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I hereby recommend that the thesis prepared under my supervision by George W. Pickral

entitled The Chemistry of Some Nitroso and Nitro Complexes of Ruthenium

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

J. B. Cameron

Joseph W. Sanders

Wayland M. Burgess

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THE CHEMISTRY OF SOME NITROSO AND NITRO COMPLEXES OF RUTHENIUM

A dissertation submitted to the
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of the University of Cincinnati
in partial fulfillment of the
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by

George M. Pickral

B.S. Virginia Military Institute 1943

M.A. Miami University 1950

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ABSTRACT

By the use of modern methods a study was made of some nitroso and nitro compounds of ruthenium. The production of ruthenium in high yield in uranium and plutonium fission has focused attention on the chemistry of ruthenium. The anionic nitroso and nitro complexes of ruthenium had not been studied for about sixty years.

Analytical methods were developed for the determination of ruthenium and potassium in the same sample; and for nitrogen and halide in the same sample.

The chloro, bromo, and iodo salts of the complex series, $K_2[Ru(NO)X_5]$, and the chloro and bromo salts of the simple series, $Ru(NO)X_3$, were prepared and analyzed. Analyses of the bromo and iodo salts of the series, $K_2[Ru(NO)X_5]$, and the bromo salt of the series, $Ru(NO)X_3$, had not been previously reported. In the same series an unsuccessful attempt was made to isolate $Ru(NO)I_3$, $Ru(NO)(NO_3)_3$, and $H_2[Ru(NO)Cl_5]$ --the parent acid of these compounds.

Three nitro compounds of probable formulas, $K_4[Ru(NO_2)_6] \cdot H_2O$, $K_2[Ru(NO)(OH)(NO_2)_4]$, and $K_3[Ru(NO_2)_5]$ were prepared and analyzed. The first two compounds had been previously reported but were poorly characterized. $K_3[Ru(NO_2)_5]$ is a new compound which has not been mentioned in the literature.

Instrumental and radioactive tracer studies were made to aid in the characterization of these compounds and the

elucidation of their properties.

The relative stability of the ruthenium compounds in aqueous solution was determined by measuring the molecular conductivity at 25 ±0.1° C. as a function of aging time at room temperature. The number of ions yielded by the salts was confirmed by measuring the molecular conductivity of freshly prepared aqueous solutions at 25 ±0.1° C. at a dilution of 1024 liters.

The reaction of sodium hydroxide with boiling aqueous solutions of $Ru(NO)Cl_3$, $K_2[Ru(NO)Cl_5]$, and $K_2[Ru(NO)(OH)(NO_2)_4]$ was studied by potentiometric titration. The first two compounds gave a precipitate of"ruthenium nitroso hydroxide", whereas no precipitate was obtained from the third compound.

All of the nitroso and nitro complexes prepared were "finger-printed" by taking X-ray diffraction powder patterns.

Dr. Allen B. Scott of Oregon State College made magnetic measurements on representative compounds and found them all to be diamagnetic.

Radioactive ruthenium-106 was used as an indicator to demonstrate that no exchange of ruthenium occurs between $K_2[Ru(NO)Cl_5]$ and $RuCl_x$ in HCl; or between $K_2[Ru(NO)Cl_5]$ and $Ru(SO_4)_x$ in H_2SO_4.

The tracer method was used to make a preliminary investigation of the extractability of ruthenium by hexone from a hydrochloric acid solution of ruthenium chloride and from a nitric acid solution of "ruthenium nitroso nitrate".

A considerable body of experimental evidence was adduced to show that NO probably coordinates as a positive group in the anionic ruthenium nitroso complexes.

CONTENTS

Part I

HISTORICAL BACKGROUND

Ruthenium, the rarest of the platinum metals, was discovered by C. Claus in 1844 (44). Crude native platinum contains from 0.5-2.0% ruthenium, and it was from platinum residues that Claus extracted pure ruthenium.

The element was first reported by G.W. Osann in 1827, but the compounds obtained by him were very impure and did not establish with certainty the existence of the element. It was Osann who gave the element the name ruthenium which is derived from Ruthenia, meaning Russia.

A. The Nitroso Halides and Nitrate of Ruthenium

Claus, in his investigation of the chemistry of ruthenium, prepared a series of chloro compounds, which he considered to be analogous to the chloro compounds of four-valent platinum (6,7,8,9). By reacting ruthenium chloride with aqua regia and treating the solution with potassium chloride Claus obtained a well-crystallized, raspberry colored compound which he characterized by analysis as $K_2[RuCl_6]$, the analogue of potassium chloroplatinate. Claus also reported a series of halides of the type, RuX_4, where X represents chloride, bromide, or iodide.

After a lapse of about thirty years A. Joly became interested in these compounds and undertook a systematic study of them (25,26). The credit for revealing the true nature of this series of compounds belongs to Joly. It was he who

showed that a nitric oxide molecule was present and that Claus' $K_2[RuCl_6]$ was actually $K_2[Ru(NO)Cl_5]$, and the type, RuX_4, was $Ru(NO)X_3$.

Claus' error was his failure to make a direct halogen determination. In analyzing $K_2[Ru(NO)Cl_5]$ he reduced the salt with hydrogen and obtained a residue of potassium chloride and ruthenium metal. The difference in weight between the original salt and the residue was considered to represent chlorine. Ruthenium was obtained and weighed by washing potassium chloride from the residue, and the difference in weight between the residue and ruthenium metal was taken as potassium chloride. Since the difference in weight of a chlorine atom and nitric oxide molecule is small, Claus' analytical data appeared to fit $K_2[RuCl_6]$, and his mischaracterization of the salt was not apparent.

Joly's method of analysis was also to reduce the salt with hydrogen to obtain a residue of potassium chloride and ruthenium metal. But hydrogen chloride formed during the reduction was absorbed in an alkaline solution, and after acidification with nitric acid the chlorine lost on ignition was determined by precipitation as silver chloride. Ruthenium in the residue was determined by removing potassium chloride by washing with water, drying, heating again in hydrogen, and weighing as metallic ruthenium. The wash water was evaporated to obtain potassium chloride. Nitrogen was determined directly, as if the compound were an organic material. Prob-

ably the Dumas method was used.

Joly's characterization of this salt as $K_2[Ru(NO)Cl_5]$ was verified by J. L. Howe (22), whose method of analysis was similar to that of Joly except nitric oxide was determined by difference.

By a similar approach Joly showed that Claus' ruthenium tetrachloride, $RuCl_4$, was nitroso chloride, $Ru(NO)Cl_3$.

The best discussion of Joly's work on the nitroso complexes of ruthenium is his summary in Fremy's "Encyclopedie Chimique" (28). Joly gave complete analytical data for $Ru(NO)Cl_3 \cdot 5H_2O$, $Ru(NO)Cl_3 \cdot H_2O$, and $K_2[Ru(NO)Cl_5]$. The bromo and iodo complexes of the series, $Ru(NO)X_3$ and $K_2[Ru(NO)X_5]$ were prepared by Joly, but no analytical data were reported on these compounds.

When $Ru(NO)Cl_3$ is treated with a base, a poorly characterized substance, which is referred to as ruthenium nitroso hydroxide, $Ru(NO)(OH)_3$, precipitates. This brown colored base is formally the parent substance of the simple nitroso salts, $Ru(NO)X_3$, and the complex salts, $M_2[Ru(NO)X_5]$. It dissolves readily in acids to give, presumably, salts of the type $Ru(NO)X_3$, and the complex acids, $H_2[Ru(NO)X_5]$. The substance, $Ru(NO)(NO_3)_3$, has not been isolated but may be present in the bright red solution obtained by dissolving $Ru(NO)(OH)_3$ in nitric acid (26,45). Ruthenium nitroso hydroxide dissolves in strong alkalies to give products of unknown composition.

Apparently the nitroso halides of ruthenium have received

little attention since 1900. The best known salt of the series is $K_2[Ru(NO)Cl_5]$. In 1894 Howe investigated the chemistry of this salt (22). He found that an aqueous solution of the salt is very stable. Conductivity studies indicate that the salt ionizes to give three ions. When a solution is heated with strong alkalies, a black precipitate, usually formulated as $Ru(NO)(OH)_3$, slowly precipitates. On heating with excess ammonia, complex nitrosoammines are formed. Hydrogen sulfide apparently precipitates the ruthenium quantitatively from a cold solution, but precipitation is incomplete from a hot solution. Sulfur dioxide gives a dark green product of unknown composition. Potassium thiocyanate, when heated, yields a dark blue solution. Potassium ferrocyanide gives an intense brown color. Silver and mercury (I) nitrates give reddish and light yellow precipitates respectively. Potassium cyanide decolorizes the raspberry-colored solution.

The solubility of $K_2[Ru(NO)Cl_5]$ is 12 parts per 100 parts of water at 25°C. and 80 parts per 100 at 60°C. The rubidium and cesium salts are difficultly soluble.

R. Charannot in 1931 prepared the chloro and iodo nitroso complexes of the series $M_2[Ru(NO)X_5]$ (3). No analyses were reported. The compounds were used by him as starting materials for the preparation of oxalato complexes of the type, $K_2[Ru(NO)X(C_2O_4)_2]$.

In 1938 Cambi and Malatesta prepared $K_2[Ru(NO)Cl_5]$ and used it to prepare dialkyldithiocarbamates of the type,

$Ru(NO)(S_2CNR_2)_3$, where R represents the methyl or ethyl radical (2).

No study of the nitroso halides of ruthenium has been reported since the work of Howe.

B. The Nitrites of Ruthenium

W. Gibbs in 1862 reacted potassium nitrite with ruthenium chloride and obtained an orange compound which he described as a "double nitrite" (13,14). Further work was done on the ruthenium nitrites from 1884 to 1894 by A. Joly and his coworkers (29,30). Joly prepared a ruthenium nitrite, apparently the same compound that Gibbs had reported, by adding a solution of ruthenium chloride to a hot solution of potassium nitrite, until the precipitate which first forms had just dissolved. The orange-red easily soluble salt obtained from the solution was characterized by analysis as $4\ KNO_2 \cdot Ru_2(NO_2)_6$ and has been referred to in the literature as $K_2[Ru(NO_2)_5]$.

When ruthenium chloride is added to an excess of potassium nitrite, a yellow, difficultly soluble compound, which Joly formulated as $8KNO_2 \cdot Ru_2O_3(N_2O_2)(N_2O_3)$, is precipitated. The properties of this compound have not been studied.

D. D. Deford in his critical survey of ruthenium chemistry points out that the formulation proposed by Joly and his coworkers for both of these nitro compounds is undoubtedly in error (10). The published analytical results do not correspond well with simple formulas and further investigation is necessary to clarify the structure and properties of these compounds.

Part II

THE PROBLEM

The object of this investigation was to prepare, characterize by analysis, and study by modern methods including radioactive tracer techniques, the nitroso ruthenium complexes of the types $K_2[Ru(NO)X_5]$ and $Ru(NO)X_3$, and the complex nitrite obtained when ruthenium chloride is treated with hot potassium nitrite solution. The complex nitrites might well belong to the $K_2[Ru(NO)X_5]$ class of compounds.

Since these compounds have received little attention since 1900 the time is ripe for a careful examination of the ruthenium-nitric oxide system of compounds to expand our fundamental knowledge of both ruthenium and nitric oxide chemistry.

Ruthenium is produced in high yield in uranium fission, and for this reason interest in the chemistry of ruthenium has recently revived.

Nitric oxide compounds are of interest due to the peculiar structural problems which they present. Compounds are known in which the nitric oxide molecule apparently coordinates as a negative radical, a neutral molecule, and as a positive radical. No study has been made of the strength of the metal nitric oxide bond in nitroso complexes using isotope exchange techniques. The availability of radioactive ruthenium of very desirable radiation characteristics makes the ruthenium-nitric oxide system of compounds a good system in which to initiate such a study.

Part III

ANALYTICAL METHODS

A. Ruthenium and Potassium

The work of Gilchrist and Wichers (15) on the separation and estimation of the platinum metals provided a basis for the development of a reliable gravimetric method for the quantitative determination of ruthenium.

In the method of Gilchrist and Wichers, osmium was first removed by distillation as the tetroxide from a nitric acid solution. The solution remaining from the osmium distillation was repeatedly evaporated with hydrochloric acid until oxides of nitrogen were no longer evolved. The residue from the last evaporation was dissolved in sulfuric acid and evaporated to fumes of sulfur trioxide. The sulfuric acid solution was transferred to an all glass distilling apparatus and a 10% sodium bromate solution added to oxidize ruthenium to the volatile tetroxide. The solution was distilled for two and one-half hours and the ruthenium tetroxide was collected in a train of three receivers which contained 6 M hydrochloric acid saturated with sulfur dioxide. After the completion of the distillation, the absorbing solution was evaporated to a moist residue, digested with concentrated hydrochloric acid, diluted, heated to boiling, and treated with a filtered solution of 10% sodium bicarbonate until a precipitate formed. Bromcresol purple indicator was then introduced and the bicarbonate solution added until the indicator changed from

yellow to blue. After boiling for five minutes to coagulate the precipitate, the solution was filtered and the precipitate washed with ammonium sulfate. The filter and precipitate were then transferred to a porcelain crucible and carefully dried and ignited. After ignition in air, the residue was strongly ignited in a hydrogen atmosphere and allowed to cool in hydrogen. The metallic ruthenium residue was thoroughly leached with water and again ignited in air and in hydrogen. After cooling in hydrogen, the residue was weighed as metallic ruthenium.

The method of Gilchrist and Wichers described above is lengthy, but the results are reliable. Ayres and Young (1) made a study of the method of Gilchrist and Wichers, as well as several "short cut" methods which have been proposed, for the quantitative determination of ruthenium. Of the methods studied the distillation of ruthenium as the tetroxide, precipitation of hydrous oxides, and reduction to metallic ruthenium with hydrogen was the only method which gave satisfactory results. The "short cut" methods which Ayres and Young investigated included:

1. Precipitation of ruthenium by active metals. It was found that the precipitated ruthenium absorbed the reducing metal giving high results.

2. Precipitation of ruthenium as a sulfide and conversion to an oxide. In this method the exact composition of the precipitate is unknown and sulfur is retained by the

oxide.

3. Precipitation of hydrous ruthenium dioxide from a faintly alkaline solution, ignition in air, and reduction with hydrogen. The hydrous dioxide is difficult to coagulate and filter, and there is a possibility of coprecipitation.

4. Precipitation of ruthenium with thionalide gave results which were 10% low.

5. Reduction of ruthenium IV to ruthenium III with stannous chloride gave low results.

In view of the report of Ayres and Young on quantitative methods for ruthenium it was decided to develop a method for ruthenium determination based on the procedure of Gilchrist and Wichers. The first change made was the use of perchloric acid instead of sulfuric acid-sodium bromate to volatilize ruthenium as the tetroxide from a ruthenium solution. Since Hoffman and Lundell (21) reported that perchloric acid will oxidize ruthenium compounds to the volatile tetroxide, this method has been generally recognized as the best and most rapid method of obtaining ruthenium tetroxide. The perchloric acid distillation requires only fifteen to twenty minutes compared to two to three hours for other distillation methods. Thiers, Graydon, and Beamish (42) have shown by use of tracer radioactive ruthenium that ruthenium is quantitatively removed from the distilling flask by perchloric acid. Although this change introduces the unpleasantness and danger of handling perchloric acid, it is more than justified by the time saved in distillation, the assurance that

ruthenium is completely removed, and by the fact that potassium can be determined as potassium perchlorate in the residue.

The second time-saving change was to absorb the ruthenium tetroxide in 6M sodium hydroxide rather than a hydrochloric acid solution saturated with sulfur dioxide. When ruthenium tetroxide is absorbed in sodium hydroxide an orange solution of "sodium ruthenate" is formed. Addition of alcohol reduces the ruthenate ion to hydrous ruthenium oxides, and boiling for five minutes coagulates the precipitate. This step eliminates the necessity of evaporating a large volume of solution, digesting with hydrochloric acid, and titrating with sodium bicarbonate.

The precipitated oxides of ruthenium are separated from the sodium hydroxide solution by centrifugation and washed with water until the precipitate no longer settles when centrifuged. A 1% ammonium chloride solution is added and the mixture boiled until the oxides of ruthenium coagulate again. In early determinations, the ruthenium oxides were collected on ashless filter paper and washed with 2.5% ammonium chloride. When the precipitate and paper were ignited in air, unless the greatest precautions were taken, severe deflagrations often occurred, and the results of the determination were low. To overcome this difficulty the ruthenium oxides were collected in a Selas crucible. After washing, ignition in air, and reduction

and cooling in a stream of hydrogen in a Rose crucible, the metallic ruthenium was washed by pouring hot water through the Selas crucible and the ignition and reduction steps repeated. The ruthenium metal was cooled to room temperature in a hydrogen atmosphere, placed in a desiccator for 30 minutes, and weighed as metallic ruthenium.

The accuracy of the ruthenium determination was established by analyzing $K_2[Ru(NO)Cl_5]$ as a standard. This compound is the best known of the nitroso halides of ruthenium and has been analyzed for ruthenium by Claus, Joly, and Howe (6,28,22)

$K_2[Ru(NO)Cl_5]$

%Ru			Average
	Calculated:	26.26	
	Found:	26.05, 26.31	26.18
Values from literature:			
	Claus:	25.95 26.54	26.25
	Joly:	26.14, 26.12, 26.08 26.25, 26.14	26.15
	Howe:	26.65 25.99	26.32

The results show that the percent ruthenium found experimentally is slightly lower than calculated. In general the results of the ruthenium analyses had a tendency to be a little low. The determination proved difficult to run, but with some experience the precision obtained improved; any deviations from calculated percentages were usually on the low side.

Procedure: Set up the apparatus as shown in Figure 1.

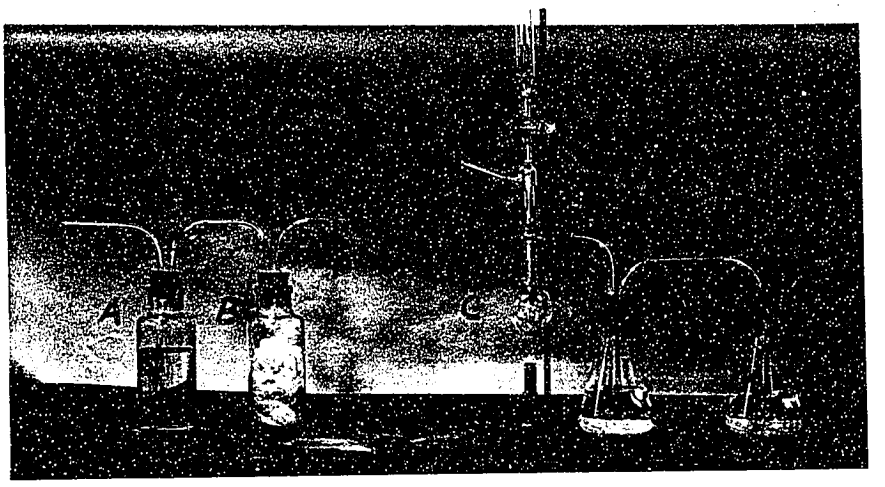

Figure 1

Apparatus for Ruthenium Distillation

A. 8 oz. glass bottle containing conc. H_2SO_4

B. 8 oz. glass bottle containing glass wool

C. All-glass ruthenium still (similar to Scientific Glass Apparatus Co., still No J 1306)

D. Receiving Flask containing NaOH

E. Receiving Flask containing NaOH

Place 200 ml. of 6N sodium hydroxide in flask D and 50 ml. in flask E.

Raise ruthenium still, C, from the receiving train. Pour 4 ml. of 70% perchloric acid into the ruthenium still. Weigh a sample which is equivalent to approximately 100 milligrams of metallic ruthenium. Dissolve the sample in the minimum volume of water and add solution to ruthenium still, C. (If the sample is a potassium salt a white precipitate of potassium perchlorate will form.) Lower still into receiving flasks.

Turn on air and adjust flow to obtain one bubble every three to four seconds. Warm still, C, gently with a micro burner until the potassium perchlorate dissolves, and the solution begins to boil. Heat strongly with micro burner. After all the water has distilled over ruthenium tetroxide starts to distill. Continue heating strongly until the residue in still, C, is colorless and perchloric acid distills up the neck of the still. Increase the air flow slightly and remove the burner. Allow to cool and disconnect receiving flasks. Turn off air. Save residue in still, C, for potassium determination.

Pour the contents of receiving flask, D, into an unetched 400 ml. beaker. Wash down the delivery tubes and rinse flask, D. Add rinse water to the ruthenate solution in the beaker. If the sodium hydroxide in flask, E, has become colored add its contents to the ruthenate solution. Allow the ruthenate solution to come to room temperature.

