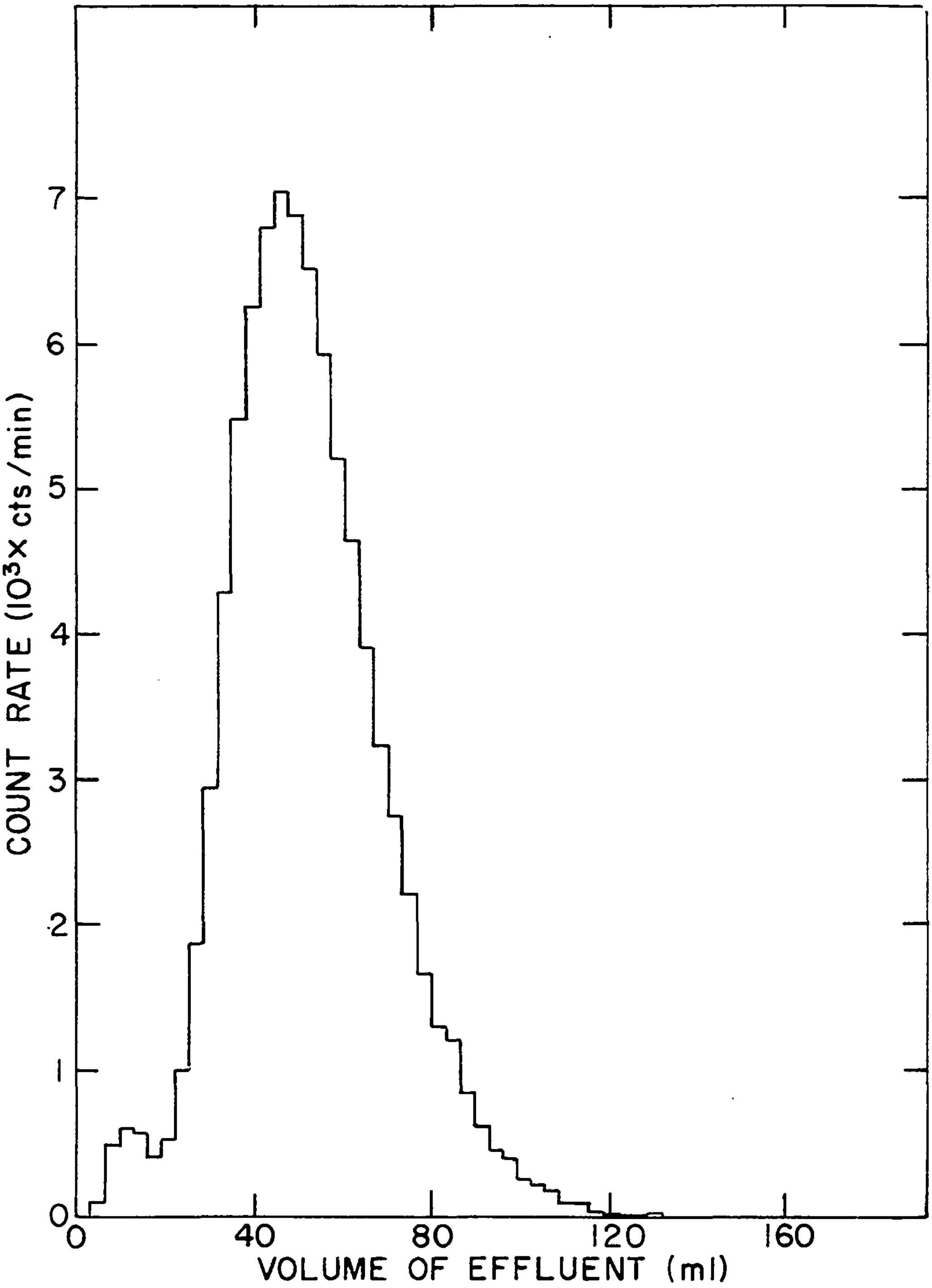


Figure 2.6. Elution curve of activity from an irradiated sample of DOHMO after refluxing for one hour, then separated on a Sephadex G-10 column with 1.5 N HCl as the eluant

in the first peak was obviously not stable to the heating. The positions of the molybdate peak relative to the effluent volume did not change as the area of this peak increased. Apparently the refluxing had converted the unknown species into molybdate.

