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# RACEMIZATION OF OPTICALLY ACTIVE COMPLEXES.

I. CATALYTIC RACEMIZATION OF tris(ETHYLENEDIAMINE)COBALT(III) IODINE.

II. CATALYTIC RACEMIZATION OF tris(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE AND TRIS(ETHYLENEDIAMINE)RHODIUM(III) CHLORIDE.

by

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# RACEMIZATION OF OPTICALLY ACTIVE COMPLEXES.
# I. CATALYTIC RACEMIZATION OF tris(ETHYLENEDIAMINE)COBALT(III) IODIDE.

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## SUMMARY

Catalytic racemization of the tris(ethylenediamine)cobalt(III) iodide has been studied in the presence of active carbon, platinum black and silica gel. Exchange studies of the cobalt complex with the $C^{14}$-labeled ethylenediamine were also made in order to find some clue to the mechanism of the racemization process. It was concluded that the complex first is activated and then racemizes. This process is accompanied by partial decomposition of the complex.

## INTRODUCTION

Douglas

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Douglas, B. E., J. Am. Chem. Soc. 76, 1020 (1954).

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reported that when optically active samples of $[Coen_3]Cl_3$ solution were heated with active carbon at 90°, they become inactive within 5 min. The absopption spectrum of the solution after treatment was found to be the same as the original sample between 330 mμ to 725 mμ. It was of interest to determine whether $[Coen_3]I_3$ solution behaves similarly with other catalysts, such as platinum black and silica gel, and also whether the racemization takes place via any sort of decomposition.

## EXPERIMENTAL

Tris(ethylenediamine)cobalt(III) chloride was prepared by the method of Work

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Work, J. B., Inorganic Synthesis 2, 221 (1946).

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and resolved by the fractional crystallization of the chloro-d-tartrate salt.

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Werner, A., Ber. 45, 121-30 (1912).

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Since L—chloro-d-tartarate is much less soluble, it can be obtained in the pure state very easily by fractional crystallization. The chloro-d-tartrate was then treated with hot saturated KI solution whence $[Coen_3]I_3$ precipitated out of the solution in fine needles. The specific rotation for the iodide with sodium light was -154° which is almost equal to the value obtained by Werner (-155°). The optical rotations were measured with a Schmidt-Haensch double field polarimeter which read to ±0.01° by means of the Vernier Scale.

The racemization studies are made as follows: 15 ml. of the solution of $[Coen_3]I_3$ was taken in a conical flask with reflux condenser and heated to the desired temperature. Then the charcoal was added to the solution and kept at that temperature for the desired time. At the end of the period, the conical flask was removed from the heat source and the solution filtered from charcoal through a quick filtering filter paper. Then it was again filtered, this time through a No. 42 Whatman filter paper to get rid of any charcoal particles which may have escaped provious filtration. The solution was then evaporated under an infrared lamp and weighed to determine the amount of compound that has been absorbed by charcoal. When complete racemization occurred this procedure of evaporation was not done. The activity of the treated compound was then determined in the polarimeter.

Exchange between the complex and $C^{14}$ labeled ethylenediamine. - Labeled ethylenediamine dihydrochloride prepared by Dr. W. G. Gehman

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Gehman, W. G., and Fernelius, W. C., NYO-7709.

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was used for all the exchange experiments. An aqueous solution of $[Coen_3]I_3$ and labeled ethylenediamine hydrochloride were mixed together and heated to the temperature of the racemization experiment. Active carbon was then added and the heating continued for the desired time. The solution was then filtered and $[Coen_3]I_3$ was precipitated from the filtrate by the addition of saturated potassium iodide solution.

The manipulation of the solid precipitate was carried out as follows: A Büchner funnel with sintered glass base was sawed apart, flush with the top surface of the sintered disc. The two portions were then ground with carborundum to give a smooth fit. A piece of filter paper (Schleicher and Schuell #576) can be placed on the sintered disc and the glass chimney replaced. After filtration, the filter paper can be removed for drying, counting and weighing.

Calvin, M., and others, "Isotopic Carbon", John Wiley and Sons, Inc., New York, 1949, p. 115.

For counting purposes the filter paper with the precipitate was mounted between two aluminum plates, one of which was solid and the other had a hole in the center with slightly smaller diameter than the filter paper.

The activities were counted with a scaling unit made by Nuclear Instrument and Chemical Corp. (Model 165) and a Geiger-Müller counting tube with a 2.88 mg./cm$^2$ window thickness (made by Dr. W. W. Miller).