The solution should be dark-colored and strongly basic. If the color is light orange there is a possibility of incomplete reduction. Add 6M sodium hydroxide if necessary. Heat the solution and add 4 to 5 ml. of alcohol with stirring. The solution becomes black almost immediately due to the formation of hydrous ruthenium oxides. Boil the solution for five minutes to coagulate the precipitate. Cool to room temperature, and let solution stand 2 to 4 hours. Separate hydrous ruthenium oxides by centrifugation. Wash precipitate with water until it becomes colloidal. Add 5 ml. of 1% ammonium chloride and boil until the precipitate coagulates. Cool and centrifuge. Transfer the precipitate to a previously ignited and weighed Selas crucible, using a 2.5% solution of ammonium chloride to aid in the transfer. Police the centrifuge tube with a small piece of ashless filter paper and put the paper in the crucible. Wash the contents of the Selas crucible twice with water. Place the Selas crucible in a five centimeter Rose crucible and heat with an infra red lamp until the paper is charred. Ignite the precipitate in air, heating slowly with a Bunsen burner and then strongly with a Meker burner. Cool.

To purify the hydrogen from a cylinder of electrolytic hydrogen use a "DEOXO" catalytic purifier. (The Deoxo purifier is designed to remove oxygen with less than one part per million oxygen remaining). Pass the purified hydrogen through a drying tube containing anhydrone to remove water

vapor.

Ignite the stream of hydrogen from a Rose delivery tube and regulate stream so that a flame about one-half an inch long is produced. Insert the delivery tube through the opening in the lid of the Rose crucible. The flame goes out. Pass hydrogen through the crucible for five minutes and relight the hydrogen by placing a Bunsen burner with a small flame under the crucible. The hydrogen will burn as it emerges from under the lid of the crucible. Gradually increase the size of the flame until the crucible is at red heat. Replace the Bunsen burner with a Meker burner and ignite the crucible at red heat for thirty minutes. Remove the burner and allow the crucible to cool for ten minutes. Momentarily break the stream of hydrogen to put out the hydrogen flame. Cool in hydrogen to room temperature. Wash the metallic ruthenium thoroughly with hot water. Repeat the ignition in air and reduction with hydrogen. After cooling the precipitate to room temperature in hydrogen, place the crucible in a desiccator for thirty minutes. Weigh as metallic ruthenium.

Potassium: After the distillation of ruthenium tetroxide from a potassium salt of ruthenium, the perchloric acid residue, when cooled, always contained solid potassium perchlorate. Potassium was determined by evaporating this residue to dryness, dissolving in the minimum amount of hot water, and precipitating potassium perchlorate by the addi-

tion of n-butyl alcohol. G. F. Smith (31) found this to be an effective method for separating potassium perchlorate from sodium perchlorate. The separated potassium perchlorate must be heated to 350°C. before weighing to expel occluded water.

The n-butyl alcohol method was tried and compared with the results obtained by omitting the n-butyl alcohol treatment and merely evaporating the residue in the distilling flask to dryness. The results were the same in both cases. The precipitate obtained by evaporation to dryness was shown by a flame test to be free of sodium. Therefore the n-butyl alcohol separation precedure was omitted.

Potassium in $K_2[Ru(NO)I_5]$ could not be determined by this method. The white solid obtained by evaporating the perchloric acid residue was not potassium perchlorate, but probably potassium iodate or periodate as shown by the fact that the percentage potassium was high and the precipitate was easily soluble in water.

When the standard salt, $K_2[Ru(NO)Cl_5]$, was analyzed to develop the ruthenium determination, potassium was not determined. At a later date one potassium determination was run on the standard to check the accuracy of the method.

$K_2[Ru(NO)Cl_5]$

% K	Calculated	20.2
	Found	20.0

Although the experimental percent potassium was low, this is not the general trend of the results. In most cases the po-

tassium analysis gave high results as illustrated by the following data:

$K_2[Ru(NO)Br_5]$

% K	Calculated	12.8
	Found	13.0, 13.1

$K_2[Ru(NO)(OH)(NO_2)_4]$

% K	Calculated	19.0
	Found	19.6, 19.3, 19.1

Procedure: Add 25 ml. of water to the distilling flask and heat until the potassium perchlorate dissolves. Decant the solution into a 250 ml. beaker. Rinse the distilling flask several times with water and combine all the rinsings. Evaporate the solution on a hot plate to a volume of about 10 ml. Transfer the solution to a weighed 50 ml. beaker which has been dried to constant weight at 350° C. Evaporate to dryness under an infra red lamp. Heat the beaker briefly at 120° C. and then dry to constant weight at 350° C. Cool in a desiccator and weigh as potassium perchlorate.

B. Nitrogen and Halogens

The first method attempted to determine nitrogen was the Friedrick method for N-N, NO and NO_2 linkages (5). In this method the sample is refluxed with constant-boiling hydroiodic acid to reduce the nitrogen-containing group and excess hydroiodic acid is removed by distillation. Potassium sulfate and sulfuric acid are added to the concentrate and the mixture is heated on a digester until most of the water has been removed. The mixture is cooled, water is added, and then the mixture is distilled. The purpose of this operation is to remove with steam the liberated iodine. The digest is then cooled, mercuric oxide is added, and the Kjeldahlization and distillation are completed in the usual manner.

The results of the Friedrick method were unsatisfactory. Potassium nitrate contains 13.96% nitrogen and only 3.4% nitrogen was found by this method. $K_2[Ru(NO)Cl_5]$ contains 3.62% nitrogen and only a trace could be detected by the Friedrick method.

The next method tried, and the one which was developed into a satisfactory analytical method for nitrogen in ruthenium nitroso and nitro complexes, was Devarda's method for nitrogen in simple nitrates and nitric acid which was reported in 1894 (11). In this method the nitrate radical is reduced to ammonia in 20% potassium hydroxide by an alloy containing 50% copper, 45% aluminum, and 5% zinc. This alloy is available commercially under the name "Devarda's Metal". The ammonia is

distilled from the reduction flask and collected in standard excess sulfuric acid which is back-titrated with standard sodium hydroxide in the usual Kjeldahl method, or the ammonia may be collected in boric acid and titrated directly with standard hydrochloric acid as in the Winkler modification of the Kjeldahl method.

Devarda's method gave satisfactory results for nitrogen in potassium nitrate and $K_2[Ru(NO)Cl_5]$ --the ruthenium complex which was selected as a standard.

KNO_3	Calculated	13.96%
	Found	13.75%, 13.81%
$K_2[Ru(NO)Cl_5]$		
	Calculated	3.62%
	Found	3.63, 3.56, 3.51, 3.42, 3.47%

All nitrogen determinations were slightly low.

The halogen in complexes of the type, $K_2[Ru(NO)X_5]$ and $Ru(NO)X_3$, was determined by acidifying the residue from the nitrogen determination and precipitating the halide as a silver salt by adding silver nitrate. In the case of chloride and bromide, nitric acid was added to the potassium hydroxide residue until the hydroxides of aluminum and zinc which formed had just redissolved, and then silver chloride or silver bromide was precipitated and handled in the usual manner.

The nitrogen-halogen precedure had to be modified for compounds containing the iodide ion, since nitric acid oxi-

dized the iodide ion to iodine causing the results to be low. For $K_2[Ru(NO)I_5]$ the initial reduction of the nitroso group was carried out in a saturated solution of sodium hydroxide, and the residue was acidified with perchloric acid instead of nitric acid. Sodium hydroxide was used since sodium perchlorate is soluble whereas potassium perchlorate would precipitate and interfere. Perchloric acid was chosen since silver perchlorate is soluble and would not precipitate under the conditions of the determination.

A blank was run on both the nitrogen and halide determinations. The blank on the nitrogen determination was the same order of magnitude as an indicator blank. The halide determinations were blanked by adding a known weight of pure, dry sodium chloride to the mixture of reagents and determining the weight of silver chloride obtained. The weight obtained was 6.2 milligrams more than the calculated weight, and this correction was applied in all halide determinations.

The results for the standard compound are as follows:

$K_2[Ru(NO)Cl_5]$	%Cl	Calculated:	45.8
		Found:	45.5, 45.6, 45.6

All halide determinations were slightly low.

Procedure: Set up a nitrogen apparatus as shown in Figure 2. Use a 50 ml. separatory funnel, 500 ml. three-neck round bottom flask, Kjeldahl trap, water-cooled condenser, adapter, and a 250 ml. Erlermeyer flask.

Put 50 ml. of 3% boric acid in receiving flask, D.

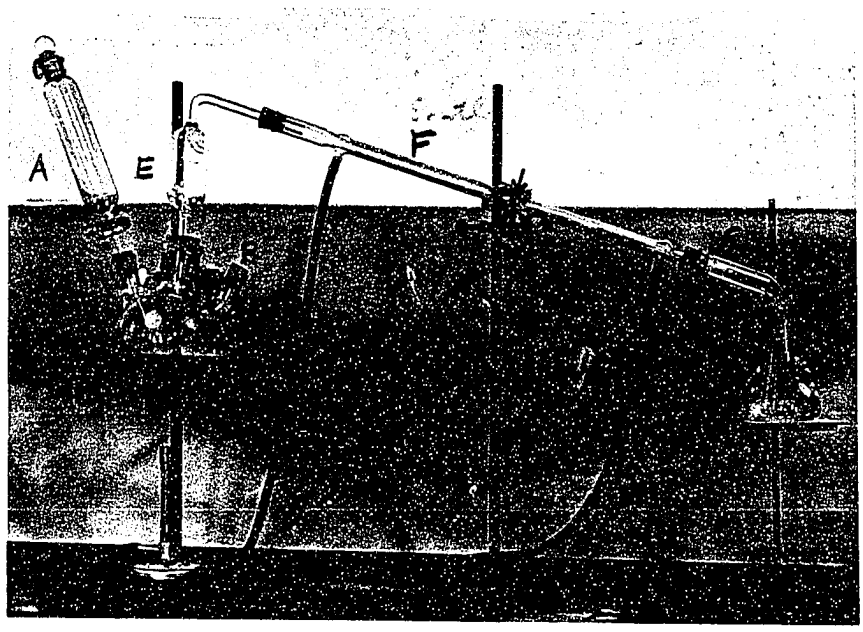

Figure 2

Apparatus for Nitrogen Determination

A. Separatory Funnel

C. 500 ml., 3 neck, round bottom flask

D. 250 ml. Erlenmeyer flask

E. Nitrogen trap

F. Water Cooled condenser

G. Adapter

Introduce into reaction flask, C, by means of neck, B, the weighed sample, 50 ml. of water, 2 ml. of alcohol, and one gram of reagent grade Devarda's Alloy. Seal all rubber stopper connections. Start the flow of water through the condenser. Introduce into flask, C, by means of separatory funnel, A, 20 ml. of freshly prepared 20% reagent grade potassium hydroxide solution. Rinse separatory, A, with a few milliliters of water and quickly close the stop cock. Gently warm flask, C, until hydrogen is rapidly evolved. Let the reaction proceed for several hours until hydrogen is no longer formed. Heat flask, C, until the reaction mixture boils and one-half its contents has distilled into the 3% boric acid. Remove stopper from neck, B, and introduce a steady stream of compressed air, which has been purified by bubbling through concentrated sulfuric acid and glass wool. Flush the system with air for five minutes. Lower flask, D, and remove flame from flask, C. Rinse the adapter and interior of the condenser into flask, D. Titrate the ammonium borate solution in flask, D, with standard hydrochloric acid, using 2 drops of methyl red and 2 drops of bromcresol green as an indicator.

To determine the halide, transfer the liquid portion of the residue from flask, C, to an unetched 400 ml. beaker. This is best done by decanting the solution into a 50 ml. centrifuge tube, centrifuging, and decanting the clear centrifugate into the beaker. Rinse the flask several times with 10 ml. portions of water, centrifuge, and add the rinse water to the beaker. During the transfer of the solution

most of the copper from the alloy and ruthenium produced by the reaction will remain in the flask with only a small portion in the centrifuge tube. Slowly add concentrated nitric acid to the solution until the hydroxides of aluminum and zinc which form redissolve. The remaining steps should be carried out in subdued light. Add 0.1 N silver nitrate slowly with stirring until a 10% excess has been added. Heat almost to boiling and stir for 1 to 2 minutes. Test for complete precipitation. Allow the solution to stand for 2 to 4 hours. Collect the precipitate in a weighed sintered glass crucible which has been dried at 140° C. Wash the precipitate with small portions of 0.01 N nitric acid until a few milliliters of the washings collected in a test tube give no turbidity when tested with 1 drop of 0.1 N hydrochloric acid. Wash the precipitate with 1 or 2 portions of water to remove the nitric acid. Dry to constant weight at 140° C.

C. Hydrogen

Hydrogen was determined directly by igniting the sample in a stream of air and absorbing the water evolved in magnesium perchlorate (31). The combustion tube contained a mixture of lead oxide and lead dioxide to retain the oxides of nitrogen emitted when the sample decomposed.

The apparatus used is shown in Figure 3. Bottle, A, contains concentrated sulfuric acid and bottle, B, (not shown) glass wool. The sulfuric acid removes most of the water from the air which is forced through the train and also

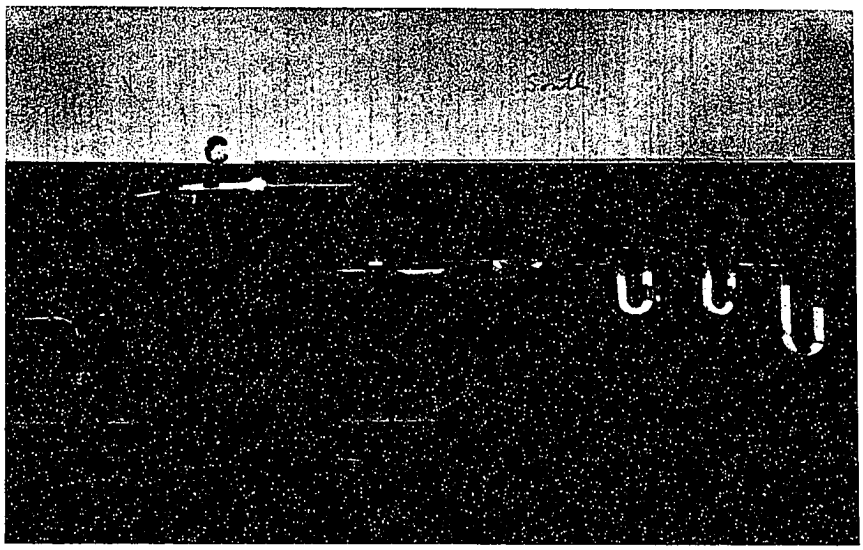

Figure 3

Apparatus for Hydrogen Determination

A. 8 oz. bottle containing conc. H_2SO_4

B. 8 oz. bottle containing glass wool (not shown)

C. Drying tube containing anhydrone

D. Pyrex combustion tube

E. Porcelain boat

F. Mixture of PbO, PbO_2, and glass wool

G,H,& I U-tubes containing anhydrone

indicates the rate of flow of the air. Drying tube, C, contains magnesium perchlorate which removes the traces of water in the air stream. Tube, D, is a pyrex or quartz combustion tube, and E is a porcelain boat. F is a mixture of lead oxide and lead dioxide intermixed with glass wool. U-tubes, G, H, and I, contain magnesium perchlorate.

Hydrogen, when present in small amounts, in inorganic complexes is very difficult to determine with any degree of accuracy. The determination was undertaken to attempt to distinguish between co-ordinated aquo and hydroxy groups in complexes of the type $K_2[Ru(NO)(OH)(NO_2)_4]$ and $K_2[Ru(NO)(H_2O)(NO_2)_4]$. These compounds have molecular weights of 411 and 412 respectively and differ by only one hydrogen atom. It is very doubtful that these compounds can be distinguished by ordinary analytical methods.

In 1927 J. L. Howe (23) made a study of complexes of the type $M_2[Ru(OH)Cl_5]$ and $M_2[Ru(H_2O)Cl_5]$, where M represents an alkali metal. Hydrogen was determined by the combustion method. The analytical results reported are as follows:

	% H Calculated	Found
$K_2[Ru(OH)Cl_5]$	0.27	0.31, 0.25
$Rb_2[Ru(OH)Cl_5]$	0.22	0.29
$Cs_2[Ru(OH)Cl_5]$	0.18	0.66, 0.39
$K_2[Ru(H_2O)Cl_5]$	0.53	0.69, 0.53, 0.78 0.77, 0.78

The results reported by Howe were erratic and the per-

cent hydrogen found usually much higher than the calculated amounts.

In view of the uncertainty of hydrogen determinations the values obtained in the present work were not used to distinguish between co-ordinated aquo and hydroxy group, but merely as a very rough indication of the hydrogen content of the compounds.

Procedure: With U-tubes, G and H, disconnected heat the central part of tube, D, with an empty boat, E, in place with a Meker burner until the system is thoroughly dry. Pass air through A, B, C, and D for 10 minutes at the rate of 2 or 3 bubbles per second. Then connect G and H and continue to pass air through the hot tube for 10 minutes. Stop the air flow, close G and H and place G and H in the balance case. After 15 minutes open U-tubes, G and H, momentarily and weigh tube G using H as a tare. Repeat the above steps until constant weight is obtained.

Dry the system, connect U-tubes, G and H, and remove drying tube, C, from combustion tube, D, and introduce an empty boat which has been handled exactly as the boat containing the sample. Connect C and D as quickly as possible. Heat the empty boat, cool, weigh U-tube, G, as before, and record the gain in weight as the "boat blank". (Usually about 0.8 mg.)

Repeat the process and introduce the boat containing the sample. Gradually heat the sample until it decomposes

and then heat strongly with a Meker burner. Heat the oxides of lead to about 350°C. Brush the combustion tube with a flame until all visible water droplets have passed into U-tube, G. Cool, disconnect G and H, and weigh as before.

The efficiency of lead oxide and lead dioxide for trapping oxides of nitrogen was determined by passing dry oxides of nitrogen, formed by reducing nitric acid with arsenious anhydride, into tube, D, and duplicating the experimental procedure. The oxide of nitrogen blank obtained was negligible.

Part IV

PREPARATIONS AND ANALYSES

A. Nitroso Compounds

The starting material for the preparation of all compounds was commercial ruthenium chloride which was obtained from the American Platinum Works. Commercial ruthenium chloride is a mixture of ruthenium (III) and ruthenium (IV) chlorides and is reported to be free of osmium and other platinum metals. In all preparations the materials used were of C.P. or reagent grade.

Potassium Nitroso Pentachlororuthenate*, $K_2[Ru(NO)Cl_5]$.

When commercial ruthenium chloride is dissolved in concentrated nitric acid and the dark opaque solution refluxed for four to six days, the solution becomes bright red and transparent. The composition of the bright red solution is unknown, but it is probable that a nitroso group has been attached to the ruthenium. When concentrated hydrochloric acid is repeatedly added and the solution evaporated until oxides of nitrogen are no longer evolved, the probable composition of the solution is $H_2[Ru(NO)Cl_5]$ --the parent acid of $K_2[Ru(NO)Cl_5]$ and $Ru(NO)Cl_3$. When potassium chloride is added and the solution concentrated, crystals of $K_2[Ru(NO)Cl_5]$

*In nitroso compounds of ruthenium since the oxidation states of the NO group and ruthenium are debatable a system of nomenclature is used which does not commit as to whether NO is NO^+, NO, or NO^- or to the oxidation state of ruthenium. If the NO is NO^+ then the proper name for this compound according to the Modified I.U.C. system is potassium pentachloronitrosyliumruthenate (II).

precipitate. This is the method used by Howe, Joly, and Wenner and Smirnoff for the preparation of this salt (22, 25, 46). A modification of this method was introduced to shorten the initial reflux time. If the nitric acid solution of commercial ruthenium chloride is saturated with oxides of nitrogen, formed by reducing nitric acid with arsenic (III) oxide, the reflux time for introducing the nitroso group is reduced from four to six days to two to four hours.

$K_2[Ru(NO)Cl_5]$ was also prepared from ruthenium nitro complexes by the method of Joly (28). In this method an aqueous solution of ruthenium chloride is heated to 80° C., and potassium nitrite is added until the solution becomes yellow or orange. When hydrochloric acid is added and the solution warmed, the color gradually changes to raspberry. Crystals of $K_2[Ru(NO)Cl_5]$ and potassium chloride precipitate when the solution is concentrated. The mixture can be separated by recrystallization, potassium chloride being the more soluble compound.

Joly's potassium nitrite method has the advantage of being much quicker than the nitric acid method, but the pure product is more difficult to isolate and the yield is lower. The compound which was analyzed was prepared by the nitric acid method. The salt prepared by the potassium nitrite method gave the same X-ray diffraction pattern as that made by the nitric acid method.

Analytical Data:

$K_2[Ru(NO)Cl_5]$ prepared by nitric acid method.

	Calculated	Found	Average
K(%)	20.2	20.0	
Ru(%)	26.26	26.05, 26.31	26.18
N(%)	3.62	3.56, 3.51, 3.42, 3.63, 3.47	3.51
Cl(%)	45.8	45.5, 45.6, 45.6	45.6

Data from literature:

a. Claus (6) (Claus characterized the compound as $K_2[RuCl_6]$)

Ru(%)	25.84	26.25 (two determinations)
4 Cl(%)	36.18	35.03 (by difference)
2 KCl(%)	37.98	38.72 (by difference)

b. A. Joly (28)

Ru(%)	26.20	26.15 (five determinations)
3 Cl(%)	27.53	26.54 (one)
2 KCl(%)	38.51	38.77 (three)
N(%)	3.62	3.45 (one)

c. Howe, (22)

Ru(%)	26.20	26.32 (two)
3 Cl(%)	27.53	27.02 (two)
2 KCl(%)	38.51	38.41 (one)

Although this compound has been analyzed by Claus, Joly, and Howe, the only direct comparisons that can be drawn between their data and the present experimental data are with respect to the percentages of ruthenium and nitrogen since the methods of analyzing the complex and reporting the results differ. In all cases the average percent ruthenium falls between 26.15% and 26.32%, and the percent nitrogen between 3.42% and 3.63%.