Further separation of the radioactive species was attempted using P-2 gel. An elution curve of the activity obtained with this gel is illustrated in Figure 2.7. This time the molybdate peak position on the effluent volume axis was reversed with the smaller peak. This suggested that the interaction between the gel and the radioactive components must be different from that of the Sephadex gel. One can furthermore observe a small but very broad peak much further out in the elution curve. It was observed that this broad peak corresponded to the slow migration of the yellow cluster band through the gel bed. Since there was not a clean break in the activity between the cluster and the preceding peaks, the P-2 gel could not be used to determine retention of activity by the cluster.

Molybdenum blue was tested on the P-2 gel as possibly one of the radioactive species eluting off the column. The molybdenum blue was made by adding a small amount of hydrazine to a solution of ammonium molybdate. The molybdenum blue was mixed with the dissolved material from an irradiated sample of DOHMO and placed on a P-2 gel column. After adding 300 ml of 1.5 N HCl eluant, the blue band had not migrated from the top of the gel, while the cluster and all other activity had been stripped from the column. This observation ruled out molybdenum blue as one of the radioactive components.

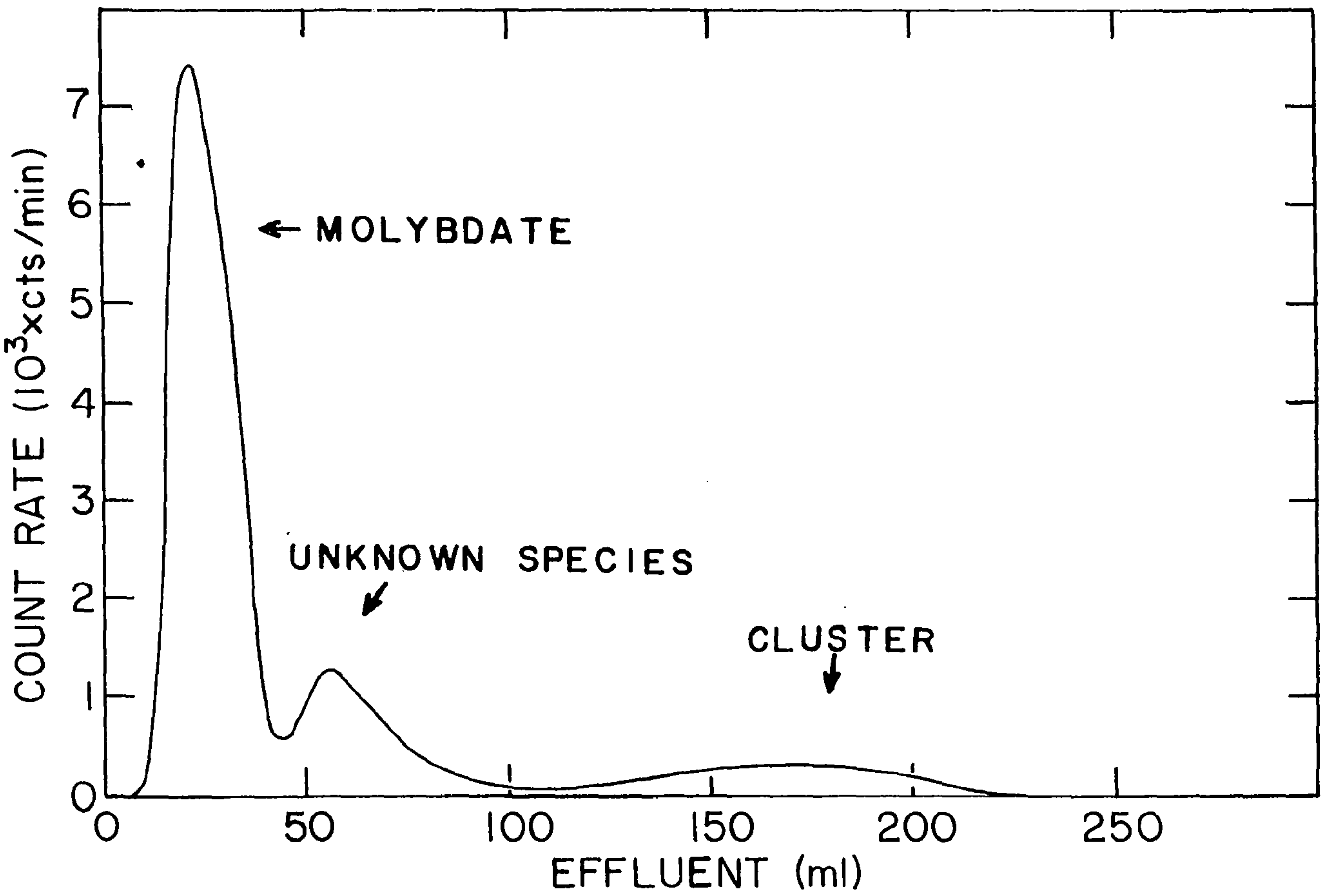


Figure 2.7. Elution of curve of activity from an irradiated sample of DOHMO being separated on a P-2 gel column with 1.5 N HCl as the eluant