Spectrophotometric Studies. - Spectrophotometric studies were done in a Beckman DU model Quartz spectrophotometer. The absorption curves of the original solution of $[Coen_3]I_3$ as well as of those which were treated with active carbon for the racemization reaction were studied at various experimental conditions.

Active Carbon. - A quantity of powdered wood charcoal (Fisher) was activated by the following treatment. The charcoal was first refluxed with concentrated hydrochloric acid for about six hours. It was then filtered and thoroughly washed with water to remove hydrochloric acid. It was dried and finally heated to 700° in a loosely covered crucible for about two hours. It was then cooled and bottled in a stoppered bottle. This carbon usually remains active for months.

Platinum Black. - Potassium chloroplatinate solution was warmed on a water bath with alcohol and a little potassium hydroxide solution. There was a black precipitate which was filtered, washed thoroughly with water and dried.

Silica gel. - The silica gel was heated to about 200° for three hours, cooled and kept in a dessicator over concentrated sulphuric acid.

## RESULTS AND DISCUSSION

It has been found that optically active $[Coen_3]Cl_3$ when treated with active carbon loses its optical activity very easily. On the other hand, it has been pointed out by various workers

See Douglas, B. E., loc. cit.

that without active carbon this compound can be boiled for hours without any loss of optical activity, and a solution of $[Coen_3]Cl_3$ remains for months without any noticable change in optical rotation.

As pointed out by Douglas, it is not possible to analyze mathematically any of the data available from the charcoal treatment. The charcoal loses most of its activity within a few minutes and it is almost impossible to know how much of the active charcoal has become inactive at a particular time.

The case of the exchange studies was similar. The active carbon adsorbed considerable radioactive ethylenediamine and the amount adsorbed was dependent on the temperature of the reaction and the amount of charcoal and ethylenediamine added. However, an attempt has been made to calculate the amount of exchange by subtracting the total amount of ethylenediamine adsorbed by charcoal. This gives the order of magnitude of the exchange reaction though not the exact values.

When the complex is boiled in the presence of charcoal for about five minutes and then filtered, a definite color change is observed. The color of the solution first changes from yellow to reddish brown. This points to the possibility of the formation of a bis(ethylenediamine) aquo complex of cobalt(III). To solve this, the absorption spectra of the original complex salt solution and the solution after treatment with active carbon at different temperatures and different time lengths were studied. These are shown in Fig. I. It is found from the study of the curves that the sample which was boiled for ten minutes in the presence of charcoal is definitely decomposed and most probably it has been converted into a bis(ethylenediamine) aquohydroxocobalt(III) complex. The sample which has been boiled for five minutes shows less of a shift from the original curve. The sample which was heated to 80° for fifteen minutes is not decomposed much as seen from the curve. However, all these three samples underwent complete racemization. It is to be concluded from the above observations that although the recemization can take place without decomposition, there is a definite tendency for the compound to undergo decomposition under these experimental conditions.

Table I

| Catalyst Used | Reaction time in min. | Reaction Temp. | % Exchange |
|---|---|---|---|
| Charcoal (active) | 10 | 100° | 15 |
| Charcoal (active) | 15 | 80° | 22 |
| Pt. black | 75 | 100° | 28 |