Procedure for Nitric Acid Method: Dissolve one gram of commercial ruthenium chloride in 100 ml. of concentrated nitric acid. Saturate this solution with oxides of nitrogen formed by reacting 25 grams of arsenic (III) oxide with 20 ml. of 12N nitric acid. Transfer the solution to a 250 ml. round bottom flask which is fitted through a ground glass joint to a water-cooled condenser. Reflux gently until the dark opaque solution becomes bright red and transparent. Filter or centrifuge to remove a black insoluble residue which sometimes forms. Add an equal volume of concentrated hydrochloric acid and evaporate to about 10 ml. Repeat until oxides of nitrogen are no longer given off. Add 1 gram of potassium chloride dissolved in 3.0 ml. of water to the 10 ml. hydrochloric acid solution. Cool slowly to room temperature and then in refrigerator. Collect the precipitate by suction filtration. Evaporate the filtrate to half its volume, add 0.5 grams potassium chloride dissolved in 1.5 ml. of water, cool, collect a second crop. Wash the precipitate with sat-

urated potassium chloride, alcohol, ether, and carefully with cold water. Cold water will dissolve all of the potassium chloride and only a small amount of $K_2[Ru(NO)Cl_5]$. Dry at 110°C.

Procedure for Potassium Nitrite Method: Dissolve 2.0 grams of commercial ruthenium chloride in water and heat to 80°C. Add a saturated solution of potassium nitrite in small portions until the resulting solution is orange or yellow. Add concentrated hydrochloric acid dropwise until the solution has a pH of 1.0. Heat slowly until oxides of nitrogen are no longer evolved. Concentrate the solution by evaporation to about one-half its volume. Cool. Wash the precipitate as in the nitric acid method.

Potassium Nitroso Pentabromoruthenate, $K_2[Ru(NO)Br_5]$.

The bromide of the series, $K_2[Ru(NO)X_5]$ was prepared from the corresponding chloride by repeatedly boiling in hydrobromic acid to replace the chloride ion by the bromide ion. The compound was purified by recrystallization from hydrobromic acid.

Analytical Data: (No analysis reported in literature)

$K_2[Ru(NO)Br_5]$

	Calculated	Found	Average
K(%)	12.83	13.0, 13.1	13.1
Ru(%)	16.68	16.57, 16.49	16.53
N(%)	2.30	2.29, 2.27	2.28
Br(%)	65.57	65.3, 65.2	65.3

Procedure: Dissolve 2.0 grams of $K_2[Ru(NO)Cl_5]$ in 50 ml. of hydrobromic acid and evaporate to about 5 ml. Remove the dark colored crystals by filtration, dissolve again in hydrobromic acid, and evaporate to a small volume. Repeat twice more. Stop the last evaporation at a volume of 20 ml. Cool slowly. Collect the precipitate by filtration and wash with alcohol and then cold water. Dry at 110° C.

Potassium Nitroso Pentaiodoruthenate, $K_2[Ru(NO)I_5]$.

This salt was prepared by repeatedly treating $K_2[Ru(NO)Cl_5]$ with hydroiodic acid and evaporating the solution until crystallization occurred. The product contained the easily soluble $K_2[Ru(NO)I_5]$ and a black insoluble powder which is believed to be $Ru(NO)I_3$. Pure $K_2[Ru(NO)I_5]$ was obtained by treating the mixture with water, filtering, adding hydroiodic acid to the filtrate and concentrating.

Analytical Data: (No analysis reported in literature)

$K_2[Ru(NO)I_5]$

	Calculated	Found	Average
K(%)	9.26	--	--
Ru(%)	12.04	12.07, 12.04	12.06
N(%)	1.66	1.69, 1.68	1.69
I(%)	75.1	74.7, 74.9	74.8

Procedure: Dissolve 1.5 grams of $K_2[Ru(NO)Cl_5]$ in 30 ml. of hydroiodic acid and evaporate until crystals form. Dissolve the precipitate in 30 ml. of hydroiodic acid and evaporate. Repeat evaporation in presence of hydroiodic

acid. Collect the precipitate in a sintered glass crucible, and pour 30 ml. of water through the crucible. Add 10 ml. of hydroiodic acid to the filtrate, evaporate to 20 ml., and cool. Separate the precipitate by filtration. Repeat until a precipitate is obtained which is completely soluble in water. Wash with alcohol, ether, and cold water. Dry at 110° C.

Ruthenium Nitroso Chloride--$Ru(NO)Cl_3 \cdot H_2O$.

The first member of the simple salts of the series, $Ru(NO)X_3$, was prepared by the method of Joly (25, 26). Commercial ruthenium chloride was refluxed with nitric acid until the nitroso group was introduced, excess nitric acid was removed by evaporation in the presence of hydrochloric acid, and the hydrochloric acid solution finally evaporated to a moist residue which probably contains the unstable acid, $H_2[Ru(NO)Cl_5]$. The residue was dried over calcium chloride until visible moisture was removed. When heated at 110° C. hydrochloric acid fumes were rapidly evolved and the brick-red powder which formed slowly reached constant weight. Analysis showed the powder to be $Ru(NO)Cl_3 \cdot H_2O$.

Analytical Data:

$Ru(NO)Cl_3 \cdot H_2O$

	Calculated	Found	Average	Joly (28)
Ru(%)	39.70	39.60, 39.80	39.70	39.72
N(%)	5.47	5.31, 5.41 5.42	5.38	5.55
Cl(%)	41.6	41.4, 41.3	41.4	41.42
H_2O(%)	7.03	--	--	7.26

Procedure: Dissolve 2.0 grams of commercial ruthenium chloride in 200 ml. of concentrated nitric acid and reflux until the solution becomes bright red. Filter. Add an equal volume of hydrochloric acid and evaporate to a moist residue. Add hydrochloric acid and evaporate again. Repeat until oxides of nitrogen are no longer given off. Dry the moist residue over calcium chloride until no visible moisture remains. Dry carefully at 110° C. until hydrochloric acid fumes are no longer expelled. Continue to dry at 110 degrees or at any temperature up to 140 degrees until constant weight is reached. Handle as an extremely hydroscopic compound.

Ruthenium Nitroso Bromide--$Ru(NO)Br_3$.

When ruthenium nitroso chloride was dissolved in hydrobromic acid and the solution evaporated almost to dryness a dark colored powder formed. After several evaporations in the presence of hydrobromic acid, the product was dried to constant weight at 140° C. and shown by analysis to be $Ru(NO)Br_3$.

Analytical Data: (No analysis reported in literature)

$Ru(NO)Br_3$

	Calculated	Found	Average
Ru(%)	27.36	27.49	--
N(%)	3.77	3.61, 3.60	3.61
Br(%)	64.5	64.4, 64.6	64.5

Procedure: Dissolve 1.0 grams of $Ru(NO)Cl_3 \cdot H_2O$ in 25 ml. hydrobromic acid and evaporate almost to dryness.

Add 25 ml. of hydrobromic acid and again evaporate. Repeat twice more. Dry the moist residue by heating carefully with an infra red lamp. Dry to constant weight at 140° C. Handle as a hydroscopic compound.

Attempt to prepare Ruthenium Nitroso Iodide, Ru $(NO)I_3$.

When ruthenium nitroso chloride was dissolved in hydroiodic acid and the solution evaporated, a coal-black powder was obtained. When dried at 110° C., the powder appeared to decompose by losing iodine. Unlike the chloride and bromide of the series, $Ru(NO)X_3$, the iodide is quite unstable. Another preparation was attempted in which the product was dried in a desiccator over calcium chloride. Even under this mild drying condition the product was not $Ru(NO)I_3$ as shown by the fact that the desiccator product contained about 34% ruthenium compared to a calculated 19.8% ruthenium for $Ru(NO)I_3$.

Attempt to isolate $H_2[Ru(NO)Cl_5]$

An attempt was made to isolate $H_2[Ru(NO)Cl_5]$ --the parent acid of the series of compounds, $K_2[Ru(NO)X_5]$ and $Ru(NO)X_3$. This acid probably exists in the solution from which $K_2[Ru(NO)Cl_5]$ can be precipitated by adding potassium chloride. A solution of $H_2[Ru(NO)Cl_5]$ was prepared as previously described in the preparation of $K_2[Ru(NO)Cl_5]$. The acid solution was evaporated to dryness in a vacuum desiccator over sodium hydroxide and calcium chloride. The residue was taken up in water and the evaporation repeated in order to remove

excess hydrochloric acid. After three such evaporations the residue was again dissolved in water and evaporated over anhydrone until most of the water was removed. The product was then allowed to stand over calcium chloride until constant weight was reached. The desiccator product was analyzed for nitrogen and chlorine:

	Found
N(%)	4.33, 4.22
Cl(%)	43.64, 43.68

Atomic ratio, Cl to N: 3.94 to 1.00

The ratio of Cl to N of 3.94 to 1.00 indicated that the desiccator product was partially decomposed $H_2[Ru(NO)Cl_5]$, and was probably a mixture of $H_2[Ru(NO)Cl_5] \cdot XH_2O$ and $Ru(NO)Cl_3 \cdot XH_2O$. Other observations which lead to the same conclusion are:

1. The desiccator product dissolved readily in water giving a strongly acid solution. $Ru(NO)Cl_3$ is only slightly soluble in cold water, but dissolves readily in an acid solution.

2. An aqueous solution of the desiccator product gave precipitates with cesium, silver, and mercury (I) ions which were similar to the precipitates that a solution of $K_2[Ru(NO)Cl_5]$ gave, but in no case was precipitation of ruthenium complete as it was from the latter solution.

3. When heated to 140° C. the desiccator product liberated a considerable amount of hydrochloric acid fumes. The

140° C. product was several shades darker than the desiccator product and was shown by analysis to be $Ru(NO)Cl_3.H_2O$.

Calculated for $Ru(NO)Cl_3.H_2O$		Found
N(%)	5.47	5.36, 5.43
Cl(%)	41.56	41.82, 41.71

Attempt to isolate Ruthenium Nitroso Nitrate, $Ru(NO)(NO_3)_3$.

The bright red solution obtained when ruthenium chloride was refluxed with nitric acid was believed by Joly and Werner to contain ruthenium nitroso nitrate (26, 45). However, all attempts by Joly to isolate this compound failed.

In the present investigation of the nitroso compounds of ruthenium an attempt was made to isolate a nitroso nitrate. Commercial ruthenium chloride was refluxed with concentrated nitric acid until a bright red solution was obtained. The solution was evaporated to a small volume, nitric acid added, and the evaporation was repeated. This process was continued until a solution was obtained which gave a negative test for the chloride ion when silver nitrate was added. The chloride-free solution was evaporated under an infra red lamp until a moist residue was obtained. When the moist residue was placed in a desiccator over sodium hydroxide and calcium chloride a red glassy material formed. The red glass dissolved readily in water to give a bright red aqueous solution. Aliquots of this solution were analyzed for nitrogen and ruthenium, and the atomic ratio of nitrogen to ruthenium was found to be

5.68 to 1.00. The high nitrogen content suggested that excess nitric acid might be present. The product was dissolved in water and evaporated to a red glass over ascarite and anhydrone. This process was repeated several times and finally the residue was placed in a desiccator for about six weeks. The atomic ratio of nitrogen to ruthenium was again determined and found to be 5.67 to 1.00, showing that excess nitrate ion, if present, had not been removed.

A portion of the "ruthenium nitroso nitrate" solution was titrated with sodium hydroxide to see if free nitric acid could be detected. As base was added the solution rapidly decomposed and precipitated a brown gelatinous precipitate which is referred to in the literature as ruthenium nitroso hydroxide. Other members of the series, $K_2[Ru(NO)X_5]$ and $Ru(NO)X_3$, give a similar precipitate with sodium hydroxide, but the precipitate forms slowly even when the solutions are boiled.

Ruthenium nitroso chloride is stable at temperatures up to 140 degrees. When ruthenium nitroso nitrate was heated to 110 degrees the red glass quickly became dark colored and finally turned black before constant weight was reached. The black residue contained 14.2% nitrogen compared to a calculated value of 17.6% for $Ru(NO)(NO_3)_3$.

From the work done on this substance it appears that the isolation of a ruthenium nitroso nitrate is probably impossible, and that the existence of the species, $Ru(NO)(NO_3)_3$, in solution is very doubtful.

B. Nitro Compounds

In 1889 A. Joly reported the preparation and analysis of two nitro compounds of ruthenium (29, 30). By treating ruthenium chloride with excess potassium nitrite, Joly obtained a yellow difficultly soluble salt which he characterized as $8KNO_2 \cdot Ru_2O_3(N_2O_2)(N_2O_3)$. In the present investigation this compound was prepared and recharacterized as $K_4[Ru(NO_2)_6] \cdot H_2O$.

Joly prepared an easily soluble orange nitro compound which he characterized as $4KNO_2 \cdot Ru_2(NO_2)_6$. This compound has been referred to in the literature as $K_2[Ru(NO_2)_5]$. The present work on this compound indicates that a better formulation for this compound is $K_2[Ru(NO)(OH)(NO_2)_4]$.

In addition to recharacterizing the two nitro compounds reported by Joly, another member of the series has been isolated. When $K_2[Ru(NO)(OH)(NO_2)_4]$ is treated with a 10% solution of potassium hydroxide at 0 to 10° C. the nitroso group probably converts to a nitro group forming $K_3[Ru(NO_2)_5]$.

Potassium Hexanitroruthenate (II) --$K_4[Ru(NO_2)_6] \cdot H_2O$

When ruthenium chloride is added to a boiling solution of potassium nitrite, and the potassium nitrite is present in large excess, a yellow crystalline powder slowly precipitates from the solution. The yellow powder is sparingly soluble and can be readily freed of chloride ion by washing with water.

Analytical Data:

$K_4[Ru(NO_2)_6] \cdot H_2O$

	Calculated	Found	Average	Joly (29)
K(%)	28.3	28.2, 28.0, 28.0	28.1	28.7
Ru(%)	18.4	18.11, 18.25, 18.06	18.14	18.55*
N(%)	15.2	15.0, 15.1, 14.9	15.0	15.05
H(%)	0.36	0.57, 0.55	0.56	--

*Joly's ruthenium analyses were 19.16, 18.17 and 18.31 for an average of 18.55. The high value for ruthenium was probably retained to support his formula, $8KNO_2 \cdot Ru_2O_2(N_2O_3)_2$, which has a calculated ruthenium content of 19.03%.

The analytical data allow, within experimental error, the assignment of the formula $K_4[Ru(NO_2)_6] \cdot H_2O$ or $K_4[Ru(NO_2)_6] \cdot 1\frac{1}{2} H_2O$.

	Found	Calculated	
		$K_4[Ru(NO_2)_6] \cdot 1\frac{1}{2} H_2O$	$K_4[Ru(NO_2)_6] \cdot H_2O$
K(%)	28.1	27.9	28.3
Ru(%)	18.14	18.11	18.42
N(%)	15.0	15.0	15.2
H(%)	0.56	0.54	0.36

The formula, $K_4[Ru(NO_2)_6] \cdot H_2O$, was choosen for this salt after evaluating the usual trends in the analytical data. Other evidence to support the formulation of the complex is developed later. The salt is hereafter in this report referred to as $K_4[Ru(NO_2)_6] \cdot H_2O$.

Procedure: Dissolve 20 grams of potassium nitrite in

30 ml. of water. Dissolve 1.0 grams of commercial ruthenium chloride in 10 ml. water. Heat the potassium nitrite solution to boiling and add the ruthenium chloride solution in 0.5 ml. portions. After each addition of ruthenium chloride wait until the solution becomes yellow before adding another portion. As ruthenium chloride is added the solution at first is dark brown, and then becomes green before turning yellow. After adding all of the ruthenium chloride, cool the solution overnight in a refrigerator. Approximately 0.2 grams of a yellow crystalline powder will form. Collect the precipitate in a sintered glass crucible and wash with water until a negative chloride ion test is obtained. Add 5.0 grams of potassium nitrite to the filtrate, cool overnight, and collect a second crop of crystals. Finally no more precipitate will form when potassium nitrite is added to the filtrate, although the filtrate still contains ruthenium.

Potassium Nitroso Hydroxotetranitroruthenate, $K_2[Ru(NO)(OH)(NO_2)_4]$.

This orange-colored, easily soluble nitro complex is very difficult to prepare. When the compound is made by Joly's method (29) of adding an aqueous solution of ruthenium chloride to a boiling solution of potassium nitrite until the solution is "neutral", several difficulties are encountered. The orange compound is more soluble than potassium chloride, and when the solution obtained by adding ruthenium chloride to potassium nitrite is concentrated by evaporation potassium chloride will precipitate first, followed immediately by the orange nitro

compound. The mixture is difficult to separate. Another difficulty is the contamination of the orange compound by the difficultly soluble yellow nitro complex, $K_4[Ru(NO_2)_6]$-$\cdot H_2O$. When attempts were made to separate this mixture and isolate the pure orange compound by the usual methods of recrystallization, a satisfactory product could not be obtained.

Since impure $K_2[Ru(NO)(OH)(NO_2)_4]$ converts to $K_4[Ru(NO_2)_6]\cdot H_2O$ when treated with excess potassium nitrite an attempt was made to use $K_4[Ru(NO_2)_6]\cdot H_2O$, which can be easily freed of chloride ion, as a starting material for the preparation of pure $K_2[Ru(NO)(OH)(NO_2)_4]$. This provides a chloride free system and eliminates the difficulty of having the product contaminated with potassium chloride.

When $K_4[Ru(NO_2)_6]\cdot H_2O$ was heated in boiling water, it dissolved slowly giving a yellow solution which had a pH of 10.0. After continued boiling the solution became orange and the pH of the solution slowly decreased. After refluxing for four hours the pH was 7.0 and showed no further change when boiling was continued. When the solution was concentrated by evaporation a crystalline product was not obtained, but rather an orange-colored sticky mass.

The next step undertaken was to determine the best pH for the precipitation of the orange nitro compound. A solution of potassium nitrite was prepared which had a pH of 8.0. Portions of this solution were treated with ruthenium

chloride until various pH values were reached and the solutions evaporated and the residue examined with a microscope. In all cases the residue contained potassium chloride, but the object was to determine at what pH the orange compound could be obtained free of $K_4[Ru(NO_2)_6] \cdot H_2O$. At a pH of 6.5 pure $K_4[Ru(NO_2)_6] \cdot H_2O$ was precipitated; at a pH of 4.7 a mixture of $K_4[Ru(NO_2)_6] \cdot H_2O$ and the orange compound was obtained, but at a pH of 4.0 the orange compound was obtained free of $K_4[Ru(NO_2)_6] \cdot H_2O$. At a pH of 1.0 which was obtained by adding hydrochloric acid, the solution became raspberry colored and $K_2[Ru(NO)Cl_5]$ precipitated.

The most logical approach to isolate the pure orange compound seemed to be to start with $K_4[Ru(NO_2)_6] \cdot H_2O$ and convert it to a solution of pH 4.0. $K_4[Ru(NO_2)_6] \cdot H_2O$ was dissolved in hot water and the solution was refluxed for several hours until the pH was 7.0. An acid had to be added to lower the pH to 4.0. Hydrochloric acid could not be used since potassium chloride would precipitate first. Nitric acid and sulfuric acid presented similar problems. It was decided to try perchloric acid to see if an orange nitro compound could be obtained after precipitating the relatively insoluble potassium perchlorate. When perchloric acid was added until the pH was 4.0, and the solution concentrated by slow evaporation a large amount of potassium perchlorate precipitated. However, a crystalline ruthenium compound

could not be obtained from the filtrate. It was shown by calculation that the amount of potassium remaining in the solution after precipitating potassium perchlorate was very small. Since a large amount of perchloric acid had to be added to lower the pH to 4.0 this method was unsuccessful.

The next method attempted was to convert $K_4[Ru(NO_2)_6]\cdot H_2O$ to $H_4[Ru(NO_2)_6]$ by an ion exchange resin. A solution of $K_4[Ru(NO_2)_6]\cdot H_2O$ was treated with a cation exchange resin, Amberite IR-120, by the batch process, and a solution of $H_4[Ru(NO_2)_6]$ with a pH of 1.7 was obtained. Potassium hydroxide was added to provide potassium ions and to raise the pH to 4.0. A crystalline product was not obtained.