A second means of determining retention in the cluster compound was recrystallization; however, this procedure had the drawbacks mentioned in the Procedure section. To compare the results from the two procedures, retention of the parent compound of DOHMO was determined after aging the irradiated samples 24 hours at room temperature. The average of three Sephadex column experiments gave a retention of 8.86 ± 0.21% of the total activity remaining on the columns after HCl elution. Recrystallization of two separate samples gave a retention of activity in the parent DOHMO compound of 7.03 ± 0.18%. In other series of experiments, the column separation always resulted in higher retention for the activity on the gel than the retention found by recrystallization. This difference was attributed to a radioactive species which interacted with the Sephadex gel in a manner similar to that of the parent cluster, yet possessed sufficiently different characteristics to be excluded from incorporation into the DOHMO crystals grown from acid solutions.

Even though retention of the parent compound could not be determined by gel separation, this procedure played a significant role in probe experiments where relative changes in activity distribution could be monitored. If a significant change in activity distribution was observed in column separations or a set of experimental conditions were deemed critical for the overall results of this study, recrystallization was performed to separate the cluster fraction.

In summary, the formation of several different radioactive species was demonstrated from the separation procedures. Activity was found in the parent cluster compound and in a component considered to be molybdate. The radioactive component breaking through within the void volume of the Sephadex gel comprised another species. However, the possibility that the molybdate component resulted simply from the decomposition of the component which had no affinity for the Sephadex was not ruled out. Still another radioactive component was the activity remaining with the cluster compound on the gel.

A separation based on ethanol may provide a more promising avenue of research for the identification of the radioactive components in the future. Electrophoresis could be applied to separate components in the ethanolic solution as has been reported for hydrated sodium hexachloroiridate(IV) (121-123) in which thirteen species have been identified.

Component Yield

Component yield is defined as the per cent of total activity found in one particular chemical species. Retention, i.e. the component yield of the target complex, is expressed as the per cent of total activity remaining in the target compound.

The retentions found for a 1% DOHMO solution are listed in Table 2.2. In the column experiments, three duplicate separations resulted in an average retention of 0.65 ± 0.02%. A recoiling atom which has broken away from the coordination site in the parent species is more likely to encounter only water molecules during the

Table 2.2. Retention of activity in the cluster compounds at dry ice and room temperatures. Comparison of the results for separation by recrystallization and Sephadex columns

Compound	Number of Experiments Column	Number of Experiments Recry	Aging Column Temp	Aging Column Time (hrs)	Aging Recry Temp	Aging Recry Time (hrs)	Encapsulation Column	Encapsulation Recry	Retention (per cent) Column	Retention (per cent) Recry
Solution[a]	3	1	RT[b]	24	RT	24	P[c]	VV[d]	0.65±0.02%	0.63%[e]
DOHMO	3	1	DI[f]	24	DI	24	P	P	8.67±0.23%	6.94%
OHMOD	3	1	DI	24	DI	24	P	P	14.8±0.1%	11.1%
OHMO	-	1	-	-	DI	24	-	P	-	25.0%
DOHMO	3	2	RT	24	RT	21	P	P	8.86±0.21%	7.03±0.18%
OHMOD	3	1	RT	22	RT	20	P	P	16.5±0.1%	12.6%

[a] 1% solution of DOHMO in 1.5N HCl.

[b] Room temperature.

[c] Heat-sealed polyethylene vial.

[d] Vycor tube under vacuum.

[e] Error corresponding to the difference between the second and third recrystallizations less than 4% of the retention value in all cases.

[f] Dry Ice temperature.

slowing-down period. The recoiling atom is, therefore, most likely to react with the water and not be incorporated back into the parent component. Thus the 0.65% retention may be indicative of failure of primary bond rupture. This view has been supported by Campbell (55). In other systems such as benzene solutions of ruthenocene (124) and various organic solutions of manganese carbonyl compounds (125), small primary retentions of the parent compound were observed. For example, in a 1% solution of $C_5H_5Mn(Co)_3$ in tetrahydrofuran, the parent retention was 0.02%. Therefore the parent retention in the 1% solution of DOHMO may indicate a rather large failure of bond rupture after the (n,γ) reaction. Furthermore, recrystallization data in Table 2.2 support the observed retention found in the column experiments. The retention was 0.63%. If the retention is due to a relatively large failure of bond rupture, then this failure may be due to the complex bonding of the molybdenum atom in the cluster. A more speculative factor may be a rather low recoil energy distribution of the gamma cascade; however, the energy distribution for the gamma cascade has not been fully characterized for ^{99}Mo.