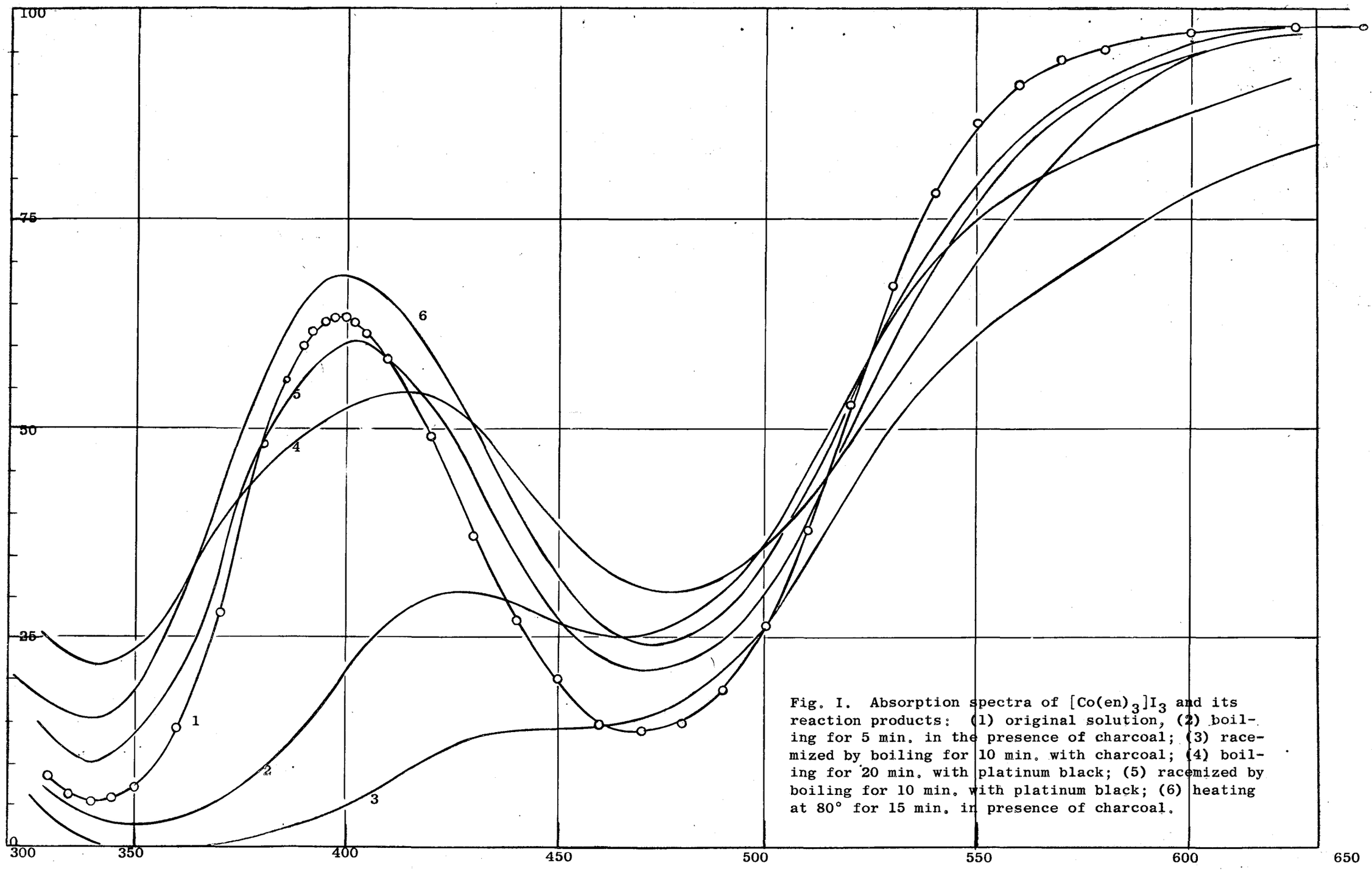


Fig. I. Absorption spectra of $[Co(en)_3]I_3$ and its reaction products: (1) original solution, (2) boiling for 5 min. in the presence of charcoal; (3) racemized by boiling for 10 min. with charcoal; (4) boiling for 20 min. with platinum black; (5) racemized by boiling for 10 min. with platinum black; (6) heating at 80° for 15 min. in presence of charcoal.

The study of the exchange reaction with radioactive ethylenediamine showed that, in every case, a considerable amount of exchange took place. The sample which was boiled for ten minutes gave a 15% exchange after treatment with active carbon when it is calculated on the basis that the complex is the tris(ethylenediamine) compound. When calculated as the bis(ethylenediamine) compound we get 18% exchange. The sample heated to 80° for fifteen minutes gives an exchange of 22% (calculated as tris(ethylenediamine) compound).

Similar observations were made both spectrophotometrically and in exchange reactions when the complex was treated with platinum black, though to a lesser extent. The exchange observed here was 27.7% only when boiled for seventy five minutes. Considering the above facts it seems that the racemization processes involved in these two cases are similar. The optically active complex when similarly boiled with silica gel does not lose any optical activity.

Under the experimental conditions, the racemization can take place according to any of the following schemes:

(1) Simple dissociation and subsequent decomposition of the tris(ethylenediamine) compound to form bis(ethylenediamine) aquo compound.

(2) Intramolecular dissociation with five-coordinate intermediate.

(3) Activated six-coordinate intermediate without bond rupture.

By process (1), the complex can first decompose to form a bis(ethylenediamine) aquo complex. The tendency for the decomposition of the complex was noticed when the complex was boiled for 10-15 minutes in the presence of active carbon. By this process, the complex can lose its optical activity, only, by decomposition.

By the second method, one of the links of the ethylenediamine molecule may be broken. This can rearrange itself causing the loss of optical activity. Under this condition no exchange is expected. However, another ethylenediamine molecule may come over and take the vacant coordination position and displace one of the former ethylenediamine molecules. Under these conditions exchange and racemization may take place together and they will depend on one another. The place of the attacking en molecule may also be taken up by water, then the whole process will resemble (1) - the $H_2O$ occupying the vacant position first and then, by knocking out the loose ethylenediamine, will form the bis(ethylenediamine) aquo cobalt complex.