Joly apparently had no difficulty preparing a pure orange nitro compound by adding ruthenium chloride to hot potassium nitrite solution. The major difference in his procedure and the initial unsuccessful attempts of the author was in the quantity of materials used. Joly worked with kilogram quantities of ruthenium chloride, whereas in the first unsuccessful attempts about 1.0 gram of ruthenium chloride was used. The ruthenium chloride-potassium nitrite method was tried again using 5.0 grams of ruthenium chloride and a pure compound was isolated. Ruthenium chloride was added to potassium nitrite at 70 degrees until oxides of nitrogen were no longer evolved, and the solution was at a pH of 4.5. It was found that if this solution was cooled suddenly, or concentrated only slightly by evaporation, and then cooled sud-

denly that crystals of $K_2[Ru(NO)(OH)(NO_2)_4]$ would precipitate and potassium chloride would remain in solution. The precipitate was freed of traces of $K_4[Ru(NO_2)_6]$ by recrystallizing rapidly from water. To prepare the compound in a pure state the procedure given below must be followed very carefully and recrystallization must be performed very quickly.

Analytical Data:

$K_2[Ru(NO)(OH)(NO_2)_4]$

Calculated		Found	Average	Joly (29)
K(%)	19.0	19.6,19.3,19.1	19.3	19.3
Ru(%)	24.75	24.92,24.93,24.93	24.93	24.98
N(%)	17.03	16.81, 16.94	16.88	17.13
H(%)	0.24	0.50, 0.50	0.50	- --

The analytical data allow the assignment of the formula (1) $K_2[Ru(NO_2)_5]$, (2) $K_2[Ru(NO)(OH)(NO_2)_4]$ or (3) $K_2[Ru(NO)(H_2O)(NO_2)_4]$.

	Found	Calculated		
		(1)	(2)	(3)
K(%)	19.3	19.0	19.0	18.9
Ru(%)	24.93	24.83	24.75	24.71
N(%)	16.88	17.07	17.03	16.99
H(%)	0.50	- --	0.24	0.48

For reasons to be developed later the orange nitro salt was assigned the formula, $K_2[Ru(NO)(OH)(NO_2)_4]$, and hereafter in this report will be referred to as such.

Procedure: Dissolve 12.0 grams of potassium in 30 ml. of water and heat to 70° C. Dissolve 5.0 grams of commercial ruthenium chloride in 30 ml. of water. Add the ruthenium chloride solution in 2.0 ml. portions to the hot nitrite solution. The nitrite solution turns yellow after the first addition of ruthenium chloride and becomes orange after 6 ml. of ruthenium chloride are added. From this point on allow the solution to stand undisturbed until oxides of nitrogen are no longer emitted after each addition of ruthenium chloride. After 20 ml. of ruthenium chloride are added the solution becomes quite cloudy and contains a yellow insoluble substance. After all of the ruthenium chloride is added the solution is almost clear and most of the yellow insoluble substance redissolves. If gases are still emitted after adding 30 ml. of ruthenium chloride, dissolve 0.5 grams of ruthenium chloride in 10 ml. of water and add this solution in 2 ml. portions until gases are no longer emitted. The addition of ruthenium chloride requires about four hours.

Evaporate the reaction mixture to a volume of not less than 30 ml. under an infra red lamp. The solution becomes slightly cloudy. Filter or centrifuge when hot, and cool the clear filtrate quickly in an ice bath. A large amount of precipitate will form quickly when precipitation starts. Collect the precipitate in a sintered glass crucible and wash with alcohol until a negative test of chloride ion is obtained when a portion of the precipitate is dissolved in nitric acid

and silver nitrate added. The yield is 4.3 grams.

Place 4.3 grams of chloride-free orange nitro compound in a 15 ml. centrifuge tube and add 2 ml. of hot water. Place the tube in a beaker of boiling water and add hot water and stir until the orange compound dissolves. The total volume of the solution is 8 ml. Quickly centrifuge and decant the clear filtrate into a 20 ml. beaker. (A small residue of a yellow insoluble substance is removed by centrifugation). Place the beaker in ice. When crystals begin to form, stir the solution and precipitation will be rapid. Collect the precipitate by filtration, wash with alcohol and ether, air dry until the alcohol and ether are removed, and then dry at 110° C. The yield is 2.3 grams. The entire recrystallization requires 15 to 20 minutes. Collect a second crop of crystals by adding alcohol to the mother liquid.

Potassium Pentanitroruthenate (II), $K_3[Ru(NO_2)_5]$

When a solution of $K_2[Ru(NO)(OH)(NO_2)_4]$ is treated with 10% potassium hydroxide at a temperature of 0 to 10° C. a yellow precipitate rapidly forms. The yellow precipitate has a pearly luster and forms in small plates, but when it is air dried or dried over calcium chloride, the product changes to a tan colored powder. The tan powder gives an X-ray diffraction powder pattern which is distinctly different from $K_2[Ru(NO)(OH)(NO_2)_4]$ or $K_4[Ru(NO_2)_6] \cdot H_2O$. It is more soluble than $K_4[Ru(NO_2)_6] \cdot H_2O$, but not as soluble as $K_2[Ru(NO)(OH)(NO_2)_4]$. The tan colored powder gave the following analysis which

corresponds to the formula: (1) $K_3[Ru(NO_2)_5]$ or (2) $K_3[Ru(NO)(OH)(NO_2)_4]$

Analytical Data: (No analysis reported in literature)

	Calculated		Found	Average
	(1)	(2)		
K(%)	26.1	26.1	26.6,26.0,25.8	26.1
Ru(%)	22.65	22.59	22.50, 22.44	22.47
N(%)	15.59	15.56	15.4,15.5,15.4	15.4

The formula, $K_3[Ru(NO_2)_5]$, was choosen for the tan salt for reasons to be developed later.

Procedure: Dissolve 3.3 grams of $K_2[Ru(NO)(OH)(NO_2)]$ in 33 ml. of water and cool to 5° C. Cool 33 ml. of freshly prepared 10% potassium hydroxide solution to 5° C. Rapidly mix the two solutions. Stir the mixture and maintain at a temperature not greater than 10° C. After about five minutes crystals begin to form and after 15 minutes a large crop will have formed. Filter immediately. (If the reaction is allowed to proceed for a longer period of time a yellow insoluble powder will form). Wash the precipitate with alcohol and then with ether. Air dry until all the ether is removed. Dry to constant weight over calcium chloride. The product can not be purified by recrystallization since it rapidly decomposes in a hot aqueous solution. An attempt was made to recrystallize from a 5% potassium hydroxide solution but the compound would not reprecipitate.

Chemical Relation of the Nitro Complexes.

When a solution of the orange salt, $K_2[Ru(NO)(OH)(NO_2)_4]$, is treated with excess potassium nitrite, the yellow salt, $K_4[Ru(NO_2)_6] \cdot H_2O$ slowly precipitates. A solution of the orange salt has an approximate pH of 6.0. When excess potassium nitrite is added the pH of the solution is 10.5. As the yellow salt slowly precipitates the pH of the solution decreases to 7.0 and no more precipitate forms. When potassium hydroxide is added to increase the pH to 10.5 more yellow salt starts to form as long as potassium nitrite is present in excess.

When a solution of the orange salt, $K_2[Ru(NO)(OH)(NO_2)_4]$, is treated with 10% potassium hydroxide at 0-10° C., the tan salt, $K_3[Ru(NO_2)_5]$, rapidly precipitates.

A solution of the yellow salt, $K_4[Ru(NO_2)_6] \cdot H_2O$, has a pH of about 10.0. When the yellow solution is refluxed for 3 or 4 hours, the solution becomes orange and the pH decreases to 7.0. Attempts to isolate a crystalline product from this solution were unsuccessful.

Part V

INSTRUMENTAL STUDIES

A. Conductance Measurements.

Theory: The molecular conductance, u, of an electrolyte in solution is defined by the equation

$$u = \frac{1000\ L}{m}$$

in which m is the concentration of the electrolyte in moles per liter, and L is that part of the specific conductivity of the solution which is due to the electrolyte. L is obtained by subtracting the specific conductivity of the pure solvent, L_o, from that of the solution, L.

Measurement of the conductivity of a solution is made with a modified Wheatstone bridge, in which a conductance cell is placed in one arm of the bridge circuit and the resistance of the electrolyte is measured. The relation between the measured resistance across the terminals of the conductivity cell and the specific conductivity of the solution depends upon the geometry of the cell. Formally, the specific conductance of a solution is equal to the reciprocal of its resistance, when measured between electrodes one square centimeter in area and one centimeter apart. In practice cell dimensions differ, but the measured resistance of a solution is related to its specific conductivity by a constant factor, K, depending on the geometry of the cell, which is known as the "cell constant". The cell constant is determined by measuring the resistance, R, of a solution of known specific

conductance and using the relationship

$$K = LR$$

The primary standard for determining cell constants is pure mercury, due to the fact that mercury is used in defining the international ohm. The specific conductivity of mercury is so high that solutions of potassium chloride are generally used as secondary standards in determining the cell constants of cells designed for the study of electrolytes.

After the cell constant is determined, the specific conductance of any solution can be obtained by measuring its resistance and using the relationship

$$L = K/R$$

The molecular conductance can then be calculated by using the defining equation

$$u = \frac{1000\ L}{m}$$

Usually dilution is used to express concentration rather than molarity. The equation for the calculation of the molecular conductivity of a solution then becomes

$$u = 1000\ (L_{soln.} - L_{water})\ D$$

where D equals the volume in liters to which one mole of the solute has been diluted.

Experimental: All resistance measurements were made with a Model RC Conductivity Bridge manufactured by the Industrial Instruments, Inc., of Jersey City, New Jersey. The cell constant was determined by measuring the resistance of a 0.0200 N solution of potassium chloride at $25 \pm 0.1^{\circ}$ C. The water used

to prepare all solutions was distilled water which was boiled to remove dissolved carbon dioxide. Samples of each salt were weighed and diluted directly to a dilution of 1024 liters for determining the number of ions. Variation of molecular conductivity with dilution was determined by preparing a stock solution of each sample and diluting to various concentrations. The temperature of each solution was maintained at 25 ± 0.1° C. by means of a thermostatically controlled water bath.

Determination of number of Ions in a Salt:

The number of ions in a salt can be determined by measuring the molecular conductivity of the salt and comparing the value obtained with the molecular conductivity of known salts. The standard conditions chosen for comparing molecular conductivity values are at a temperature of 25° C. and at a dilution of 1024 liters. At this dilution 100% ionization is assumed. The following ranges for salts containing two, three, and four ions have been established by comparing conductance values for a large number of salts:

Number of Ions	Range of Molecular Conductivity (Mhos)
2	118-131
3	235-273
4	408-435

The only common five ion salt which has been studied is potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$, and molecular conductivity values ranging from 558 to 596 mhos have been

reported for it. (See Table I)

Table I shows that all the three ion salts of the series, $K_2[Ru(NO)X_5]$, and the knowns measured to check the accuracy of the measurements, fall well into the accepted range of 235 to 273 mhos.

The four ion salt, $K_3[Ru(NO_2)_5]$, gave a value of 405 mhos which is slightly lower than the established range of 408 to 435, but is well above the upper limit for 3 ion salts of 273 mhos.

The five ion salt, $K_4[Ru(NO_2)_6] \cdot H_2O$, has a molecular conductivity of 582 mhos compared to a measured value of 600 mhos for C.P. doubly recrystallized potassium Hexacyanoferrate (II). The published values for potassium hexacyanoferrate (II) vary widely. The experimental values for potassium hexachloroplatinate (IV), potassium hexacyanoferrate (III), and potassium hexacyanoferrate (II) agree well with the data obtained by Walden.

The data obtained with the ruthenium salts are seen to be completely in accord with the formulas postulated on the basis of their analysis.

Table I

Relation of Molecular Conductivity, u, to

Number of Ions

Temperature 25±0.1° C.

Dilution (D) 1024 Liters.

	Experimental u (mhos)	Values from literature u (mhos)	D (liters)	Reference
3 Ion Salts:				
$K_2[PtCl_6]$	269 ± 3	268.8	1024	c
$Na_2[Fe(NO)(CN)_5].2H_2O$	223	236.4	1024	d
$K_2[Ru(NO)Cl_5]$	254	252*	640	a
		260*	1280	a
$K_2[Ru(NO)Br_5]$	254	None		
$K_2[Ru(NO)I_5]$	255	None		
$K_2[Ru(NO)(OH)(NO_2)_4]$	245	None		
4 Ion Salts:				
$K_3[Fe(CN)_6]$	469±5	468.1	1024	[redacted]
		435	1024	g
$Na_3[Co(NO_2)_6]$	425	405	640	e
		467	1280	c
$K_3[Ru(NO_2)_5]$	405	None		
5 Ion Salts:				
$K_4[Fe(CN)_6]$	600±7	596.4		c
		583		b
		558		g
$K_4[Ru(NO_2)_6].H_2O$	582	None		

*Converted to 25° C. by assuming a temperature coefficient of 2.2% per degree.

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Table II

Molecular Conductivity Values of Freshly Prepared Solutions of Ruthenium Salts at Various Dilutions.

Temperature 25 ± 0.1° C.

Compound	Dilution in Liters				
	256	512	1024	2048	4096
$K_2[Ru(NO)Cl_5]$	236	245	254	259	---
$K_2[Ru(NO)Br_5]$	241	247	254	259	---
$K_2[Ru(NO)I_5]$	247	262	280	306	---
$K_2[Ru(NO)(OH)(NO_2)_4]$	---	231	245	255	---
$K_3[Ru(NO_2)_5]$	---	---	405*	---	---
$K_4[Ru(NO_2)_6] \cdot H_2O$	---	---	573	576	575

*dilution 1033 liters

Table II shows the variation of the molecular conductivity of freshly prepared solutions with dilution. The increase of conductivity with dilution is a general behavior.

Variation of Molecular Conductivity with Aging Time of Solution:

The relative stability of complex ions in solution can be determined by measuring molecular conductivity as a function of time. If an ion of the type, $[MX_6]^{-a}$ decomposes in solution by reacting with water according to the equation

$$[MX_6]^{-a} + bHOH = [MX_{6-b}(OH)_b]^{-a} + bH^+ + bX^-$$

the molecular conductivity of the solution will increase, due to the liberation of hydrogen ions and X^- ions. As the solution ages the conductivity will increase and the pH of the solution will decrease.

Variation of molecular conductivity with time was studied for the nitroso and nitro complexes of ruthenium. Measurements were made at a dilution of 1024 liters and a temperature of 25°C. at various intervals up to 300 hours. The solutions were stored in glass stoppered bottles at room temperature (25-30°C.) between measurements. Figure 4 shows the results.

In the series, $K_2[Ru(NO)X_5]$, the orange nitro complex, $K_2[Ru(NO)(OH)(NO_2)_4]$ is extremely stable, the chloro complex fairly stable, whereas the bromo and iodo complexes decompose rapidly.

$Ru(NO)Cl_3.H_2O$ decomposes at about the same rate as the

Variation of Molecular Conductivity at 25 ±0.1°C. with Aging Time at Room Temperature (25-30°C.) of Aqueous Solutions of Nitroso and Nitro Complexes at a Dilution of 1024 Liters.

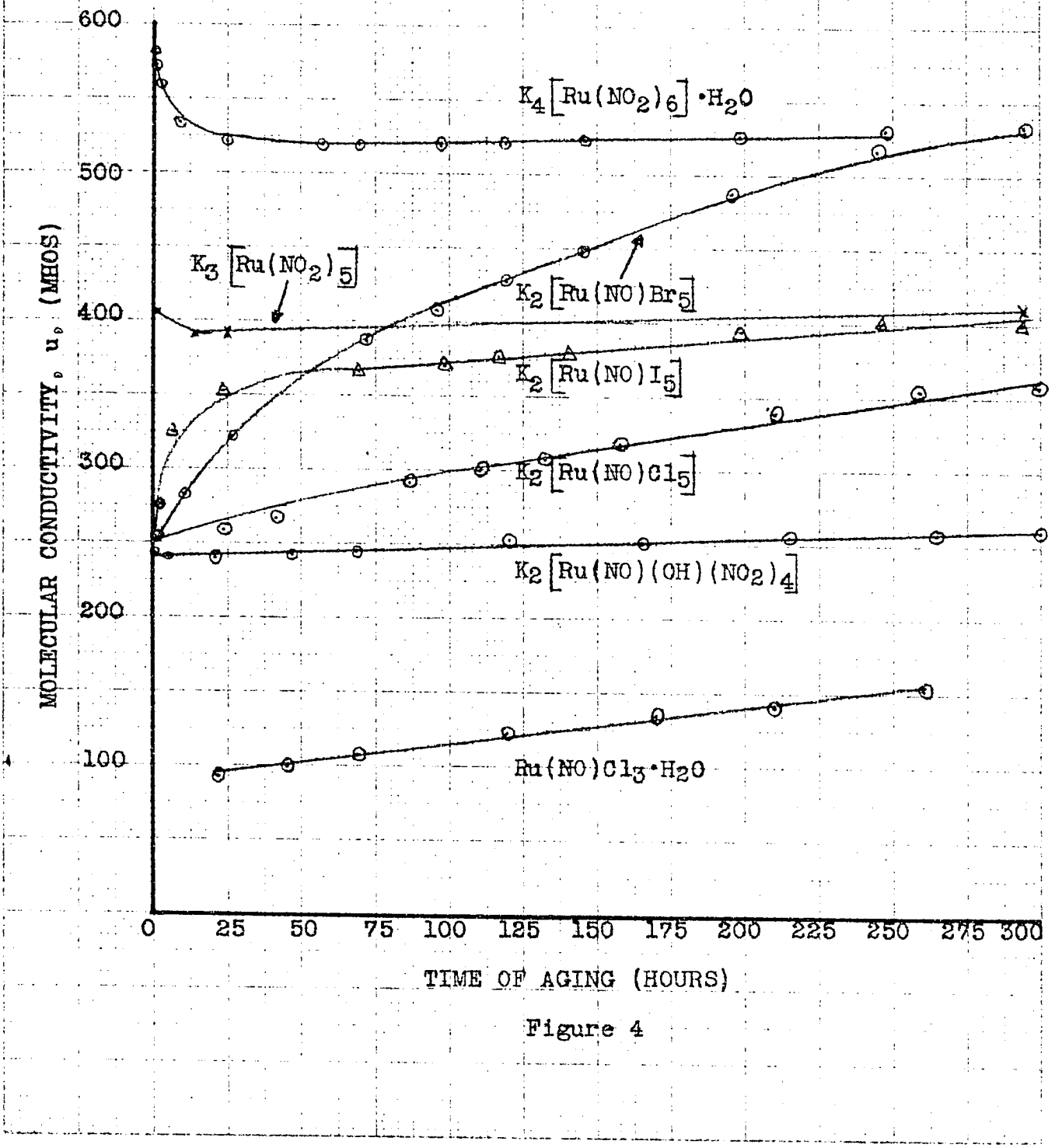


Figure 4

complex ion, $[Ru(NO)Cl_5]^{-2}$. $Ru(NO)Cl_3 \cdot H_2O$ dissolves very slowly at 25° C., so it was impossible to obtain a conductance value for a freshly prepared solution. If it is a completely covalent compound its solution should have a very low conductivity. The value of 100 mhos at 23 hours is probably due to the fact that as the compound dissolves it forms a complex acid which then hydrolyzes.

The yellow nitro complex, $K_4[Ru(NO_2)_6] \cdot H_2O$, and the tan nitro complex, $K_3[Ru(NO_2)_5]$ gave an initial decrease in conductance and then showed very little change. Since a decrease in conductance with time is unusual, the yellow salt was studied further. The conductance of the nitroso complex, $K_2[Ru(NO)I_5]$, increases with aging time at about the same rate that the conductance of the nitro complex, $K_4[Ru(NO_2)_6] \cdot H_2O$, decreases. The change in conductance of these two complexes was followed for several hours and each time a conductance reading was taken the pH of the solution was also measured. Figure 5 shows that as the conductance of $K_2[Ru(NO)I_5]$ increases from 255 to 300 mhos, the pH of the solution decreases from 5.0 to 3.3, whereas as the conductance of $K_4[Ru(NO_2)_6] \cdot H_2O$ decreases from 572 to 520 mhos the pH of the solution decreases from 10.5 to 7.5.

As the reaction

(1) $[Ru(NO)I_5]^{-2} + n\ HOH = [Ru(NO)I_{5-n}(OH)_n]^{-2} + n\ H + nI^-$

proceeds, the conductance increases, due to the iodide and

Variation of Molecular Conductivity and pH at 25 ± 0.1°C. with Aging Time at Room Temperature (25-30°C.) of Aqueous Solutions of $K_2[Ru(NO)I_5]$ and $K_4[Ru(NO_2)_6]\cdot H_2O$ at a Dilution of 1024 Liters.