Different solid forms of the molybdenum(II) chloride cluster were bombarded with neutrons at the reactor and then stored at either dry ice or room temperature for 24 hours before separation was begun. The results for both column and recrystallization separations of the compound are listed in Table 2.2. The difference in the retention measured by the recrystallization procedure and the activity remaining on the gel becomes more evident as the less hydrated compounds' retentions are compared.

The most striking feature of the data in Table 2.2 is the variation in retention with the amount of water present in the target material. DOHMO gave a retention of 6.94% when stored in dry ice for the 24 hours before separation. OHMOD gave 11.1% and OHMO's retention under identical conditions was 25.0%. Other systems (91-95, 126) have given similar reductions in retention for hydrated compounds.

Examples of these systems include the results on $NaMnO_4$ by Bolton and McCallum (92). They found a retention of 11% for a H_2O:$NaMnO_4$ mole ratio of 2.98 and a retention of 15% for a H_2O:$NaMnO_4$ mole ratio of 0.05. Cabral and Maddock (95) reported retentions of 3.5%, 12.0% and 20.8% for Ir in Na_2IrCl_6 containing 6, 2 and 0 moles of H_2O/mole Na_2IrCl_6, respectively. In Ambe and Saito's iodate systems (126), $Ca(IO_3)_2$ had a reported retention of 63 ± 2%, whereas the monohydrate gave a retention of 51 ± 1% upon neutron irradiation.

Harbottle and Sutin (54) have suggested the reduction of the hot atom in hydrated metal oxyanions as the cause of lower retention. This suggestion has been expanded to include other hydrated systems such as the ones previously discussed. Possibly, the dependence of retention upon the degree of hydration in the molybdenum(II) chloride system may be the consequence of in situ oxidation of the recoil fragment by the water. When the recoil fragment (i.e. a molybdenum atom) is oxidized, the atom in the higher oxidation state may not be able to exchange with the Mo(II) in the cluster matrix. Thus the chemical characteristics of the recoiled fragment are changed sufficiently that it becomes unable to exchange with an unexcited target atom.

Dimotakis et al. (96) have suggested that the lower retentions found in the hydrates reflect a lower tendency to annealing than the corresponding anhydrous material possesses. There appears to be little evidence in the literature to support this proposal, however. Little or no annealing was noted for either DOHMO or OHMOD between dry ice and room temperature, so a difference in annealing does not seem to be a factor for the molybdenum clusters studied. Annealing effects will be discussed in more detail in the next section.

There exist exceptions to the trend that the anhydrous compounds always have higher retentions. $Co(dipy)_3(ClO_4)_3$ system (97) and $Co(en)_3Cl_3$ system (96) have shown lower retentions for the anhydrous material under identical conditions. For example, $Co(en)_3Cl_3$ gave a retention of 66.8%, but $Co(en)_3Cl_3 \cdot 3H_2O$'s retention was 88.5% under identical conditions utilizing neutrons for activation (96). These exceptions support Fenger's contention (53) that general models may not be possible for many diverse systems involving Szilard-Chalmers effects.

Annealing Results

The possibility of annealing radioactive fragments into the original compound exists at any temperature. In Table 2.2, the results reflect little change in retention between Dry Ice and room temperatures for DOHMO and OHMOD. A small difference for OHMOD stored at dry ice and room temperature following irradiation possibly suggests a slight annealing effect at room temperature. This relatively small change from 11.1% to 12.6% in retention could, however, be a consequence of a small difference in the amount of water present in the two specimens used for the experiments. Furthermore, retentions determined by recrystallization in experiments at 120°C or following treatment by gamma ray irradiation were found to occur between the values of 11.1% and 12.6% which indicates the difference is probably not an annealing effect.

Higher temperatures were apparently needed in order to explore the possibility of a more marked change in retention upon annealing. Several thermogravimetric tests were performed on DOHMO and OHMOD to test the feasibility of various annealing treatments. Water loss was rapid from DOHMO even at temperatures as low as 40°C; therefore, DOHMO could not be studied at higher temperatures for annealing effects.

