The Identification of Neutral Ruthenium(III) Chloride Complexes: Equilibria Involving Neutral and Cationic Species

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Previous work on chloride complexes of ruthenium in the +3 oxidation state has resulted in the separation and identification of the cationic species $RuCl^{++}$ and the two isomeric $RuCl_2^+$ species. In the present study two neutral (uncharged) complexes have been obtained in pure form in solution and characterized. The formulas of the species were determined by use of freezing-point lowering experiments to establish the number of metal atoms per species and direct analysis to establish the number of chloride ions bound to each metal atom. The species were both found to have the formula $RuCl_3$ and are presumed to be isomers. The species were separated by elution from ion-exchange columns. Values were obtained for equilibrium quotients involving these species and the cationic ruthenium(III) chloride complexes.

Introduction

In previous studies on the ruthenium(III) chloride complexes formed in aqueous solution the monochloro complex $RuCl^{++}$ and the two isomeric dichloro complexes $RuCl_2^+$ were separated and identified using ion-exchange techniques.[1,2] The present paper extends the investigation to the two neutral trichloro species, $RuCl_3$, dissolved in aqueous solution. The methods employed previously for the identification are not applicable to neutral species; however, the formulas of neutral species can be established by the usual methods of freezing-point lowering and analyses. In applying the method, the principal problem was to prepare sufficiently pure and concentrated solutions of the ruthenium species.

Experimental

Apparatus.—Absorption spectra were measured on a Cary Recording Spectrophotometer Model 11, Serial 4. Measurements of pH were made with a Beckman Model G pH meter. The $\log^{-1} (-pH)$ was divided by the mean activity coefficient of hydrochloric acid at the same ionic strength to yield an approximate value for the hydrogen ion concentration. Freezing-point determinations were made by means of a calibrated Western Electric 14B Thermistor, used with a Leeds and Northrup Test Set No. 5305 and a Rubicon galvanometer 3830. A Beckman thermometer was employed in some of the determinations.

Solutions.—The water used in all experiments was normal distilled water which gave a negative test for chloride ion.

Stock solutions of Ru(III) chloride species were prepared by refluxing a solution of Chemical Commerce ruthenium chloride over mercury. The solution which yielded the highest proportion of the species referred to as species "A" in this paper contained 9.2 g. ruthenium chloride in 50 ml. 0.5 M HCl and was refluxed about 24 hr. The solutions which proved most fruitful for obtaining the species referred to as species "B" contained 0.6–0.8 M ruthenium in 1.5, 2 and 2.5 M HCl and were refluxed 3–9 hr.

Freezing-point Determinations.—About 3 cc. of solution was placed in a jacketed test tube fitted with a stopper; the stopper had holes for thermistor leads and for a mechanical stirrer. The apparatus was immersed in an ice-salt-bath in a dewar. The thermistor, with its tip immersed in the ruthenium solution, was connected to a Wheatstone bridge. The bridge circuit included an external galvanometer of sensitivity 0.03 μamp. per mm. The cooled stirred solution was seeded with a small ice crystal. The attainment of a constant current in the galvanometer was considered to indicate the attainment of the freezing-point temperature of the solution. The resistance of the thermistor at that temperature was measured. The freezing-point of the solution was then known, the thermistor having been calibrated against ice-salt mixtures. In the case of species B, the freezing-point measurements were made with a Beckman thermometer. About 4 cc. of solution was used for each determination. A constant temperature was attained in every determination, and this temperature was taken as the freezing-point of the solution.

Analysis.—The ruthenium concentration in solution was determined by making the solution alkaline with sodium hydroxide, oxidizing the ruthenium to a mixture of RuO_4^- and RuO_4^- with excess hypochlorite, reducing the RuO_4^- to RuO_4^- and the ClO^- to Cl^- with excess sodium iodide and determining the RuO_4^- spectrophotometrically.[2]

Analysis for total chloride in ruthenium solution was accomplished by precipitating the chloride with excess silver nitrate, oxidizing the ruthenium to RuO_4 with ceric perchlorate and filtering and weighing the silver chloride precipitate.[2]

Qualitative tests for Ru(IV) were made by addition of sodium iodide and starch to the ruthenium solution. Appearance of the starch-iodine color was considered to indicate the presence of Ru(IV).[3]

Ion-Exchange Resins.—The ion-exchange resins were analytical grade resins obtained from Bio-Rad Laboratories. Specific resins used were Dowex 50W×8, hydrogen form and Dowex 1×10, chloride form. Particle size was 200–400 mesh.