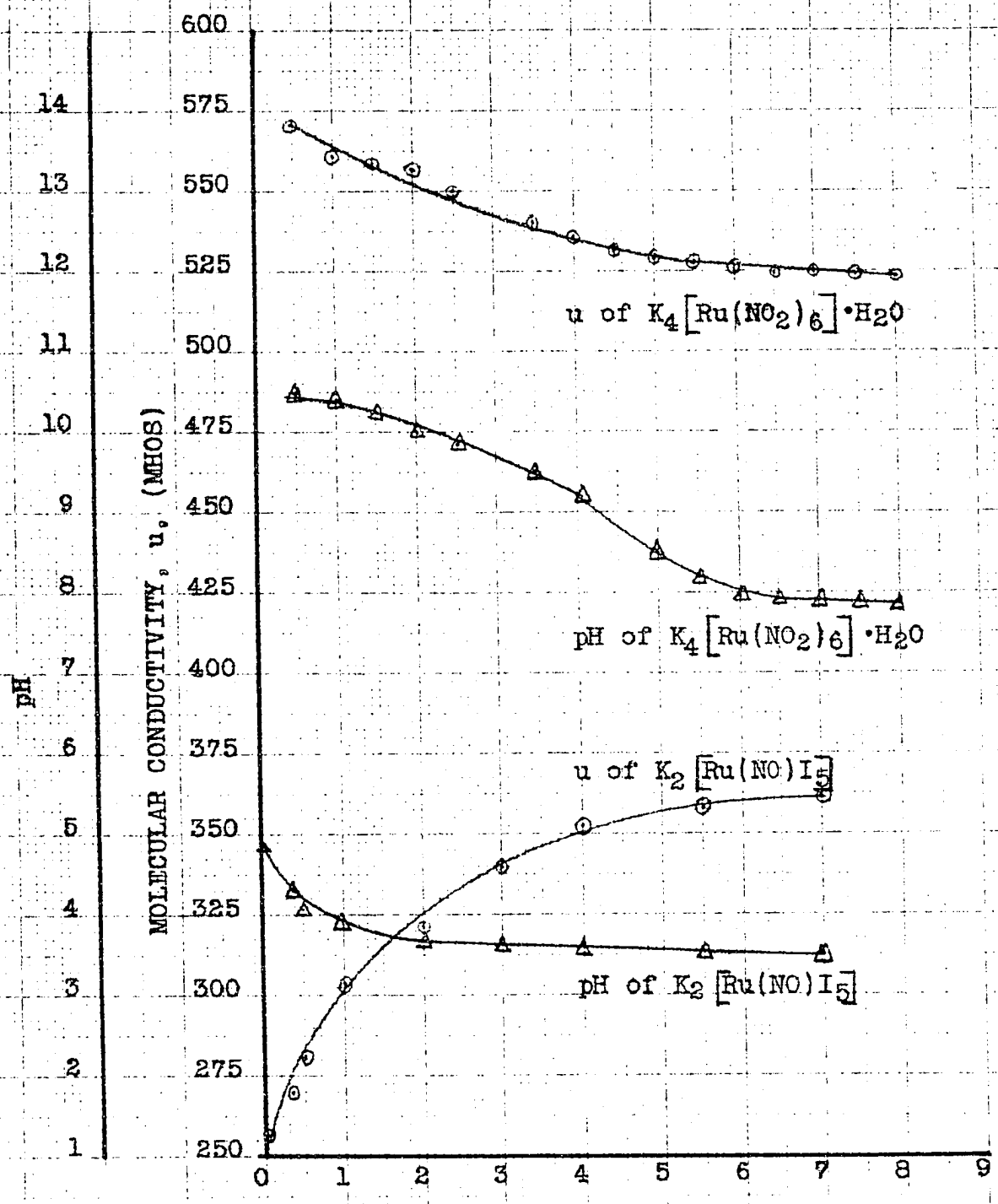


Figure 5

especially the hydrogen ions formed as reaction products. Any difference in the conducting ability of $[Ru(NO)I_5]^{-2}$ and $[Ru(NO)I_{5-n}(OH)_n]^{-2}$ could not be detected, due to the effect of the hydrogen ions. The decrease of the pH to 3.3 confirms the presence of hydrogen ions in the solution.

The reaction

(2) $[Ru(NO_2)_6]^{-4} + n\ HOH = [Ru(NO_2)_{6-n}(OH)_n]^{-4} + n\ HNO_2$

is accompanied by a decrease in conductance. The effect of the hydrogen and nitrite ions in reaction 2 is small in comparison with the hydrogen and iodide ions in reaction 1, because nitrous acid, a weak acid, is formed. The decrease in conductance with time may be attributed to the possibility that $[Ru(NO_2)_{6-n}(OH)_n]^{-4}$ is a poorer conductor than $[Ru(NO_2)_6]^{-4}$. The molecular conductivity decreases 50 mhos, which is the order of magnitude of the difference in conducting ability of various ions.

B. Potentiometric Titrations

Reaction of Nitroso Ruthenium Complexes with NaOH Solution:

By treating a boiling solution of $Ru(NO)Cl_3 \cdot H_2O$ with alkali in just the right amount, Joly obtained a brown gelatinous material which he called ruthenium nitroso hydroxide, $Ru(NO)(OH)_3$. This hydrous base is soluble in excess alkali to give a brown solution of unknown composition and readily soluble in dilute acids forming a red solution.

In the present investigation the reaction of sodium hydroxide with $Ru(NO)Cl_3 \cdot H_2O$, $K_2[Ru(NO)Cl_5]$, and $K_2[Ru(NO)(OH)(NO_2)_4]$ was studied by means of potentiometric titrations. Solutions of each compound containing 0.30 millimoles of ruthenium were titrated with standard sodium hydroxide. Base was added to the boiling solutions and the solutions maintained at a temperature near boiling until a constant pH was reached. All pH measurements were made at a temperature of $60 \pm 0.1^{\circ}$ C. The reactions proceeded slowly. Approximately 30 minutes was required for constant pH to be reached after each addition of base. The results of the titrations are shown in Figure 6.

$Ru(NO)Cl_3 \cdot H_2O$ and $K_2[Ru(NO)Cl_5]$ gave identical reactions. In both cases precipitation of $Ru(NO)(OH)_3$ started at a pH of 5.5. At a pH between 8.0 and 8.5, precipitation of ruthenium was almost quantitative, as shown by the fact that the raspberry colored solutions became almost colorless. At a

Potentiometric Titration of Nitroso Ruthenium Complexes with Sodium Hydroxide Solution.

Solution Concentrations: Ruthenium Complexes--0.30 millimoles Ru per 25-30 ml. water.

NaOH--0.1205N NaOH

Reaction Temperature: 100°C.

Temperature of pH Measurement: 60 ± 0.1°C.

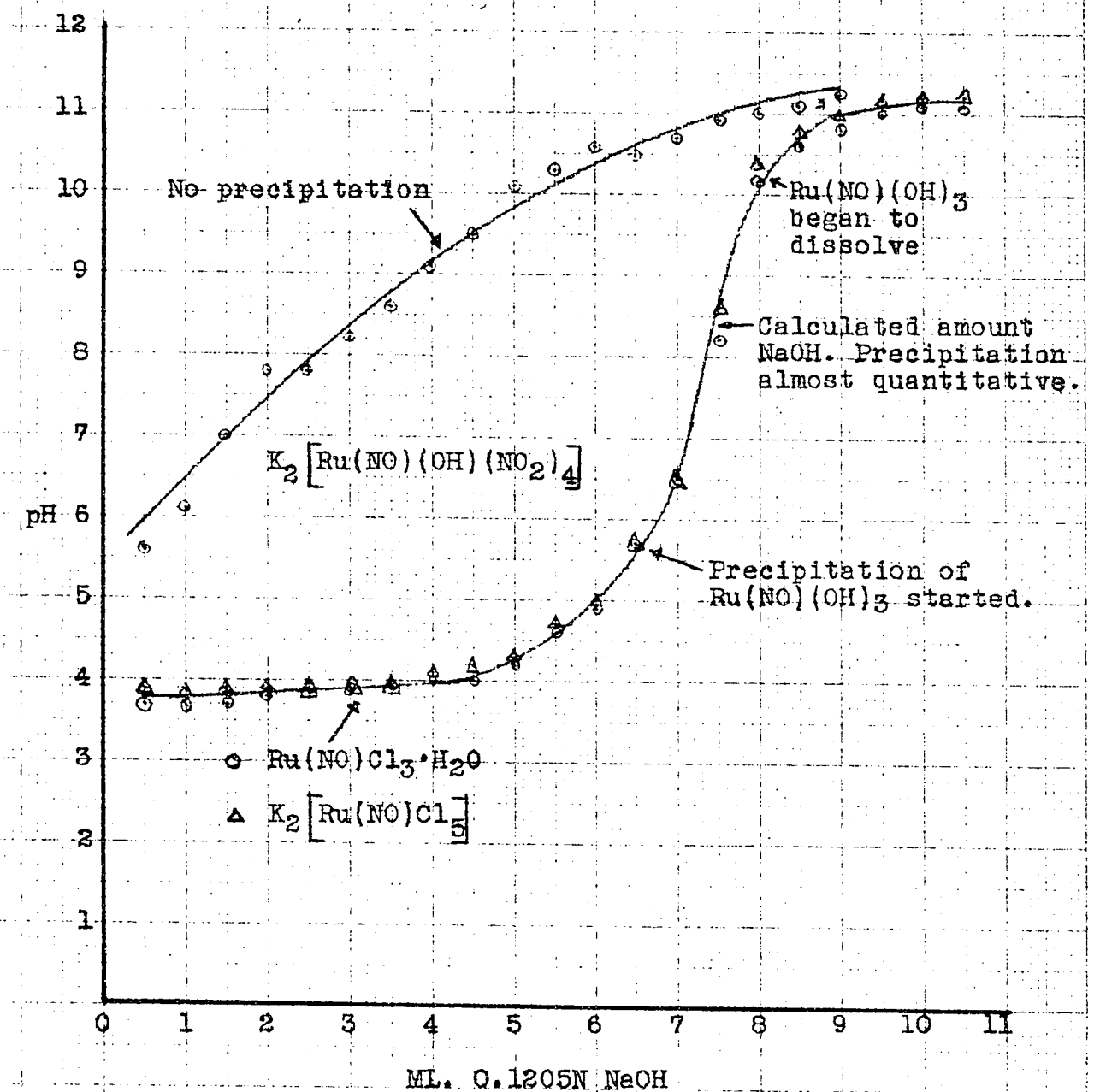


Figure 6

pH slightly above 10.0 ruthenium nitroso hydroxide began to dissolve. Solution was rapid as more base was added.

The theoretical amount of sodium hydroxide required for the reactions

$$Ru(NO)Cl_3.H_2O + 3NaOH = Ru(NO)(OH)_3 + 3NaCl + H_2O$$

and

$$K_2[Ru(NO)Cl_5] + 3NaOH = Ru(NO)(OH)_3 + 3NaCl + 2KCl$$

was 7.5 ml. It is interesting to note that after the calculated amount of sodium hydroxide was added the precipitation of ruthenium was almost complete.

$K_2[Ru(NO)(OH)(NO_2)_4]$ was unaffected by sodium hydroxide even after several hours of boiling. This fact shows the difference in the stability of the ruthenium to chloride and ruthenium to nitro nitrogen bonds in the complexes. Nitro complexes are among the most stable and frequently are stable even in boiling alkali.

Detection of a coordinated aquo or hydroxy group:

A solution of $[Co(NH_3)_5H_2O]_2(SO_4)_3$ was titrated with standard base to determine if the hydrogen of the coordinated water molecule in the complex cation shows acidic properties. Figure 7 shows that when 0.012 N sodium hydroxide was added to an approximately 0.01 N solution of the cobalt complex, a break occurred at a pH of about 8.0. Since the titration was run rapidly, the inflection of pH is probably due to the acid-base reaction:

$$[Co(NH_3)_5H_2O]^{+3} + OH^- = [Co(NH_3)_5OH]^{+2} + H_2O$$

Potentiometric Titration of 0.01N Solutions of $K_2[Ru(NO)(OH)(NO_2)_4]$ and $[Co(NH_3)_5H_2O]_2(SO_4)_3$ with 0.012N NaOH and 0.012N HCl at Room Temperature.

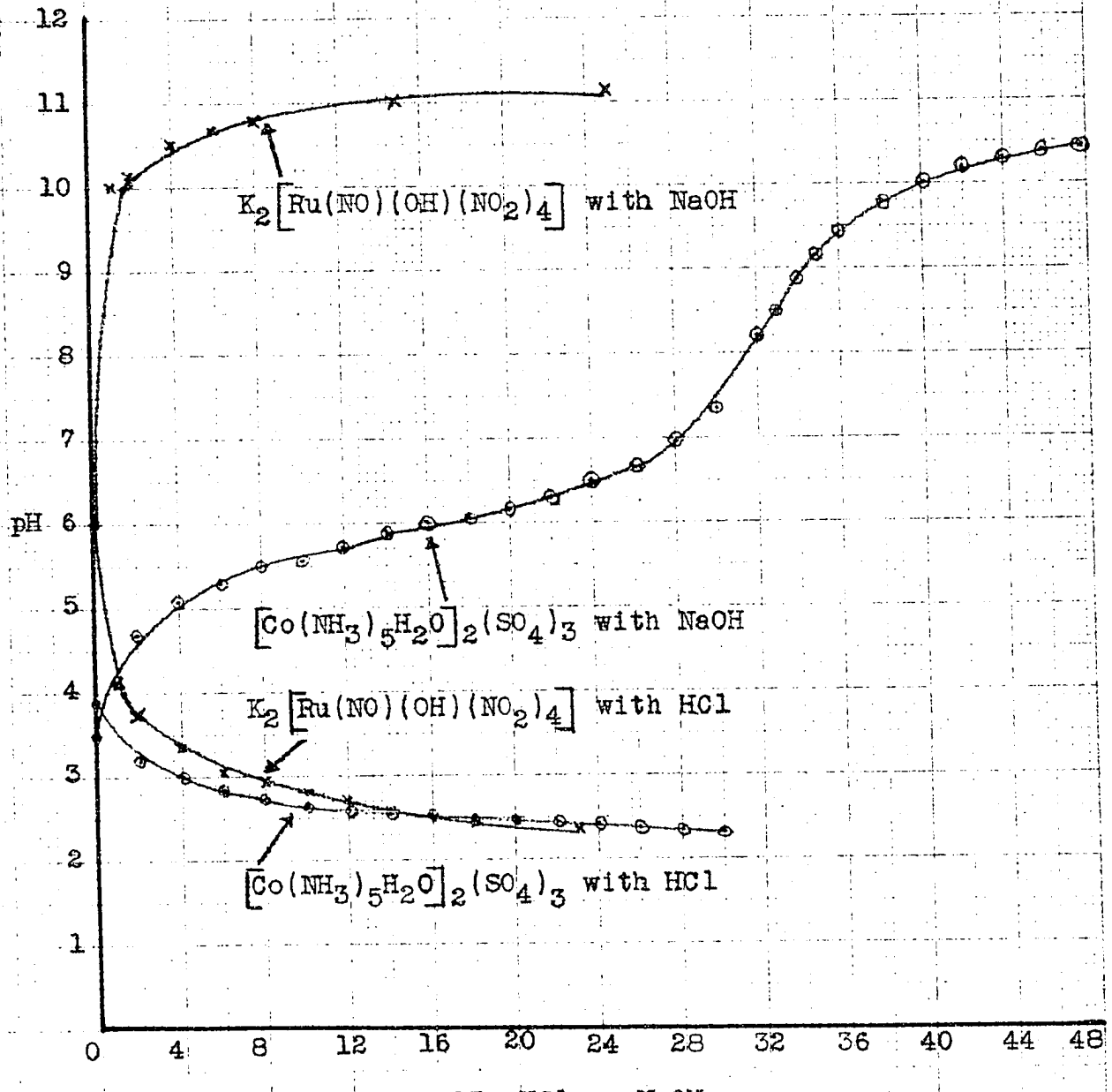


Figure 7

rather than a replacement reaction which usually proceeds at a slower rate.

When the cobalt complex was titrated with hydrochloric acid, apparently no reaction occurred. No record could be found of the use of acid-base reactions to detect the presence of coordinated aquo or hydroxy groups in complex ions. This method should be investigated further as it might offer a simple means to aid in the characterization of complex cations.

Similar reactions were run using the anionic complex, $K_2[Ru(NO)(OH)(NO_2)_4]$. Figure 7 shows that no acid-base reaction occurred with sodium hydroxide or hydrochloric acid. In his review on complex ions H. Taube (41) pointed out that complex cations containing an aquo group show acidic properties, that the higher the charge of the cation the greater the acidity, and that no work had been done on the acid-base properties of complex anions.

C. X-ray Diffraction Patterns

Theory: When a beam of X-rays strikes a crystal, the planes of the crystal diffract the beam in much the same manner as a grating diffracts ordinary light. The relationship between the wavelength, λ, the angle of diffraction, θ, and the distance between the planes in the crystal, d, is given by the Bragg equation:

$$n\lambda = 2d \sin \theta$$

where n represents the order of diffraction.

If many very small crystals, randomly oriented, are placed in an X-ray beam, a continous cone of diffracted rays will be produced. The cone will intercept a circular film surrounding the sample in curved lines. The angle, θ, may be calculated if the radius of the circular film is known and the distance between corresponding arcs of the same cone of diffracted rays is measured. If the distance between corresponding arcs is called S, then

$$\frac{S}{R} = 4\ \theta \text{ rad.}$$

where R is the radius of the camera, and θ rad is the angle of diffraction, measured in radians. The angle, θ, of the Bragg equation measured in degrees, is then:

$$\theta = \frac{S}{4\ R} \times 57.295$$

X-ray diffraction patterns are very useful for "finger printing" crystalline compounds for identification purposes. The basis of the method was stated in 1919 by A. W. Hull (24).

The basis is "That every crystalline substance gives a pattern; that the same substance always gives the same pattern; and that in a mixture of substances, each produces its pattern independently of the others, so that the photograph obtained with a mixture is the superimposed sum of photographs that would be obtained by exposing each of the components separately for the same length of time."

The most satisfactory method for the identification of unknowns is the direct comparison of negatives. Since it is not practical to publish prints, a system of classification has been developed based on the positions of lines in the pattern calculated by solving Bragg's equation, $n\lambda = 2d \sin \theta$, for d, the distance between the planes in the crystal. The relative intensity of the lines is visually estimated on a 1 to 10 scale, the most intense line being assigned a value of 10. In some cases it is difficult to estimate the relative intensities of the lines.

Procedure: A sample of each compound was ground in an agate mortar and passed through a 150 mesh screen. The finely divided sample was loaded in a thin glass capillary tube and packed in with a burette wire. The capillary tube was sealed and inserted in the pulley of the camera and held in place by modeling clay. The camera was placed on the diffraction unit, and exposed to a X-ray beam from a copper target tube, for 3 to 4 hours. The diffraction unit was operated at 32 kilovolts and 20 milliamperes.

The exposed film was developed in standard X-ray developer for 7 minutes at 20° C., fixed in hypo for 10 to 12 minutes, washed in running water for 1 hour, and dried at room temperature.

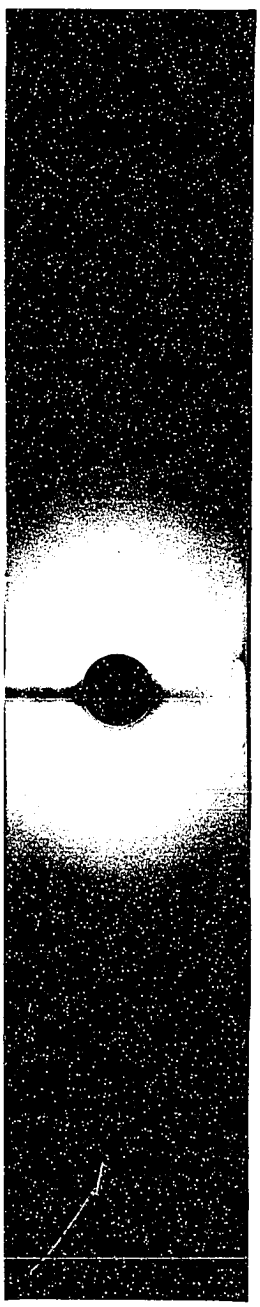
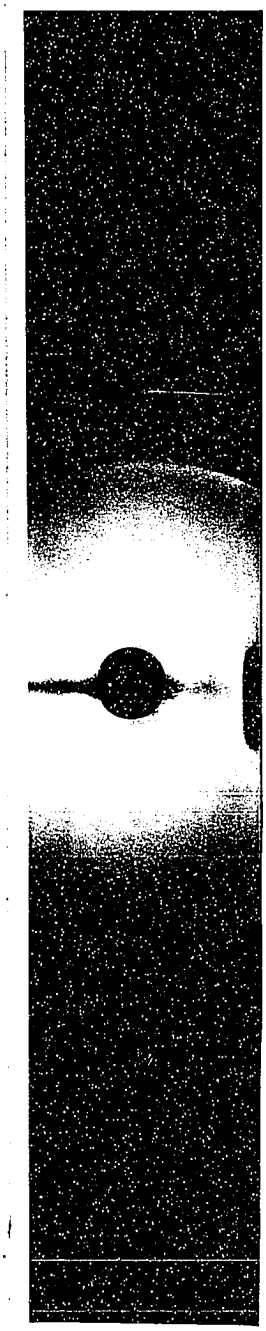
Calculations: The large camera used was designed so that one-half the distance between corresponding arcs equals the angle 2 θ. Samples which gave a weak pattern in the large camera were exposed for 3 hours in a small camera. The small camera was designed so that the distance between corresponding arcs equals the angle 2 θ. d spacings for the angle 2 θ for CuK_{α} radiation were obtained from a table published by G. Switzer et al (40).