OHMOD samples were stable during annealing in air at 120°C. However, small 0.01 g samples showed bulk reaction at 200°C in that the entire sample changed from its original pale yellow color to olive green. Furthermore, the retention of activity in the radioactive components on the gel appeared to decrease at high temperatures, as listed in Table 2.3. This decrease was apparently due to the reaction products eluting through the columns with the molybdate species. Therefore, the column separation procedure which utilized small samples was not applicable at 200°C. When 0.2-0.5 g samples were sealed in air, there was insufficient oxygen to react with the

Table 2.3. Retention of activity in OHMOD upon annealing at various temperatures. Comparison of the results for separation by recrystallization and Sephadex columns

Aging[a]				Number of Experiments		Encapsulation		Retention (per cent)	
Column		Recry							
Temp	Time(min)	Temp	Time(min)	Column	Recry	Column	Recry	Column	Recry
-	-	-	-	3	1	P[b]	P	14.8±0.1%	11.1%[d]
-	-	-	-	-	1	-	VV[c]	-	14.6%
120°	320	120°	360	1	1	G[e]	G	17.6%	12.1%
200°	120	200°	120	1	1	G	G	17.6%[f]	14.3%
200°	1980	200°	1995	1	1	G	G	15.5%	15.8%
-	-	320°	3420	-	1	-	VV	-	25.6%[g]

[a] Samples aged in Dry Ice for 24 hours before annealing.

[b] Heat-sealed polyethylene vial.

[c] Vycor tube under vacuum.

[d] Error corresponding to the difference between the second and third recrystallizations less than 4% of the retention value in all cases.

[e] Glass centrifuge tubes.

[f] Slight decomposition.

[g] Decomposition of cluster noted.

entire sample. Only a small layer at the top was discolored. The determination of retention by the recrystallization procedure is still possible on partially decomposed samples, since most decomposition products are separated out of the cluster when crystallization occurs. The decomposition products must either be soluble or must contain recoil fragment activity for the recrystallization procedure to yield a measure of retention. Therefore, recrystallization provided retention data at 200°C even when the samples were sealed under air, since the sample dissolved.

The results of annealing at 120°C, 200°C and 320°C, along with the type of encapsulation for each experiment are listed in Table 2.3. The results of experiments at 120°C and 200°C must be compared with the sample irradiated under the same conditions. This sample had an observed retention (by recrystallization) of 11.1%. The largest increase in retention at 120°C or 200°C occurred in a sample annealed at 200°C for 1995 minutes. The slight increase was from 11.1% for the samples stored in dry ice to 15.8% for the annealed sample. No comparison could be made from the gel separation data due to the reaction of the samples with oxygen.

At 320°C, it was necessary to evacuate the air from the sample in order to prevent reaction with oxygen. Even with this precaution, a brownish-black precipitate was observed when dissolution was attempted. From other experiments in which no color change was noted and in which only one transfer from the irradiation capsule to the dissolving beaker occurred, the amount calculated from spectral analysis averaged slightly more than 96.6% of the amount weighed out. However, the amount found by spectral analysis for the sample annealed at 320°C for 3420 minutes was just over 75% of the weighed amount, indicating bulk decomposition. Increased retention is still indicated by the recrystallization procedure; however, a large error may have been introduced by the decomposition.

Another observation of the OHMOD samples sealed in Vycor tubing was the bumping when the samples were first placed under vacuum. This bumping may have resulted from either loss of a small amount of water or loss of trapped gases. In Table 2.3, the results of the vacuum are seen on the sample irradiated in an evacuated Vycor tube and cooled in Dry Ice for 24 hours before separation. The observed retention for this experiment was 14.6%, compared to the 11.1% for a sample irradiated under air in a polyethylene vial. Since the sample annealed at 320°C was sealed in a vacuum, the retention must be compared to the retention of 14.6% observed for the vacuum-sealed sample stored in dry ice before separation. An increase in retention from 14.6% to 25.6% resulted after two days of annealing at 320°C.

The annealing conditions were quite severe compared to other systems which have been studied (88,99,101). For example, the highest temperature studied by Groening and Harbottle (99) for annealing in $Mo(CO)_6$ was 120°C. Samples dissolved immediately after irradiation in a solution cooled to 0°C gave a retention of 60%. The samples annealed at 120°C for ten minutes had an observed retention of 87%. E. Lazzarini and A. L. Fantola Lazzarini (88) subjected <u>cis</u>-

$[Co(en)_2(NO_2)CNS][Co(EDTA)]\cdot 2H_2O$ to a temperature range of 20°C to 162°C for purposes of studying both anionic and cationic annealing simultaneously. No attempt was made in the present study to obtain a complete isothermal annealing curve since partial decomposition was observed at 320°C.