There should not be any bond rupture if the racemization takes place by the third postulated method. A substance that autoracemizes, but gives no indication of bond rupture will be expected to undergo racemization via an activated intermediate. That the intermediate should have more energy follows from the fact that the two enantiomorphoric forms have the same energy but only slowly lose their optical activity. An example of this type of racemization has been given by Ray and Dutt

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Ray, P., and Dutt, N. K., J. Indian. Chem. Soc. 20, 81 (1943).

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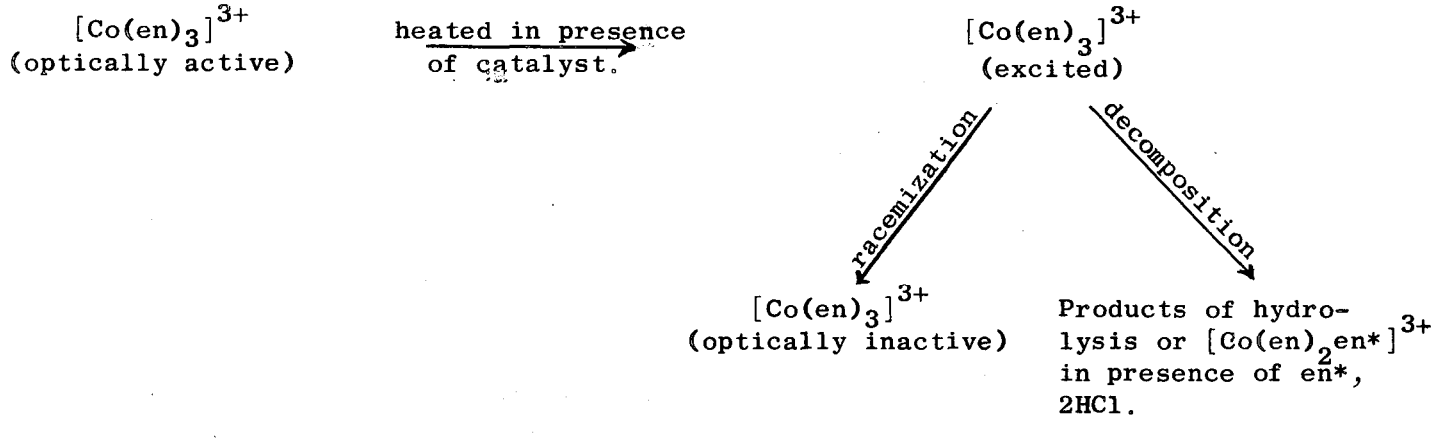
for tris(biguanidinium) cobalt cation which slowly racemizes on heating a solution of the pure salt. However, the evidence of bond rupture does not exclude the intramolecular rearrangement mechanism since racemization may proceed by a different mechanism than decomposition or exchange.

In the case of tris(ethylenediamine)cobalt(III) there is no sign of autoracemization. From the spectrophotometric investigation it has been observed that there is a definite tendency for bond rupture in the process, though it has been found that racemization and decomposition of the complex do not go side by side and they are not interdependent. If the racemization took place by any kind of bond rupture, a much higher exchange of ethylenediamine would have been expected. It has been found that when the racemization is complete, the exchange is only 20%.

Under this condition the following mechanism has been suggested for the racemization of $[Co(en)_3]^{3+}$ in the presence of charcoal and platinum black.



The excited state of the $[Co(en)_3]^{3+}$ is attained by the third postulated mechanism, the heat and the active carbon supplying the energy. In all probability there is no sharp line dividing the complete racemization process without any decomposition and with decomposition. The energy supplied by heat and charcoal may be sufficient to cause both the reactions to go on simultaneously.

## II. CATALYTIC RACEMIZATION OF tris(ETHYLENEDIAMINE)PLATINUM(IV) CHLORIDE AND tris(ETHYLENEDIAMINE)RHODIUM(III) CHLORIDE.

### SUMMARY

Catalytic racemization process of tris(ethylenediamine)platinum(IV) and -rhodium(III) has been studied in the presence of active carbon, platinum black, and silica gel. Exchange studies of the platinum compound with $C^{14}$-labeled ethylenediamine were made under similar experimental conditions for racemization. No exchange was found to occur during the process. The racemization most probably takes place through an activated six-coordinate intermediate.

### INTRODUCTION

It has been found that when optically active tris(ethylenediamine)cobalt(III) chloride is heated in the presence of charcoal catalyst it loses all its optical activity.