Results: The d spacings and relative intensity of the lines for the nitroso and nitro complexes of ruthenium prepared in this research are shown in Table III. A print of the negatives is also shown.

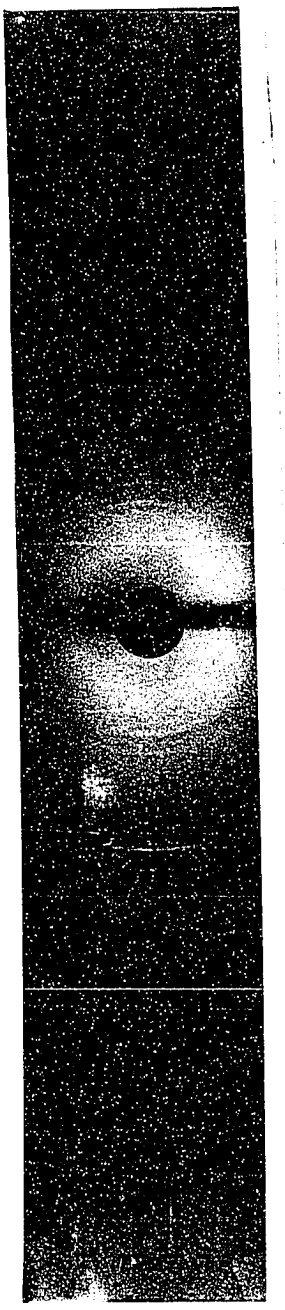
Table III

Powder X-ray Patterns of Ruthenium Complexes

$K_2[Ru(NO)Cl_5]$

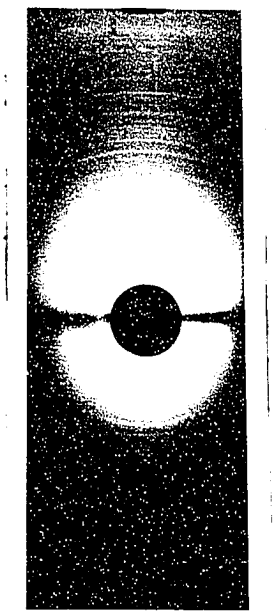
Prepared by Nitric Acid Method.	Prepared by Potassium Nitrite Method.	d (A°)	Relative Intensity
		5.50	5
		5.01	2
		4.67	1
		3.43	3
		3.25	2
		2.82	1
		2.75	10
		2.69	10
		2.56	10
		2.37	4
		2.24	1
		2.08	1
		2.04	1
		1.97	1
		1.86	5
		1.74	4
		1.69	1
		1.66	1
		1.63	1

$K_2[Ru(NO)Br_5]$



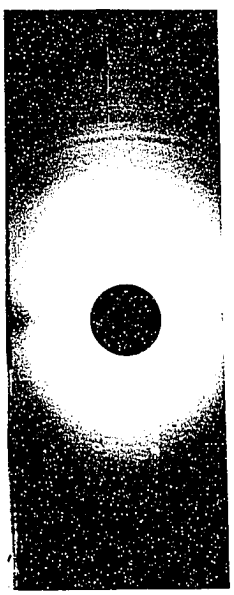
d (A°)	Relative Intensity
5.68	5
4.87	3
3.10	1
2.96	2
2.88	10
2.82	4
2.67	5
2.47	5
2.35	2
2.20	1
2.14	1
1.94	4
1.82	4
1.78	2
1.73	2
1.70	3
1.59	3

$K_2[Ru(NO)I_5]$



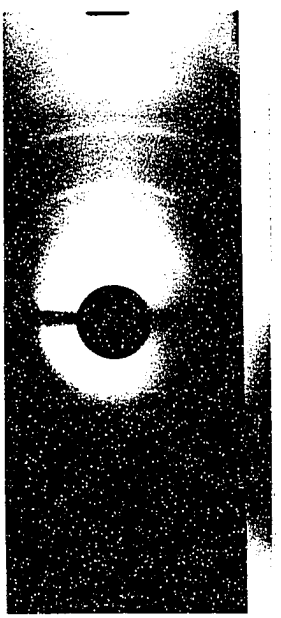
d (A°)	Relative Intensity
3.06	10
2.81	5
2.64	5
2.49	2
2.33	5
2.16	1
2.06	5
1.93	3
1.89	3
1.85	3
1.81	3
1.76	3
1.70	5
1.55	5

$Ru(NO)Cl_3 \cdot H_2O$



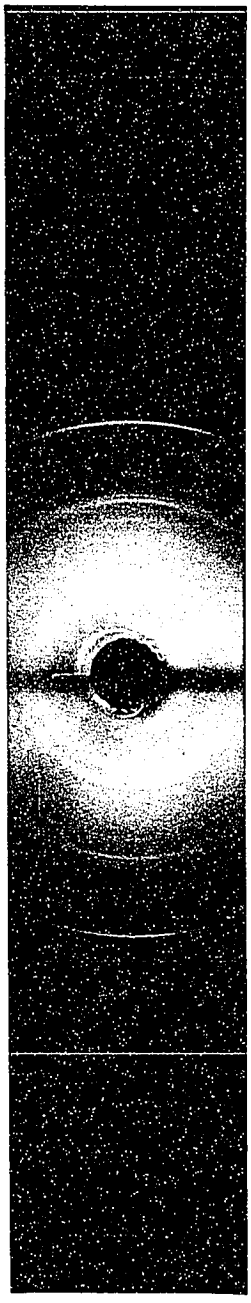
d (A°)	Relative Intensity
2.80	3
2.66	3
2.51	10
2.43	5
2.35	5
1.99	1
1.93	1
1.82	1
1.80	1
1.68	1
1.65	1
1.63	1

$Ru(NO)Br_3$



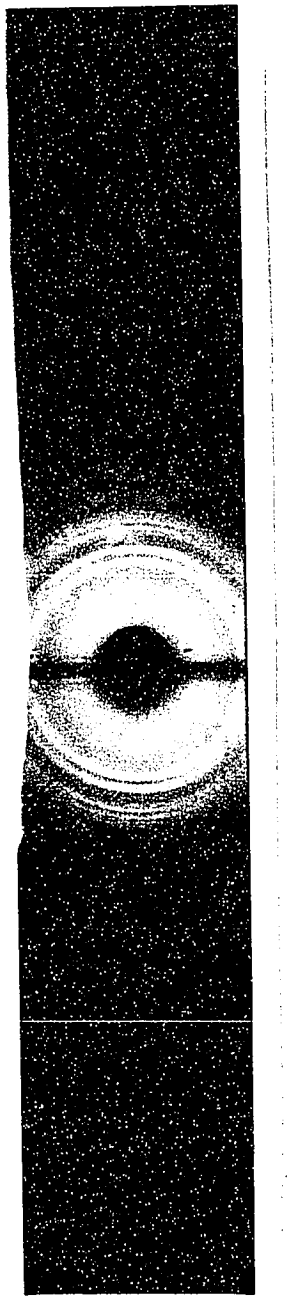
d (A°)	Relative Intensity
5.64	5
3.95	3
2.93	8
2.55	10
2.33	1
2.11	1
1.95	1
1.83	9
1.73	1
1.55	1

$K_4[Ru(NO_2)_6] \cdot H_2O$



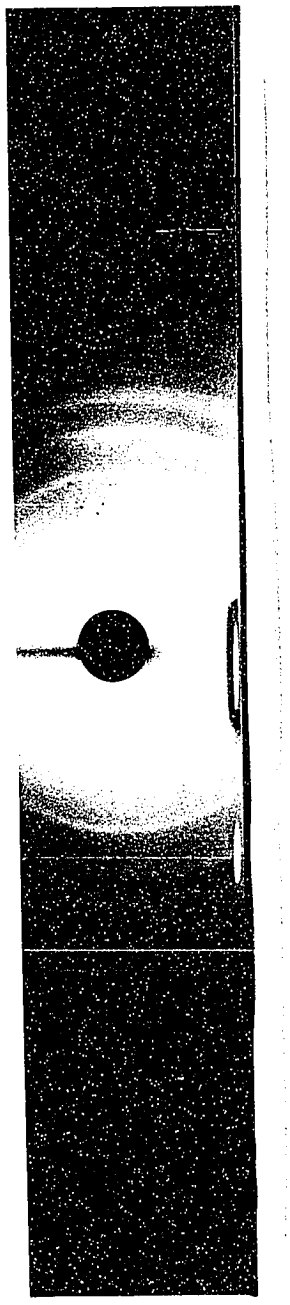
d (A°)	Relative Intensity
7.63	2
7.20	5
6.56	2
6.07	5
5.50	1
4.15	1
2.60	10
2.43	2
2.23	3
2.15	7
2.08	4
1.92	3
1.87	3
1.83	3
1.80	1
1.70	2
1.66	3
1.65	2
1.55	2

$K_2[Ru(NO)(OH)(NO_2)_4]$



d (A°)	Relative Intensity
6.15	10
5.61	2
5.44	7
4.87	1
4.72	4
4.60	2
3.52	1
3.39	2
2.90	4
2.81	3
2.59	2
2.49	2
2.40	3
2.21	2
2.02	2
1.98	1
1.94	1
1.88	1
1.84	1
1.79	1
1.75	2
1.64	1
1.60	1
1.54	1

$K_3[Ru(NO_2)_5]$



d (A°)	Relative Intensity
6.11	5
5.37	3
3.82	10
3.05	2
2.62	8
2.38	3
2.15	6
1.89	1
1.70	1
1.54	1

D. Magnetic Measurements

When a substance is placed in a magnetic field, a magnetic polarization results, due to the accelerating influence of the field on the electrons in the substance. If the direction of the polarization is negative, that is, it gives rise to a field which is opposed to the applied field, the substance is said to be diamagnetic. All substances show diamagnetic polarization. In addition to diamagnetic polarization some substances show a polarization of the opposite sign, that is, with the field. Such substances are said to be paramagnetic. Paramagnetism results when the substance contains atoms, ions, or molecules with permanent magnetic dipole moments, which in general are due to the magnetic moments, of unpaired electrons. Paramagnetism is observed in many simple and complex ions derived from the transition metals, in molecules containing odd numbers of electrons, and in a few molecules containing even numbers of electrons but unpaired electron spins.

Magnetic measurements are of importance in solving problems of molecular structure and bond type, because they afford a means of detecting the presence of singly-occupied electronic orbitals. A paramagnetic substance increases the flux due to the applied field, whereas a diamagnetic substance diminishes it. Diamagnetism is caused by an interaction of the applied magnetic field with the filled electronic orbitals of the atoms of the medium. The magnitude of diamagnetic effects

is small and diamagnetism is independent of the temperature. Substances which contain unpaired electrons have diamagnetic tendencies, but also paramagnetic tendencies due to the permanent magnetic moment caused by the unpaired electrons. The two effects are opposed and the net result is that paramagnetism always results, because the magnitude of the paramagnetic effect is much larger than that of the diamagnetic effect.

Both the spin and the orbital motion of an electron are sources of magnetic moment. In doubly occupied orbitals the magnetic moment of one electron is compensated by the equal and opposite moment of the second electron. If a compound is found to be diamagnetic then all the orbitals must contain pairs of electrons. It follows that compounds with incomplete electron shells with unpaired electrons should be paramagnetic, and that the magnitude of the paramagnetism should vary directly with the number of unpaired electrons. In those cases where these unpaired electrons are in effect the outermost ones in the species under consideration, the spin contribution becomes important and the orbital contribution may be neglected. In such cases the magnetic moment in Bohr magnetons may be calculated from the equation,

$$\text{magnetic moment} = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons. The following table shows the approximate value expected for the magnetic moment for a given number of unpaired electrons:

Number of Unpaired Electrons	Magnetic Moment (Bohr magnetons)
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

In the case of ruthenium and its simple ions the electron distributions in the higher energy levels are expected to be:

	4d	5s	5p
Ru	** ** * * *	*	
Ru^{+2}	** * * * *		
Ru^{+3}	* * * * *		
Ru^{+4}	* * * *		

In six-coordinate complexes of ruthenium, assuming a covalent $d^2 sp^3$ configuration, the electron distributions are expected to be:

		Bonding Orbitals
Ru^{+2}	** ** **	
Ru^{+3}	** ** *	
Ru^{+4}	** * *	

It is seen that the covalent six-coordinate complexes of bivalent ruthenium should be diamagnetic since there are no unpaired electrons, whereas those of trivalent and tetravalent ruthenium contain one and two unpaired electrons respectively and consequently should be paramagnetic.

Since the existence of five-coordinate complex ions has not been established with absolute certainty, little is known

of their actual electronic configurations. Regardless of the orbitals used in covalent bond formation, five-coordinate +3 ruthenium complexes must contain at least one unpaired electron and therefore should be paramagnetic. No conclusions may be drawn as to the magnetic behavior of five-coordinate +2 and +4 ruthenium complexes, since the orbitals used for bond formation will govern the number of unpaired electrons, if any.

A survey was made of the literature and the reported magnetic properties of ruthenium complexes tabulated. The results are shown in Table IV.

It is seen from Table IV that all the reported bivalent ruthenium complexes are diamagnetic, as one would expect. The complexes containing ruthenium in the +3 oxidation state are paramagnetic with moments ranging from 1.74 to 2.04 Bohr magnetons; this corresponds well to the values expected for compounds containing one unpaired electron.

Only two complexes containing +4 ruthenium have been reported. $K_2[RuCl_6]$ has a moment of 3.07 Bohr magnetons as expected for two unpaired electrons. However, $K_2[Ru(OH)Cl_5]$, although expected to show a moment corresponding to two unpaired electrons, is diamagnetic. The reason for this anomaly is not apparent, but Deford (10) has pointed out that it might be due to the formation of a double bond between the oxygen and ruthenium, as in the structures

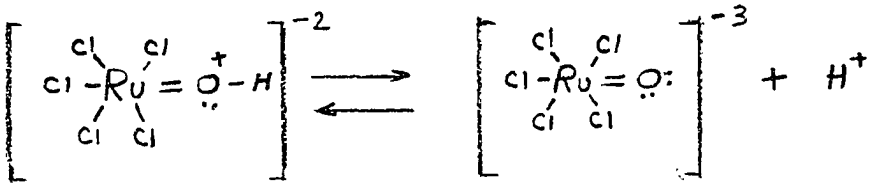


Table IV

MAGNETIC PROPERTIES OF RUTHENIUM COMPLEXES

Compound	Moment in Bohr Magnetons	Reference
+4 Oxidation State		
$K_2[RuCl_5]$	3.07	1
$K_2[Ru(OH)Cl_5]$	Diamagnetic	1
+3 Oxidation State		
$K_2[Ru(H_2O)Cl_5]$	2.04	1
$K_2[RuCl_5]$	1.8	1 (Note A)
$[Ru(NH_3)_6]^{+3}$	2.00	2 a
$[Ru(NH_3)_5Cl)]^{+2}$	2.00	2 a
$[Ru(NH_3)_5OH]^{+2}$	1.9	2 b
$[Ru(NH_3)_5(H_2O)]^{+3}$	2.0	2 b
$[Ru(S-C(S)NR_2)_3]$ (R = methyl, ethyl, butyl)	1.74 to 1.88	4
+2 Oxidation State*		
$(NH_4)_2[Ru(NH_3)_4(SO_3)_2] \cdot 4H_2O$	Diamagnetic	2 c
$[Ru(NH_3)_4SO_2Cl]^{+1}$	Diamagnetic	2 c
$[Ru(NH_3)_4SO_2Br]^{+1}$	Diamagnetic	2 c
$[Ru(NH_3)_4SO_2H_2O]^{+2}$	Diamagnetic	2 c
$[Ru(CN)_6]^{-4}$	Diamagnetic	3
$[Ru(NH_3)_4NO(H_2O)]^{+3}$	Diamagnetic	3
$[Ru(NH_3)_4Cl(NO)]^{+2}$	Diamagnetic	3
$[Ru(NH_3)_4C_2O_4]_2S_2O_6$	Diamagnetic	3
$Ru(NO)(S_2CNR_2)_3$ (R = methyl or ethyl)	Diamagnetic	5

(Table IV con't on page 84)

$[Ru(NH_3)_5NO]\ SO_4 \cdot \frac{1}{2}S_2O_8$	Diamagnetic	2 d
$[Ru(NH_3)_5NO]\ Cl_3 \cdot H_2O$	Diamagnetic	2 d
$[Ru(NH_3)_5NO]\ Br_3 \cdot H_2O$	Diamagnetic	2 d
$\left[Ru(NH_3)_4 \begin{matrix} NO \\ OH \end{matrix}\right] Cl_2$	Diamagnetic	2 d
$(NH_4)_2\ [RuCl_5\ NO]$	Diamagnetic	2 d

*Ruthenium oxidation states were assigned on the assumption that nitric oxide coordinates as a positive radical.

References

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2. a. Gleu and Rehm, Z. anorg. Chem. 227, 237 (1936).
   b. Gleu and Cuntze, Z. anorg. Chem. 237, 193 (1938).
   c. Gleu and Rehm. Z. anorg. Chem. 235, 201 (1938).
   d. Gleu and Buddicker, Z. anorg. allgem. Chem., 268, 202 (1952).
3. Landolt-Bornstein, 3 Teil, Mokekeln II, 1950, p. 530.
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5. Chemical Abstracts 34, 3200 (1940).
   Cambi and Malatesta, Rend. ist lombardo Sci. 71, 118 (1938).

Note A. D. P. Mellor quoted the value of 1.8 for $K_2[RuCl_5]$ as being found in the literature. The original source of information was not given.

or to polymerization to polymeric structures.

It should be pointed out that in assigning the oxidation states of ruthenium in nitroso ruthenium complexes in Table IV, it was assumed that the nitroso group is in a +1 oxidation state.

T. Moeller (34,35) has written a review on nitric oxide chemistry. Compounds are known in which the nitric oxide molecule is positive, neutral, and negative. The nitric oxide molecule contains an odd electron and is paramagnetic as expected. The compound, NaNO, is diamagnetic and probably contains a negative nitric oxide radical. The positive nitric oxide radical is present in compounds such as NOCl and $NOClO_4$. NOCl is diamagnetic in both the gaseous and solid states as would be expected for a positive nitric oxide ion.

Compounds of the type $Fe(NO)_2(CO)_2$ and $Co(NO)(CO)_3$ are diamagnetic, indicating that the nitric oxide molecule is not coordinated as a neutral molecule.

Of the complex anions containing the nitric oxide molecule the nitroprusside ion, $[Fe(CN)_5NO]^{-2}$, is well known. This ion is diamagnetic indicating a +2 oxidation state for iron and a +1 oxidation state for the nitric oxide group. Other evidence confirms this viewpoint. When the NO group in $[Fe(CN)_5NO]^{-2}$ is replaced by the neutral ammonia molecule $[Fe(CN)_5NH_3]^{-3}$ is formed; when replaced by a negative nitro group $[Fe(CN)_5NO_2]^{-4}$ is formed. The change of valence of the anion is as expected if the NO group were coordinated as a

positive radical.

$[Ru(NO)X_5]^{-2}$ belongs in the same class of anions as the nitroprusside ion. If the nitric oxide group is +1 and ruthenium +2 all electrons are paired and the ion should be diamagnetic. If the nitric oxide molecule were neutral, ruthenium would be +3. This arrangement would seem to require two unpaired electrons, one of which would be in the nitric oxide molecule, and the ion should be paramagnetic. If the nitric oxide group were negative, ruthenium would be +4 and there should be two unpaired electrons resulting in paramagnetism.

The same line of reasoning can be applied to the complexes of the type, $[Ru(NH_3)_5NO]^{+3}$. Complexes of this type are diamagnetic indicating +2 ruthenium and -1 nitric oxide. Moeller points out that D. P. Mellor considers these complexes to contain +4 ruthenium and -1 nitric oxide. Although this is contrary to the expected magnetic behavior the theory was probably advanced by Mellor on the basis of the pink and black cobalt salts containing the ion, $[Co(NH_3)_5NO]^{+2}$. The pink compounds are diamagnetic and are believed to contain +3 cobalt and -1 nitric oxide. The black compounds are paramagnetic and their constitution is not well understood.

In the case of the nitroso ruthenium complexes, $[Ru(NO)X_5]^{-2}$ and $[Ru(NH_3)_5NO]^{+3}$, the charge of the ions will be the same with either a +4 ruthenium and -1 nitric oxide or +2 ruthenium and a +1 nitric oxide. A distinction can not be made by magnetic measurements alone, if one is willing to

accept the fact, contrary to theory, that six-coordinate +4 ruthenium may in some cases be diamagnetic as is apparently true in the case of $K_2[Ru(OH)Cl_5]$.

On the basis of chemical behavior to be discussed later, the view of the author is that in nitroso ruthenium complexes of the nitroprusside type, $[Ru(NO)X_5]^{-2}$, the ruthenium is in a +2 oxidation state and the nitric oxide group +1.