Results in Table 2.4 compare the effects of high doses of ionizing radiation upon retention. Comparable samples treated under similar conditions without exposure to the extra ionizing radiation are also listed in Table 2.4. The observed retention for the sample receiving an ionizing radiation dose of 22.5 Mrad after being stored for 24 hours in Dry Ice was 11.8%. A sample stored for 24 hours in Dry Ice which received no subsequent ionizing radiation gave a retention of 14.6%. The sample thermally annealed at 200°C for 2000 minutes gave a retention of 26.5%, whereas the sample receiving both the extra 22.5 Mrad of ionizing radiation and subsequent heat treatment for 2000 minutes at 200°C retained only 19.4% of the activity in the cluster.

Most systems previously studied have been concerned with several Co(III) complexes. An increase in retention has normally been observed following ionizing radiation treatment, especially if subsequent thermal annealing was utilized. However, Dimotakis _et al_. (96) have observed one exception. $[Co(en)_3]Br_3$, which received an additional ionizing dose of 24 Mrad during neutron irradiation, had a retention of only 57.2%. When the compound had not received this extra ionizing radiation, the observed retention was 68.2%. Even though Dimotakis

Table 2.4. Retention of activity in OHMOD for annealing following ionizing radiation and related results

Aging[a]				Dose[b] (Mrad)		Number of Experiments		Retention (per cent)	
Column		Recry							
Temp	Time(min)	Temp	Time(min)	Column-Recry		Column-Recry		Column	Recry
-	-	-	-	-	0	-	1	-	14.6%[c]
RT[d]	4380	RT	4380	22.5	22.5	3	1	17.7±0.2%	11.8%
-	-	200°	2000	-	0	-	1	-	26.5%
200°	2000	200°	2000	22.5	22.5	3	1	26.5±0.2%	19.4%

[a] All samples aged for 24 hours in Dry Ice; all samples encapsulated in Vycor tubes under vacuum.

[b] 2 Mrad dose received by all samples during neutron irradiation not included.

[c] Error corresponding to the difference between the second and third recrystallizations less than 4% of the retention value in all cases.

[d] Room temperature.

et al. (96) did not anneal $[Co(en)_3]Br_3$ without the extra gamma ray dose, other systems have shown equal or increased retention in samples annealed after receiving an extra ionizing radiation dose compared to samples subjected to only the thermal annealing treatment. For example, Nath et al. (86) subjected tris(acetylacetonato)cobalt(III) to a temperature of 120°C for 28 hours in a vacuum with a resulting retention of 33.0%. With an additional 0.5 Mrad of ionizing radiation and with the subsequent thermal treatment, a retention of 37.0% was reported. This increase found among other studies was not the case in the molybdenum(II) chloride system.

There are several plausible explanations for the observations in radiation treatment of the OHMOD samples. One possibility is that during evacuation of the capsules, before neutron irradiation, the samples which were not subjected to extra ionizing radiation dehydrated to a greater extent than the other samples; thus the observations reflect hydration effects. However, the OHMOD samples were prepared by dehydrating DOHMO at 200°C for six hours in a dynamic vacuum; little dehydration should have occurred during the sealing of the Vycor tubes.

Another possibility exists that the samples which underwent the 22.5 Mrad ionizing radiation treatment suffered decomposition even though no observable physical change took place, e.g. discoloration. Calculations (87) have been made on the distribution of ionizing radiation within a solid. 50 Mrad of gamma ray irradiation was found to be sufficient to excite all the atoms at least once on the average, with a minimum of one electron volt of energy. Therefore, the number of atoms involved with 22.5 Mrad of ionizing radiation was sufficient to account for a significant decrease in parent retention if only a fraction of these events resulted in a decomposition.

The possible decomposition was investigated on a sample which was given identical gamma ray treatment as those carried through the recrystallization experiments, except that it was not subjected to the neutron flux. The amount of OHMOD calculated from absorbance measurements was identical (within experimental error) to the amount weighed out. Furthermore, as seen in Figure 2.8, the molar absorption of molybdate in 1.5 N HCl was less than 170 $cm^{-1}M^{-1}$ per atom of molybdenum at 310 nm. Little interference would have occurred at 310 nm for the cluster spectrum from decomposition products converted into molybdate. The molar absorptions for the cluster as a function of wavelength in the range illustrated in Figure 2.8 were compared to the spectra of the samples subjected to the extra ionizing radiation. Within the accuracy of the measurements, no difference was noted. Hence, there was no evidence of decomposition occurring in the irradiation.