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Douglas, B. E., J. Am. Chem. Soc. 76, 1020 (1954).
Sen, D. and Fernelius, W. C., previous communication.

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It seemed interesting to know whether the tris(ethylenediamine) compounds of platinum and rhodium also have the same behavior. It was found that the tris(ethylenediamine) compound of platinum racemizes when heated for about one hour in the presence of active carbon, though not in the presence of platinum black and silica gel. Tris(ethylenediamine)rhodium(III) chloride was found to remain completely unaffected by the above treatment with charcoal, platinum black and silica gel even on prolonged heating.

## EXPERIMENTAL

The tris(ethylenediamine)platinum(IV) chloride was made by the method of Werner

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Werner, A. Naturf. Ges. Zurick, 62, 553 (1917).

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and resolved into its dextro and laevo forms by the fractional crystallization of the chloro-d-tartrate salt by adding d-$NH_4$-tartrate to the racemic mixture of the platinum compound. The L-$[Pten_3]^{Cl_2}_{d\text{-}C_4H_4O_6}$ which precipitated was filtered and recrystallized. The compound was then treated with a hot, saturated solution of potassium iodide causing the precipitation of L-$[Pten_3]I_4$. This was then reconverted to chloride by treating with silver chloride.

Tris(ethylenediamine)rhodium(III) chloride was prepared by the method of Werner.

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Werner, A., Ber. 45, 1229 (1912).

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The dextro and the laevo compounds were separated by fractional crystallization of the chloride-tartrate compound L-$[Rhen_3]^{Cl}_{d\text{-}C_4H_4O_6}$ separated out first and was further purified by fractional crystallization from hot water. This product was then decomposed by adding hot, saturated potassium iodide solution to a concentrated chloride-tartrate compound. The specific rotation of the chloride-tartrate was found to be $[\alpha]_D^{25} = -48°$ which is very near to value obtained by Werner, ($[\alpha]_D^{25} = -50°$).

The determination of the change of optical activity, and the exchange reactions with labeled ethylenediamine were carried out as described in the previous communication. Active carbon, platinum black and silica gel were prepared by the method described previously.

## RESULTS AND DISCUSSION

Tris(ethylenediamine)platinum(IV) ion was found to be optically very stable. The aqueous solution of this was boiled for about six and a half hours without any change in optical rotation. It was then heated with active carbon. In five minutes there was no change in rotation. Boiling for thirty minutes caused little diminution in the

optical rotation, although in seventy minutes the complex was completely racemized. Boiling with platinum black for three hours caused no diminution in optical rotation. Boiling with silica gel for a number of hours did not produce any racemization. Moreover, $[Rhen_3]Cl_3$, was not found to be effected by boiling alone, or boiling with active carbon, platinum black and silica gel. The optical rotation remained completely unaffected by any treatment.

Ethylenediamine exchange studies. - Exchange of the labeled ethylenediamine with the complex ion in the presence of active carbon was studied. It was found that the exchange takes place to a very little extent which may easily pass for contamination.

As indicated in our previous communication recemization can take place mainly by two methods, viz. (a) dissociation or (b) formation of six-coordinate intermediate without bond rupture. If there are any decomposition or dissociation process involved in the racemization, it is expected that a large amount of exchange with active ethylenediamine, available in the system in the exchange study experiments cited above, will take place during racemization. On the contrary, very little exchange is found. Steigman

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Steigman, J., Phys. Rev. 59, 498 (1941).

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studied the exchange of tris(ethylenediamine) complexes of Rh, Ir and Pt with radiometals derived by a Szilard-Chalmers reaction. He found a slow exchange in all cases. Hence a little exchange is expected in the exchange studies with $[Pten_3]^{4+}$ and active 'en', independent of any racemization process.

Under the conditions of the present experiments, it is concluded that the racemization of optically active $[Pten_3]^{4+}$ in presence of active carbon takes place via activated six-coordinate intermediate formation without any bond rupture.

$$[Pten_3]^{4+} \text{ (optically active)} \longrightarrow \text{Heated in presence of catalyst} \longrightarrow [Pten_3]^{4+} \text{ (excited)}$$

$$[Pten_3]^{4+} \text{ (excited)} \xrightarrow{\text{racemization}} [Pten_3]^{4+} \text{ (optically inactive)}$$

The catalyst, active carbon, supplied the energy for excitation. However, platinum black and silica gel were found to be completely inactive in the racemization of the complex.

In the case of $[Rhen_3]^{3+}$ complex, even active carbon was not found to be effective.