Since magnetic measurements are very useful in determining the oxidation state of ruthenium and substantiating formulations of complexes, it was desirable to have magnetic measurements on the compounds prepared in this research. The author is extremely grateful to Dr. Allen B. Scott and William A. Smith of Oregon State College who kindly consented to make the measurements. The following compounds were found to be diamagnetic:

1. $K_2[Ru(NO)Cl_5]$
2. $K_4[Ru(NO_2)_6] \cdot H_2O$
3. $K_2[Ru(NO)(OH)(NO_2)_4]$
4. $K_3[Ru(NO_2)_5]$
5. $Ru(NO)Cl_3 \cdot H_2O$
6. $Ru(NO)Br_3$

The measurements on compounds 1, 2, and 3, which were available in large amounts, were made using a Guoy Balance. Compounds 3, 4, and 5 were available only in small quantities and were measured with a Cu-Be spring Faraday Balance. The larger samples were also checked with the Faraday Balance.

In all cases the force on the samples was negligible compared to the force on either a 30% $NiCl_2$ solution or anhydrous $MnCl_2$.

Since $K_2[Ru(NO)Cl_5]$ is diamagnetic it is very probable that the ruthenium is in a +2 oxidation state and that the nitric oxide molecule coordinates as a positive radical. This is the only configuration that can be formulated which has no unpaired electrons. This is in line with the more common nitroprussides, $M_2[Fe(CN)_5NO]$, where strong evidence has been presented for the coordination of a +1 nitric oxide radical (34, 35). While this research was in progress Gleu and Buddicker reported that $(NH_4)_2[Ru(NO)Cl_5]$ is diamagnetic (16).

$K_4[Ru(NO_2)_6] \cdot H_2O$ would be expected to be diamagnetic, since there is little doubt that it contains +2 ruthenium. $K_4[Ru(CN)_6]$ has been shown to be diamagnetic.

The magnetic criterion is very helpful in formulating the orange nitro complex, $K_2[Ru(NO)(OH)(NO_2)_4]$. Alternative formulations are: $K_2[Ru(NO_2)_5]$ and $K_2[Ru(NO)(H_2O)(NO_2)_4]$. It would be very difficult to distinguish among $K_2[Ru(NO_2)_5]$, $K_2[Ru(NO)(OH)(NO_2)_4]$, and $K_2[Ru(NO)(H_2O)(NO_2)_4]$ by analysis, because the respective molecular weights are 410, 411, and 412, and the compounds differ only by one hydrogen. If this compound were $K_2[Ru(NO_2)_5]$, as it is usually referred to in the literature, it most certainly would contain +3 ruthenium with at least one unpaired electron and would be paramagnetic.

The formulation $K_2[Ru(NO)(H_2O)(NO_2)_4]$ is undoubtedly incorrect since ruthenium would be in the unlikely +1 oxidation state and the compound would be paramagnetic. $K_2[Ru(NO)(OH)(NO_2)_4]$ is probably the best formulation, since it is confirmed by analysis and by magnetic measurements.

Analysis of the tan nitro complex permits the formulation $K_3[Ru(NO_2)_5]$ or $K_3[Ru(NO)(OH)(NO_2)_4]$. $K_3[Ru(NO)(OH)(NO_2)_4]$ is unlikely since +1 ruthenium would be required and the compound should be paramagnetic. $K_3[Ru(NO_2)_5]$ is the better formulation since it meets the magnetic requirements.

$Ru(NO)Cl_3 \cdot H_2O$ and $Ru(NO)Br_3$ are both diamagnetic. No conclusions may be drawn from this information because undoubtedly these compounds are more complex than represented by the simple formulas and are very likely to exist in polymeric forms.

Part VI

STUDIES WITH RADIOACTIVE RUTHENIUM - 106

A. Exchange Reactions.

In order to determine whether or not an exchange reaction occurs corresponding to the equation

$$AB + B^*C = AB^* + BC$$

a method must be available for distinguishing the chemically identical atoms B and B^*. A very important method is the use of radioactive nuclides of the element B.

In exchange experiments the atoms of an element, in one of its valence states or types of chemical combination, are labelled by admixture with some radioactive nuclide of the element which is in the same form of chemical combination. The element in another state of valence or form of combination is added to this system. The presence of radioactivity in this second chemical form, after it has been separated from the first, shows that an exchange of atoms between the two different states of the element has taken place. Complete exchange has been attained when the radioactivity has distributed itself between the two chemical forms in the same ratio as the amounts of the element in the two forms, i.e., when the specific activity is the same. In all exchange reactions, regardless of the order, the rate varies with time according to the law for first-order reversible reactions, since the chemical composition of the reaction mixture remains unchanged (12).

From exchange studies a large amount of information might be obtained. Exchange reactions have been helpful in the study of chemical bond types, strength and reactivity of chemical bonds and the effect of the solvent on these properties, the structure of compounds and ions, the reactivities of ions and compounds, reaction mechanisms, and the mechanism of catalysis.

Although a rigid theory of exchange reactions has not been formulated, certain generalizations have been made by Glenn T. Seaborg (38). If the exchange of a given element between two sorts of molecules or ions in which it is held by electron-pair bonds to different numbers or kinds of other atoms is considered, it may be said in general that such exchange reactions do not proceed with appreciable rates except in those cases where there are reversible reactions which enable the exchanging atoms to reach equivalent states of chemical combination. For example, there is no exchange of atoms between phosphate and phosphite ions, sulfate and sulfite ions, sulfur and carbon disulfide and iodide ion and iodoform.

On the other hand exchange of the following types has been observed: oxidation-reduction equilibrium, e.g., chlorine exchanges with the chlorate ion; ionization exchange, e.g., the exchange of lead between lead nitrate and lead chloride; formation of a symmetrical intermediate, e.g., iodide ion and iodine exchange due to the formation of I_3^- ;

transfer of an electron--when two exchanging molecules differ only in their net charge, the transfer of an electron from one to the other may become possible, e.g., there is exchange of manganese between manganate and permanganate ions.

Counting Equipment and Procedure: The relative activity (counts per minute) of all radioactive materials was determined by Geiger-Mueller counting.

A scaler, a lead-shielded tube mount and sample holder, and sample slides were constructed by the University of Cincinnati Physics Department. This equipment was of the conventional type similar in design to the Tracerlab, Inc., Model SC-2A Scaler, Model SC-10A Sample Holder and Tube Mount, and Model SC-9C Manual Sample Changer. For detection of radiation a mica, end-window Geiger tube was used. The window thickness of the tube was approximately 3.5 milligrams per square centimeter.

All solid materials which were counted were collected on 3-centimeter filter paper in a Tracerlab, Inc., E-6 precipitation apparatus. The filter paper was mounted on brass rings of 1 inch diameter, and clamped firmly onto the ring by means of a collar. The mounted samples were placed on sample slides and counted from the second shelf of the sample holder.

To determine the activity of liquid materials, a known volume was measured by a pipette and placed in a pyrex sample dish of 1 inch diameter. The liquids were slowly evaporated to dryness under an infra red lamp. The pyrex sample dishes

were placed on sample slides and counted from the second shelf of the sample holder.

The reproduction of the counting apparatus was checked at the beginning and end of each counting period by means of an uranium beta standard and found in all cases to be satisfactory.

Background was counted at the beginning and end of each counting period and found to remain constantly within the range of 14 to 16 counts per minute. All activities reported were corrected for background by subtracting 15 counts per minute.

Samples which gave an appreciable number of counts per minute were counted for a sufficient length of time that the percent relative standard deviation was in no case greater than 3.5% and in most cases no greater than 1%. Samples which had a net activity of below 12 counts per minute were counted for 15 minutes. The percent relative standard deviation was in no case greater than 34%.

The Tracer: Ruthenium-106 decays by emitting 0.04 MEV. electrons and has a half life of 1.0 year. The decay product, rhodium-106, with which the ruthenium-106 quickly comes into equilibrium, emits 3.53 MEV. electrons and has a half life of 30 seconds. The final product is palladium-106 which is stable. The energetic beta emission of rhodium is quite easy to detect and makes ruthenium-106 a very desirable tracer.

One millicurie of radioactive ruthenium-106 was received

from the Atomic Energy Commission in the form of ruthenium chloride in hydrochloric acid. The volume of the solution was 0.5 ml. and the ruthenium content was 0.05 milligrams. Commercial ruthenium chloride was added as carrier and a portion of the solution purified by distilling ruthenium tetroxide from a perchloric acid solution. The tetroxide was absorbed in sodium hydroxide and ruthenium dioxide precipitated by adding alcohol. The dioxide was washed and dissolved in hot concentrated hydrochloric acid to give a ruthenium chloride solution of high activity which was used to label other ruthenium chloride solutions.

Procedure: Two milliliters of ruthenium chloride in 6N hydrochloric acid, containing 4 milligrams of ruthenium, was added to the tracer material. The solution was mixed by shaking the bottle which was held by a pair of tongs. One milliliter of the solution was transferred by means of a long pipette into the ruthenium still and washed in, first with 3 ml. of 70% perchloric acid and then with 2 ml. of water. The distillation was performed in the usual manner. Ruthenium tetroxide was absorbed in 15 ml. of 6N sodium hydroxide in a 50 ml. centrifuge tube. A second tube containing 15 ml. of sodium hydroxide remained colorless indicating that absorption was complete in the first tube. The tube containing the dark-colored sodium hydroxide solution was heated in a beaker of hot water and 1 ml. of alcohol stirred into the solution to precipitate ruthenium dioxide, which was coagulated by heating for 15 minutes. The precipitate was

separated by centrifugation, twice washed with water, and dissolved in 2 ml. of hot concentrated hydrochloric acid. Two milliliters of water were added making the purified ruthenium chloride solution 6N in hycrochloric acid. The ruthenium concentration of the solution was approximately 0.4 mg. Ru/ml. This solution was labelled "primary stock solution" and stored behind iron bricks.

All glassware, with the exception of the distilling apparatus, that came in direct contact with the highly active solution was discarded. The distilling apparatus was cleaned by rinsing first with hot concentrated hydrochloric acid and then with water, and stored for future use.

Preparation of Labelled Solutions: A labelled solution of ruthenium chloride was prepared by adding 1.25 ml. of the primary stock solution to 50 ml. of standard ruthenium chloride. The solution was 6N in hydrochloric acid and contained 2.0 mg. Ru/ml. 0.05 ml. of this solution had an activity of 10,240 counts per minute.

A ruthenium chloride solution with an activity of 9,470 counts per minute per milliliter was made by adding 2.5 ml. of the above solution to 50 ml. of standard ruthenium chloride. This solution was 6N in hydrochloric acid and contained 2.04 mg. Ru/ml.

A labelled ruthenium sulphate solution, $Ru(SO_4)_x$, was prepared by adding concentrated sulphuric acid to a labelled ruthenium chloride solution and evaporating on a hot plate

until sulphur trioxide fumes were given off. The solution was then baked under an infra red lamp until a negative test for chloride ion was obtained when silver nitrate was added. The solution was diluted and the resulting solution was approximately 1N in sulfuric acid and contained 1.25 mg. Ru/ml. 1.0 ml. of this solution had an activity of 7,083 counts per minute.

Solid radioactive $K_2[Ru(NO)Cl_5]$ was prepared from labelled ruthenium chloride by the potassium nitrite method. The specific activity of this salt was 7.3×10^6 counts per minute per gram.

Exchange System I: The first system studied consisted of the nitroso complex, $K_2[Ru(NO)Cl_5]$ and the chloro complexes formed by dissolving commercial ruthenium chloride in 6N hydrochloric acid.

A separation could not be made by precipitating one of the pair with a simple cation since both solutions gave precipitates with silver, mercury (I), and cesium ions, whereas neither solution gave a precipitate with any other common simple cation. Several complex cobalt cations were tried and it was found that a solution of chloropentaamminecobalt (III) chloride, $[Co(NH_3)_5Cl]Cl_2$ provided a means of separation. The cobalt complex gave a precipitate with the ruthenium chloride solution and gave no precipitate with $K_2[Ru(NO)Cl_5]$.

When a freshly prepared saturated solution of $[Co(NH_3)_5Cl]Cl_2$ was added to a radioactive solution of ruthenium chloride

70% of the activity appeared in the precipitate. When the cobalt reagent was added to a radioactive solution of $K_2[Ru(NO)Cl_5]$ no precipitate was obtained. When equal volumes of $K_2[Ru(NO)Cl_5]$ and radioactive ruthenium chloride were mixed and $[Co(NH_3)_5Cl]\ Cl_2$ was added 63% of the activity of the ruthenium chloride solution appeared in the precipitate. This shows that the pair may be separated by the cobalt reagent by precipitating the ruthenium chloride complexes with a chemical yield of 63%.

Procedure: 1.0 ml. of radioactive $K_2[Ru(NO)Cl_5]$ having an activity of 4,833 counts per minute was added to 1.0 ml. of ruthenium chloride in a 15 ml. centrifuge tube. Both solution were 6N in hydrochloric acid and contained 2.04 milligrams ruthenium per milliliter. The mixture was thoroughly stirred and the ruthenium chloride complexes precipitated by adding 4 ml. of a freshly prepared saturated solution of $[Co(NH_3)_5Cl]\ Cl_2$.

The ruthenium chloride precipitate was washed five times with 2 ml. portions of water by centrifuging and decanting and then transferred and collected on filter paper in a Tracer Lab, Inc., E-6 filtration apparatus. The filter paper was mounted on a brass sample holder, clamped into position and dried by slowly heating under an infra red lamp, and then counted. The same reaction was repeated at various time intervals up to 51 hours at room temperature, 9 hours at $60 \pm 0.5^{\circ}$ C., and 7 hours in boiling water. The data collected is tabulated in Table IV.

Table IV

Exchange System I

$K_2[Ru^*(NO)Cl_5]$ - RuClx

In 6N HCl

	Time of Reaction (Hours)	Activity of Ruthenium Chloride Precipitate (Counts/Minute)
A. Room Temperature	.10	5
	1	2
	2	1
	4	1
	7½	2
	21	9
	30	7
	45	6
	51½	10
B. 60 - 0.5° C.	1	4
	2	1
	3	12
	4	8
	5	5
	7	3
	9	4
C. Boiling Water	0.5	0
	1	0
	2	5
	3	1
	4	2
	5	4
	6	4
	7	7

If an exchange of ruthenium atoms had taken place between labelled $K_2[Ru(NO)Cl_5]$ and ruthenium chloride, some of the radioactive ruthenium would have appeared in the ruthenium chloride precipitate. The results show that no exchange took place after 51½ hours at room temperature, 9 hours at 60° C., and 7 hours in boiling water. The very small activity found in the ruthenium chloride precipitate may be attributed to incomplete removal of the radioactive $K_2[Ru(NO)Cl_5]$ solution by washing.

The absence of exchange in this system indicates that the nitric oxide molecule is tightly bound to ruthenium in the nitroso complex. In studying exchange reactions of rhenium the author has shown that in a similar system exchange takes place (36). At room temperature a very rapid and almost complete exchange of rhenium occurs in the system potassium hexachlororhenate (II) and rhenium dioxide dissolved in 6N hydrochloric acid.

Exchange System II: It was demonstrated as being extremely likely that the ruthenium in a ruthenium chloride solution is capable of undergoing exchange in the following manner. 1.0 ml. of radioactive ruthenium sulphate solution having an activity of 7,083 counts per minute was mixed with 1.0 ml. of ruthenium chloride. The ruthenium sulphate solution was 1N in sulphuric acid and contained 1.2 mg. Ru/ml., whereas the ruthenium chloride was 6N in hydrochloric acid and contained 2.04 mg. Ru/ml. After 1 hour at 60° C. the ruthenium chloride

complexes were precipitated by adding cesium chloride. Although the chemical yield was small, approximately 20%, the cesium ruthenium chloride precipitate had an activity of 217 counts per minute. Thus an exchange of ruthenium takes place between $Ru(SO_4)_x$ and $RuCl_x$.

Exchange System III: Since it was shown that the ruthenium in $Ru(SO_4)_x$ will exchange with the ruthenium in $RuCl_x$ it was decided to study the system $K_2[Ru(NO)Cl_5]$ -- $Ru(SO_4)_x$.

A solution of $K_2[Ru(NO)Cl_5]$ which was 1N in sulfuric acid and contained 1.25 milligrams ruthenium per milliliter was prepared. A radioactive solution of $Ru(SO_4)_x$ in 1N H_2SO_4 having an activity of 7,083 counts per minute per milliliter and an approximate ruthenium content of 1.2 milligrams ruthenium per milliliter was prepared. 1.0 ml. portions of each solution were mixed. Separation was made by adding silver nitrate which precipitates $Ag_2[Ru(NO)Cl_5]$ almost quantitatively and precipitates only a small amount of silver sulphate. (Only silver sulphate precipitated if silver nitrate was added to the $Ru(SO_4)_x$ solution.) When the mixture of $Ag_2[Ru(NO)Cl_5]$ and Ag_2SO_4 was washed five times with 2 ml. portion of water all of the silver sulphate was removed and very little of the $Ag_2[Ru(NO)Cl_5]$ dissolved.

The precipitate of $Ag_2[Ru(NO)Cl_5]$ was collected by filtration, dried, and counted as in exchange system I.

An inspection of Table V shows that there is no ex-

change of ruthenium in this system. The absence of exchange between the ruthenium in $K_2[Ru(NO)Cl_5]$ and $Ru(SO_4)_x$ after 113 hours at room temperature and 12 hours at 60 degrees might again be attributed to the great stability of the ruthenium-nitric oxide bond. When the reaction was run at the temperature of boiling water the $[Ru(NO)Cl_5]^{-2}$ ion was destroyed and only silver chloride precipitated when silver nitrate was added. It was impossible to tell if the nitric oxide molecule was still attached to the ruthenium, since no means of separation was available.

Table V

Exchange System III

$K_2[Ru(NO)Cl_5] - Ru^*(SO_4)_x$

In 1N H_2SO_4

	Time of Reaction (Hours)	Activity of $Ag_2[Ru(NO)Cl_5]$ Precipitate (Counts/Minute)
A. Room Temperature	0.01	6
	0.5	6
	1.0	4
	2.0	2
	17.0	3
	113.0	0
B. 60 - 0.5° C.	1.0	0
	2.0	1
	3.0	0
	4.0	0
	8.5	3
	12.0	1

B. EXTRACTION STUDIES

The use of radioactive nuclides to tag a compound offers a simple and rapid method for the determination of extraction coefficients.

If to a system of two liquid layers, made up of two immiscible or slightly miscible components, is added a third substance which is soluble in both layers, then the third substance will distribute itself between the two layers in a ratio which is approximately equal to the solubility of the third substance in the two solvents.

The extraction coefficient, K, is approximately defined by the equation, $K = C_a/C_b$, where Ca is the concentration of the third substance in layer A and Cb the concentration of the third substance in layer B.

If the system consists of a ruthenium compound dissolved in an acid and an organic solvent, and if the ruthenium compound is radioactive, then the extraction coefficient of the system can be found by determining the ratio of the activity in a unit volume of each layer.

However, it should be pointed out that the Berthelot-Nernst distribution law stated above does not hold when the activity coefficient of the third substance changes on dilution. Furthermore, in extraction studies made by the tracer method the ratio of concentrations of radioactive atoms is measured, not the ratio of concentrations of particular molecular species, so that if the extracted substance exists as

a different molecular species in each layer the radioactively measured extraction coefficient will change with dilution.

A preliminary investigation was made of the extractability of ruthenium compounds in diethyl ether, hexone, (methyl isobutyl ketone), benzene, chloroform, and petroleum ether. The nitroso complexes, $K_2[Ru(NO)Cl_5]$ and $Ru(NO)Cl_3$, could not be extracted from a hydrochloric acid solution into any of the organic solvents. In all cases none of the color of the ruthenium complexes appeared in the organic solvent.

However, the ruthenium in the red solution of "ruthenium nitroso nitrate", formed by treating $Ru(NO)(OH)_3$ or $Ru(NO)Cl_3$ with nitric acid, could be partially extracted into hexone. The ruthenium chloride complexes, formed by dissolving commercial ruthenium chloride in hydrochloric acid, could not be extracted by any of the organic solvents from a 6 N hydrochloric acid solution, but appeared to be very slightly extracted by hexone from a 9 N hydrochloric acid solution. Both the ruthenium nitroso nitrate-hexone and ruthenium chloride-hexone systems were investigated further using radioactive solutions.

Extraction System I: Aqueous ruthenium chloride - hexone

The object of this experiment was to study the extractability of ruthenium chloride dissolved in hydrochloric acid by hexone as a function of the acid concentration of the ruthenium chloride solution.

Radioactive ruthenium chloride solutions which ranged

from 6N to 10N in hydrochloric acid were prepared. Each solution had a ruthenium content of 0.68 milligrams per milliliter. 1.0 ml. of hexone was added to 1.0 ml. of each ruthenium chloride solution in a 15 ml. centrifuge tube. The mixture was stirred very vigorously with a motor-driven platinum wire stirrer for 15 minutes, and then allowed to stand for 45 minutes. Equal portions of each layer were withdrawn, placed in glass sample cups, slowly evaporated to dryness under an infra red lamp, and then counted. The activity of each layer was thus determined.

The results in Table VI show that no appreciable amount of ruthenium chloride is extracted into hexone from any of the ruthenium chloride solutions. As the acid concentration of the ruthenium chloride solutions is increased, the hexone and acid solutions become partially miscible. Hexone and 12N hydrochloric acid are completely miscible.