There could have also been an oxygen effect. If the samples subjected to the extra ionizing radiation contained more oxygen than the other samples, then lower retention might be expected. Several studies (86, 127-129) have reported an oxygen effect. Nath et al. (86) have observed an oxygen effect in tris(acetylacetonato)cobalt (III). This compound had an observed retention of only 3.0% after

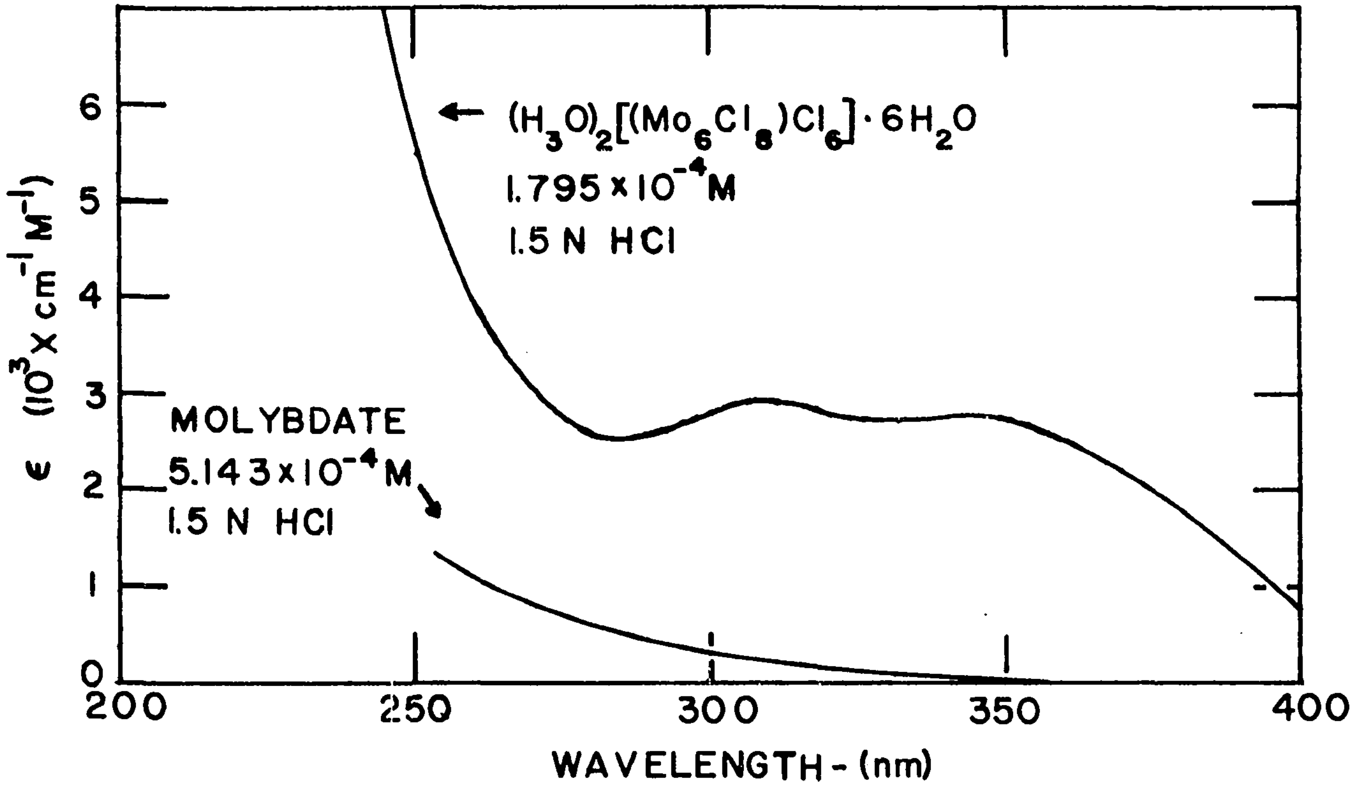


Figure 2.8. Absorbance spectra of molybdate and $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$

thermally annealing in air at 120°C for six hours. Under a vacuum, with the same conditions, a retention of 15.5% resulted. The mechanism in the Nath model (86) for the oxygen effect involved the trapping of thermally-excited electrons by oxygen molecules on the solid's surface. If the oxygen competes successfully with the recoil fragments for the electrons, then little annealing was thought to occur. Support of an oxygen effect can be found in the molybdenum(II) chloride system. In Table 2.3, the retention of a sample of OHMOD sealed in air and thermally annealed at 200°C for 1995 minutes was 15.8%. The 15.8% retention is much lower than the 26.5% retention found for the sample treated in a vacuum listed in Table 2.4. This effect appears much too large to be explained by dehydration. The investigation of a possible oxygen effect offers an excellent area for further research. Experiments designed specifically for this area would possibly be most valuable in interpreting some of the observations in this study. Both OHMOD and OHMO could be utilized.

If the gamma ray irradiation actually does decrease the extent of annealing in the molybdenum(II) chloride system, the effect can be rationalized in terms of a modification of the Nath model (86). Fenger (53) has suggested that general models may not exist; therefore, the following proposal may have very limited applicability. In the Nath model (86), the concept of electron traps was applied to interpret radiation annealing data. The energy levels of the traps were located between the conductance and valence bands. Annealing was proposed to take place when the thermal energy of the solid was sufficient to excite trapped electrons into the conductance band. The traps and recoil fragments compete for these electrons, and when the fragments were successful, the energy imparted to the fragments was sufficient to satisfy the activation needed for exchange of the fragment atoms with a site in the parent compound.

When gamma ray irradiation occurred, the effect was to form deep traps (130-132) along with electron holes in the valence band. The ejected electrons resulting from the gamma ray irradiation populated the shallow traps. Subsequent thermal treatment could easily depopulate these filled shallow traps and result in the annealing process. The gamma ray process is assumed to be the same for the molybdenum(II) chloride system as in the Nath model. Furthermore, the formation of deep traps and electron holes from the gamma ray irradiation would also occur. However, it is proposed that the deep traps and electron holes compete much more successfully than the recoil fragments for any electrons reaching the conductance band by thermal excitation than contained in the Nath model for cobalt complexes. With fewer electrons reaching the recoil fragments the result would be a decrease in the retention after a sample had been treated with ionizing radiation and subsequent thermal treatment as compared to a sample undergoing only thermal annealing. The limited observations made on OHMOD samples corresponding to these conditions follow the proposed decrease in retention.

The rate of increase in retention upon annealing for the molybdenum(II) chloride system proved to be very slow even at high temperatures in comparison to other systems which have been studied. For example, Nath et al. (86) found the retention in an untreated sample of the sodium EDTA complex of Co(III) to be 1.5%. When this complex was annealed for one hour at 150°C, the retention increased to 34.0%. In $[Co(en)_3](ClO_4)_3$, Dimotakis et al. (96) reported the retention of an untreated sample to be 33.1%, whereas, upon receiving a 10 Mrad dose of ionizing radiation and heating for 25 hours at 135°C, the retention increased to 60%. These results and conditions are typical for cobalt systems which comprise the bulk of the studies on annealing phenomena.

Further areas of research based upon this preliminary investigation have been noted. There appears to be a marked change in retention with the amount of water present in the molybdenum(II) chloride. The utilization of a dry sample of OHMO, being handled under dry conditions before dissolution, would eliminate the hydration effect. Thermal annealing and ionization irradiation effects, along with the oxygen effect, could possibly be quantitized for OHMO if further studies were undertaken.

SUMMARY

Partial separation of radioactive species in HCl solution resulting from the (n,γ) reaction on the solid-state systems containing the octa-μ_3-chloro-octahedro-hexamolybdenum(II) cluster has been obtained with the use of Sephadex G-10 gel. A suitable recrystallization method was formulated to quantitize the retention of activity in this system. In aqueous HCl solution, the ^{99}Mo recoil atom resulting from neutron bombardment was postulated to be in the form of at least four different species. The four species were the parent cluster compound, the radioactive component(s) retained with the parent cluster on the Sephadex gel and the two components which were separated from the Sephadex column using HCl as the eluant.

Both column and recrystallization data support the proposed failure of bond breaking in the ^{98}Mo(n,γ)^{99}Mo reaction to the extent of 0.64% for the cluster system in 1.5 N HCl solution. It is proposed that the recoil from the prompt gamma cascade is insufficient to break the strongly bonded molybdenum atom in the cluster in the lower energy region for only this small fraction of events. Parent retention in solution has been observed in other systems (124,125), but usually to a lesser extent.

The parent retention varied markedly with the extent of hydration in identically treated samples. The range began at 7.0% retention for DOHMO and increased to 25.0% for an OHMO sample containing 0.8% water. In this study, chemical change of the hot atom by water, which prevents annealing, is supported.

Effects of annealing were observed only under the most severe conditions. After heating a sample over a two day period at 320°C, the parent retention did increase from 14.6% to 25.6%; however, partial decomposition of the sample was observed. Annealing by ionizing radiation, followed by thermal annealing, resulted in a lower observed retention than samples which were only heated. The difference may have been a result of hydration or oxygen effects.

The octa-μ_3-chloro-*octahedro*-hexamolybdenum(II) cluster system offered a unique study in the Szilard-Chalmers effect. However, before more extensive studies are begun on this system or related cluster compounds, a rapid and efficient means of separation of the parent species from the fragments should be obtained.

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