Extraction System II: Aqueous ruthenium nitroso nitrate--hexone.

The object of this experiment was to investigate the extraction of "ruthenium nitroso nitrate" in 6N nitric acid by hexone. A radioactive solution of ruthenium nitroso nitrate containing approximately 2 to 3 milligrams of ruthenium per milliliter was prepared from solid, radioactive $K_2[Ru(NO)Cl_5]$. $K_2[Ru(NO)Cl_5]$ was treated with the calculated amount of potassium hydroxide and boiled until ruthenium nitroso hydroxide precipitated. The precipitate was washed

Table VI

Extraction System I

Aqueous $RuCl_x$ - Hexone

Acid Concentration	Volume Hexone Layer (ml.)	Volume Water Layer (ml.)	Volume Each Layer Counted (ml.)	Activity Water Layer (Counts/Minute)	Activity Hexone Layer (Counts/Minute)
6N	1.0	1.0	0.25	1138	4
7N	1.0	1.0	0.25	1116	6
8N	0.9	1.1	0.25	1088	8
9N	0.7	1.3	0.25	1010	4
10N	0.3	1.7	0.20	566	4

several times with water and dissolved in 6N nitric acid.

The hexone used was Eastman's best grade and was twice equilibrated with 6N nitric acid.

Procedure:

IA Determination of "forward" extraction coefficient.

2.0 ml. of each solution were mixed and stirred for 15 minutes with a platinum wire stirrer and allowed to stand for 1 hour. The activity of 0.100 ml. of each la yer was determined.

IB Determination of "reverse" extraction coefficient.

1.0 ml. of the hexone layer from IA was mixed with 1.0 ml. of 6N nitric acid. The solution was stirred for 15 minutes and allowed to stand for 1 hour. The activity of 0.250 ml. of each layer was determined.

IIA Effect of Age of "Nitroso Nitrate "Solution on Extraction Coefficient.

1.0 ml. of the ruthenium nitroso nitrate from IA which was 24 hours old was mixed with 1.0 ml. of fresh hexone. The solution was stirred was 15 minutes and allowed to stand for 1 hour. The activity of 0.100 ml. of each layer was determined.

The "reverse" extraction coefficient was determined by using 0.75 ml. of hexone from above and 0.75 ml. of fresh 6N nitric acid. The solution was stirred for 15 minutes and allowed to stand 1 hour. The activity of 0.250 ml. of each layer was determined.

IIB Effect of Time of Equilibration on Extraction Coefficients.

1.0 ml. of the ruthenium nitroso nitrate from IA which was 24 hours old was mixed with 1.0 ml. of fresh hexone. The solution was stirred was 15 minutes and allowed to stand for 24 hours. The activity of 0.100 ml. of each layer was determined.

The "reverse" extraction coefficient was determined by using 0.75 ml. of hexone from above and 0.75 ml. of fresh 6N nitric acid. The solution was stirred for 15 minutes and allowed to stand 24 hours. The activity of 0.250 ml. of each layer was determined.

Discussion:

From Table VII it is seen in IA that the extraction coefficient, K, which is equal to activity hexone/activity acid layer, has an average value of 0.198. When ruthenium nitroso nitrate is treated with fresh hexone 19.8% of the ruthenium goes into the hexone layer. IB shows that when the ruthenium-containing hexone layer is mixed with fresh nitric acid to test the reproducibility of the extraction coefficient, an average value of 0.293 is obtained, i.e., 29.3% of the ruthenium remains in the hexone layer. The two precentage values should be the same if the extraction coefficient represented a geniune equilibrium.

IIA shows that as the ruthenium nitroso nitrate solution ages that there is a decrease in the amount of ruthenium which passes into a fresh hexone layer and that more of

Table VII

Extraction System II

Aqueous $Ru(NO)(NO_3)_3$ - Hexone (6N HNO_3)

		Activity Water Layer (Counts/Min.)	Activity Hexone Layer (Counts/Min.)	Extraction Coefficient (Activity Hexone Layer/Activity Water Layer)
IA	Fresh Nitroso Nitrate			
	Forward Extraction Coefficient	6642	1241	0.187
		6259	1333	0.213
		6470	1252	0.194
				0.198 (Average)
IB				
	Reverse Extraction Coefficient	2337	631	0.271
		2426	731	0.301
		2592	795	0.307
				0.293 (Average)
IIA	Aged Nitroso Nitrate			
	Forward	3373	498	0.132
	Reverse	887	407	0.459
IIB	Time of Equilibration			
	Forward	3671	229	0.064
	Reverse	388	199	0.513

the ruthenium in the hexone layer remains there when treated with fresh nitric acid. For a 24 hour old ruthenium nitroso nitrate solution only 13.2% of the ruthenium goes into the hexone layer compared with 19.8% for a freshly prepared solution. Of the 13.2% ruthenium which goes into the hexone layer 45.9% remains there compared to 29.3% for the fresh solution when re-extracted with fresh nitric acid.

Since IA, IB, and IIA were run under the same conditions, i.e., 15 minutes stirring time and 1 hour standing time, the values obtained for the extraction coefficient should all be the same, provided that sufficient time was allowed for equilibrium to be reached.

Portions of the same solutions used in IIA were used in IIB. The mixture was stirred for 15 minutes and the standing time increased from 1 hour to 24 hours. This allows longer time for equilibrium to be reached and if the difference in the values obtained in IIA, 0.132 and 0.459, is to be attributed to insufficient time for equilibrium to be reached, then the values in IIB should show closer agreement. However, with the longer standing time the values were even farther apart--0.064 and 0.513 in IIB compared to 0.132 and 0.459 in IIA.

The reasons for this abnormal behavior are not apparent, unless this behavior is attributed to the assumption that the molecular species in the two layers are different. This is a system which requires further study. In order to account for

the variance of the extraction coefficient it would probably be necessary to identify the molecular species in each layer. This would be a difficult task since attempts to isolate and identify the ruthenium-containing substance in the nitric acid layer were unsuccessful.

The only general observation that can be made is that as the aqueous ruthenium nitroso nitrate solution ages, or as the equilibration time is increased, the amount of ruthenium which passes into the hexone decreases, and on re-extraction with fresh nitric acid the amount of ruthenium which remains in the hexone increases.

Part VII

SUMMARY OF RESULTS

A systematic study has been made of some nitroso and nitro complexes of ruthenium. Such a study had not been undertaken since the turn of the century. The recent revival of interest in the elements produced in uranium and plutonium fission has focussed attention on the chemistry of ruthenium and made the present investigation seem timely.

Analytical Methods

Adequate analytical methods for nitroso and nitro compounds of ruthenium were developed. The quantitative determination of ruthenium has long been recognized as being more difficult than that of most elements. The lengthy, but accurate, method of Gilchrist and Wichers (15) was modified and developed into a shorter but just as accurate method for the gravimetric determination of ruthenium. The use of perchloric acid to volatilize ruthenium as ruthenium tetroxide from the sample makes possible the determination of potassium as potassium perchlorate in the distillation residue.

Devarda's method (11) for nitrogen in simple nitrates was found to be a simple and reliable method for determining nitrogen in the nitroso and nitro complexes of ruthenium. This method is much simpler than the classical Dumas method and the conventional Kjeldahl method. It should be investigated further to determine the limits of its applicability as a general method for the determination of nitrogen in in-

organic complexes.

An additional advantage of the Devarda method for nitrogen in ruthenium complexes is that halides, if present, may be determined in the same sample.

Preparations

The most difficult problem encountered in the study of the chemistry of ruthenium is the preparation of pure compounds. In the literature on ruthenium the methods of preparation are discussed in general terms and in very few instances are adequate procedures given. In this thesis detailed procedures for the preparation of some nitroso and nitro compounds of ruthenium have been presented. These procedures will be invaluable to anyone who undertakes the preparation of these compounds, and many hours of exploratory work will be avoided.

The following compounds were prepared and analyzed:

Nitroso - $K_2[Ru(NO)Cl_5]$

$K_2[Ru(NO)Br_5]$

$K_2[Ru(NO)I_5]$

$Ru(NO)Cl_3 \cdot H_2O$

$Ru(NO)Br_3$

Nitro - $K_4[Ru(NO_2)_6] \cdot H_2O$ (yellow salt)

$K_2[Ru(NO)(OH)(NO_2)_4]$ (orange salt)

$K_3[Ru(NO_2)_5]$ (tan salt)

Unsuccessful attempts were made to isolate $Ru(NO)I_3$, $H_2[Ru(NO)Cl_5]$, and $Ru(NO)(NO_3)_3$.

In the nitroso halide series the analytical results of Joly (28) and Howe (22) for $K_2[Ru(NO)Cl_5]$ and Joly for $Ru(NO)Cl_3 \cdot H_2O$ (28) were verified by a new method of analysis.

Analytical data for $K_2[Ru(NO)Br_5]$, $K_2[Ru(NO)I_5]$ and $Ru(NO)Br_3$, such as are presented in this report, have not been previously published. Detailed procedures for the preparation of all these compounds are put in writing for the first time.

The nitro complexes of ruthenium offer an interesting and puzzling field of study. In this research Joly's (30) yellow salt, 8 $KNO_2 \cdot Ru_2O_3(N_2O_2)(N_2O_3)$, was prepared, analyzed, and recharacterized as $K_4[Ru(NO_2)_6] \cdot H_2O$; and his orange salt, 4 $KNO_2 \cdot Ru_2(NO_2)_6$, prepared, analyzed, and recharacterized as $K_2[Ru(NO)(OH)(NO_2)_5]$. In addition a new member of the nitro series, which may tentatively be formulated as $K_3[Ru(NO_2)_5]$, was isolated for the first time. This tan salt has never been mentioned in the literature. The nitro complexes of ruthenium are extremely difficult to prepare in a pure state.

Instrumental Studies

Conductance Measurements: The molecular conductivity of the nitroso and nitro complexes was measured as a function of dilution and as a function of the age of aqueous solutions at a dilution of 1024 liters. From the measurements obtained the stabilities of aqueous solutions of the nitroso and nitro complexes were compared. The nitro complexes were found to be extremely stable, whereas the nitroso halides are less stable.

The molecular conductivity of all the salts (temperature 25 ± 0.1° C.; dilution 1024 liters) were compared with values measured for knowns, for the purpose of confirming the number of ions indicated by formulations based on analysis.

The only conductance measurements found in the literature were for $K_2[Ru(NO)Cl_5]$. The values reported by Howe (22) were verified; all other conductance data represent original work.

Potentiometric Titrations:

The reactions of sodium hydroxide with $K_2[Ru(NO)Cl_5]$, $Ru(NO)Cl_3 \cdot H_2O$ and $K_2[Ru(NO)(OH)(NO_2)_4]$ at 100° C. were studied by means of potentiometric titrations. $K_2[Ru(NO)Cl_5]$ and $Ru(NO)Cl_3 \cdot H_2O$ gave identical reactions - "ruthenium nitroso hydroxide" was precipitated when the calculated amount of base was added. On the other hand the orange nitro salt, $K_2[Ru(NO)(OH)(NO_2)_4]$, gave no reaction. This difference in behavior may be attributed to strong ruthenium to nitro group bonding in the orange salt in comparison with the weaker ruthenium to chloride bonds in the chloro complexes.

In another series of potentiometric titrations it was shown that the orange nitro salt gives no fast reaction with sodium hydroxide or hydrochloric acid, whereas apparently an acid-base reaction occurs between $[Co(NH_3)_5H_2O]_2(SO_4)_3$ and sodium hydroxide.

This is an unexplored area which should be studied further for the possibility of detecting the presence of co-

ordinated aquo or hydroxy groups in both anionic and cationic complexes.

X-ray Diffraction Patterns:

X-ray powder patterns were taken and the data recorded for all of the nitroso and nitro compounds that were prepared. The powder patterns provide an excellent means of "finger printing" the compounds for future identification purposes. No X-ray data for any of the compounds have been previously reported.

Magnetic Measurements:

Dr. Allen B. Scott and Mr. William A. Smith of Oregon State College measured the magnetic susceptibility of the following compounds and found them all to be diamagnetic.

$K_2[Ru(NO)Cl_5]$

$Ru(NO)Cl_3 \cdot H_2O$

$Ru(NO)Br_3$

$K_4[Ru(NO_2)_6] \cdot H_2O$ (yellow salt)

$K_2[Ru(NO)(OH)(NO_2)_4]$ (orange salt)

$K_3[Ru(NO_2)_5]$ (tan salt)

The only other magnetic measurements on any similar compounds were reported by Gleu and Buddicker (16) while this work was in progress. They found $(NH_4)_2[Ru(NO)Cl_5]$ to be diamagnetic.

Studies with Radioactive Ruthenium - 106

Exchange Reactions: By using radioactive ruthenium as an indicator it was demonstrated that no exchange of ruthenium occurred between $K_2[Ru(NO)Cl_5]$ and the chloro complexes formed by dissolving commercial ruthenium chloride in 6N hydrochloric acid, after 260 hours at room temperature, 9 hours at 60° C., or 7 hours in boiling water.

Similarly it was shown that no exchange of ruthenium took place between $K_2[Ru(NO)Cl_5]$ and a ruthenium sulfate solution after 113 hours at room temperature or 12 hours at 60°C.

In another experiment commercial ruthenium chloride in 6N hydrochloric acid was found to exchange ruthenium with a ruthenium sulfate solution.

The failure of ruthenium in $K_2[Ru(NO)Cl_5]$ to exchange with either ruthenium chloride or ruthenium sulfate, both of which are capable of undergoing exchange, points to the great stability of the ruthenium to nitric oxide bond.

A survey of the literature revealed that no exchange reactions involving either ruthenium or coordinated nitric oxide molecules have been reported. The stability of the metal to nitric oxide bond in nitroso complexes is an area which should be further investigated by exchange studies using the tracer method.

Extraction Studies: A preliminary investigation of the extractability of ruthenium complexes from acid solutions by organic solvents was made. It was shown by the tracer method that ruthenium chloride is not extracted from a hy-

drochloric acid by hexone. On the other hand "ruthenium nitroso nitrate" in nitric acid solution is extracted into hexone. However, it was found that the extraction coefficient is not reproduced on re-extraction with fresh nitric acid, and varies widely with the age of the aqueous "ruthenium nitroso nitrate" solution and the equilibration time. No conclusions can be drawn from the data presented, except that the situation appears to be chemically complex.

Part VIII

CONCLUSIONS ON FORMULATION OF NITROSO AND NITRO RUTHENIUM COMPLEXES.

Nitroso Compounds: The series of salts, $K_2[Ru(NO)X_5]$, appear to be well characterized. The analytical data and other information obtained confirm the above formulation. The chloro complex, $K_2[Ru(NO)Cl_5]$, which is the best known member of the series, was studied in detail. This salt is diamagnetic which indicates the ruthenium is probably in the +2 oxidation state. This requires that the nitric oxide molecule be assigned an oxidation state of +1.

It has been shown that in the nitroprussides, $M_2[Fe(CN)_5\ NO]$, the iron is in the +2 oxidation state and the nitric oxide molecule is coordinated as a positive group (34). This formulation is confirmed by the diamagnetic properties of the nitroprussides and by the fact that the anion, $[Fe(CN)_5\ (NO)]^{-2}$, changes its oxidation state when the nitric oxide group is replaced by neutral or negative groups. When treated with alkali the nitroso group converts to a negative nitro group forming, $[Fe(CN)_5\ (NO_2)]^{-4}$; replacing the nitroso group with ammonia gives $[Fe(CN)_5\ (NH_3)]^{-3}$. The changes in the charge of the anion confirms the presence of a positive nitroso group. The evidence presented is thus very convincing for the assignment of a +1 oxidation state to nitric oxide in $[Fe(CN)_5NO]^{-2}$. It seems reasonable to assume that nitric oxide is also +1 in the $[Ru(NO)X_5]^{-2}$ ions.

An outstanding property of $K_2[Ru(NO)Cl_5]$ is the great stability of the ruthenium to nitric oxide bond. The inability of ruthenium in $K_2[Ru(NO)Cl_5]$ to exchange with ruthenium in the labile chloro complexes illustrates this fact. When the complex is destroyed in boiling alkali the chloride ions are completely replaced, but the precipitate, "$Ru(NO)(OH)_3$" still contains nitrogen.

Nitro Compounds: The three nitro complexes of ruthenium which were prepared and analyzed are difficult to classify. These compounds may be formulated as follows:

(1) $K_4[Ru(NO_2)_6] \cdot H_2O$ (yellow salt)

(2) $K_2[Ru(NO)(OH)(NO_2)_4]$ (orange salt)

(3) $K_3[Ru(NO_2)_5]$ (tan salt)

The chief difficulty encountered in characterizing these salts by analysis is the unreliability of the hydrogen determinations. Until a means is found to determine accurately one or two hydrogens in a compound with a molecular weight around 400 to 500, the formulation of the nitro complexes will not be firm.

All of the nitro complexes are diamagnetic, which requires +2 (or possibly +4) ruthenium. The best formulations for these compounds then must be based on the potassium, ruthenium and nitrogen analyses and the assignment of a +2 (or +4) oxidation state to ruthenium.

The yellow salt contains nitrogen, potassium, and ruthenium in the atomic ratio of 6.02: 4.02: 1.00. The analytical and conductance data allow, within experimental error, the

assignment of the formula $K_4[Ru(NO_2)_6] \cdot H_2O$ or $K_4[Ru(NO_2)_6] \cdot 1\frac{1}{2}H_2O$. Either formulation fits the experimental observation that the salt is diamagnetic. The only doubtful point is the degree of hydration. The hydrogen analysis shows 3 hydrogens are present, but since little faith can be placed in the determination, and since hydrogen analyses usually run high, the best formulation is probably $K_4[Ru(NO_2)_6] \cdot H_2O$.

The orange salt contains nitrogen, potassium, and ruthenium is the atomic ratio of 4.92: 2.03: 1.00. The analytical and conductance data allow, within experimental error, the assignment of the formula $K_2[Ru(NO_2)_5]$, $K_2[Ru(NO)(OH)(NO_2)_4]$ or $K_2[Ru(NO)(H_2O)(NO_2)_4]$. These compounds have molecular weights of 410, 411, and 412 respectively, and differ by only one hydrogen. Since no choice can be made on the basis of the analyses, heavy reliance must be placed on the fact that the compound is diamagnetic. $K_2[Ru(NO_2)_5]$ can be ruled out on the basis that it contains +3 ruthenium and should be paramagnetic; also, five-coordinate complexes are very rare. $K_2[Ru(NO)(H_2O)(NO_2)_4]$ would contain the unlikely +1 (or possibly the +3) oxidation state for ruthenium and would be paramagnetic. The only possibility which the analytical and conductance data will allow for a diamagnetic salt is $K_2[Ru(NO)(OH)(NO_2)_4]$.

This formulation of the orange salt is further supported by chemical evidence. When the orange salt is treated with excess potassium nitrite the yellow salt, $K_4[Ru(NO_2)_6] \cdot H_2O$ is produced. If the orange salt were $K_2[Ru(NO_2)_5]$ the in-

troduction of the sixth nitro group would give $K_3[Ru(NO_2)_6]$ (assuming no valence change for ruthenium). If the orange salt is formulated as $K_2[Ru(NO)(OH)(NO_2)_4]$, and if the nitric oxide molecule is present in a +1 oxidation state, then the replacement of the nitric oxide group and hydroxy group by negative nitro radicals, would lead to a change of charge on the anion from -2 to -4, i.e., $[Ru(NO)(OH)(NO_2)_4]^{-2}$ to $[Ru(NO_2)_6]^{-4}$. That this is apparently what occurs supports the assignment of +1 nitric oxide in the series of complexes, $[Ru(NO)X_5]^{-2}$, where X is a univalent negative radical.

The tan salt, which precipitates when the orange salt is treated with cold 10% potassium hydroxide, contains nitrogen, potassium, and ruthenium in the atomic ratio of 4.97: 3.01: 1.00. On the basis of the analytical and conductance data the tan salt may be formulated as $K_3[Ru(NO)(OH)(NO_2)_4]$ or $K_3[Ru(NO_2)_5]$. $K_3[Ru(NO)(OH)(NO_2)_4]$ may be discarded since it would contain +1 (or +3)ruthenium and be a paramagnetic salt. Also, it is possible to believe that the tan salt contains no nitroso group, since the nitroso group in the orange salt probably followed the general behavior of converting to a nitro group when treated with alkali. $K_3[Ru(NO_2)_5]$ is the best formulation that can be made to fit the analytical and conductance data and the fact that the compound is diamagnetic.

Several objections to this formulation arise. The existence of five-coordinate ruthenium complexes is, apriori,

doubtful. There is no reason to believe that the orange salt, $K_2[Ru(NO)(OH)(NO_2)_5]$, will lose a hydroxy group when treated with potassium hydroxide. However, the formula, $K_3[Ru(NO_2)_5]$ satisfies the presently available information. Maybe the controlling factor is the need for ruthenium to remain in the +2 oxidation state.

Until more information is available, such as might be obtained from crystal structure studies, indisputable formulations seemingly can not be made for the orange and tan nitro complexes of ruthenium.

Part IX

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