Results and Discussion

Separation of Species.—The neutral species identified in this work were obtained by charging an anion column with stock solution of Ru(III) species, eluting the column with water, charging a cation exchange column with the eluate from the anion column and again eluting with water. The species were also obtainable by charging the cation column first and then the anion column. The first method was more efficient as the species were eluted only gradually from an anion column in the chloride form and it was feared that cationic species might be formed slowly during the elution. Water elutions of anion columns charged with stock solution always yielded two distinct portions, the first being yellow colored and rich in cations and the second being orange colored and rich in neutral species. A possible explanation for this behavior is that neutral species in the stock solution attach themselves to chloride ions in the anion resin, becoming anionic, and are re-formed gradually as the column is eluted with water and the chloride concentration in the aqueous phase decreases. Another possibility is that an ion-exclusion process is operative.

Two neutral species were eluted successively in the neutral portion, species "A" coming off the column before species "B." To obtain a good yield of species B it was essential to run the column at low temperature; a jacketed column with circulating ice-water was used for this purpose. The proportion of species B decreased with increasing time and temperature. Absorption spectrum was used as a measure of purity; the spectra of the two species were quite distinct. Samples from the beginning of the elution of the anion column were consid-

(1) H. H. Cady and R. E. Connick, THIS JOURNAL, **80**, 2646 (1958).

(2) R. E. Connick and D. A. Fine, *ibid.*, **82**, 4187 (1960).

(3) W. R. Crowell and D. M. Yost, *ibid.*, **50**, 374 (1928); O. Ruff and E. Vidic, *Z. anorg. allgem. Chem.*, **136**, 49 (1924).

ered to be pure species A. Samples near the end of the elution had spectra characteristic of species B. The ruthenium concentration in the eluate tailed off very gradually; samples from the end of the elution had spectra indicating the presence of species A as well as species B. This may have been due to partial isomerization of species B or to the decomposition of anionic species in the resin. All samples were run through cation columns in the hydrogen form in order to remove any cationic ruthenium species that may have been present. The final samples were kept in a refrigerator to minimize the danger of decomposition. No changes in spectrum were observed during the time interval between the collection of the samples and the experiments on the samples; in some cases this was several days.

Determination of Ruthenium Atoms per Species. —A freezing-point lowering experiment on a solution of a neutral ruthenium chloride species serves to establish the degree of association of the species, i.e., it distinguishes between a monomer, dimer or higher polymer. The experiment establishes the moles of ruthenium species per liter; if the ruthenium concentration of the solution in gram-atoms per liter is known, the number of ruthenium atoms per species then can be calculated.

Ideally, for purposes of the experiment, one would like to obtain a solution consisting only of the ruthenium species in water. Practically, this is an impossibility, as some hydrochloric acid must be present. The species are obtained from stock solutions of ruthenium chloride in hydrochloric acid, and the HCl concentration in these stock solutions must be high enough so that a respectable proportion of the ruthenium is in the neutral form. Once the neutral species have been separated from the other species, most of the HCl could be removed by stirring the solution with anion exchange resin in the hydroxide form. This was not considered desirable, however. A drastic lowering of the hydrogen ion concentration could lead to hydrolysis effects. It was thought better to prepare a hydrochloric acid solution in which the HCl concentration was the same as in the ruthenium solution and determine the difference in the freezing-points of these two solutions. The neutral species were obtainable in concentrations sufficiently high compared to the hydrochloric acid concentration to make this method practicable.

Solutions of the pure species were analyzed for ruthenium and pH measurements were made. The freezing-points of the solutions were determined as described above. Hydrochloric acid solutions having the same pH as the ruthenium solutions were prepared, and their freezing-points were determined in the same way. Measurements were also made on pure water. A typical temperature *versus* time curve showed a continuous fall of temperature with time through a minimum followed by a rapid rise to a constant temperature which was taken to be the freezing point. The supercooling was terminated by the addition of small ice crystals. The moles of ruthenium species per liter were calculated from the difference between the freezing-points of the ruthenium and the hydrochloric acid sloutions. This quantity was compared with the

TABLE I
Ruthenium Atoms per Species

pH, Ru and HCl soln.	Difference in f.p. of HCl and Ru soln., °C.	Ru species, mole/l. (from f.p.)	Ru concn. g. atoms/l. (by analysis)
		Species A	
1.51	0.095 ± 0.006	0.051 ± 0.004	0.048
0.92	.137	.074	.072
1.32	.130	.070	.062
0.98	.141	.076	.076
0.90	.154	.083	.086
		Species B	
2.13	0.070 ± 0.01	0.038 ± 0.006	0.036
2.36	.050	.027	.027
2.47	.060	.032	.030

gram-atoms of ruthenium per liter, as determined by analysis.

The results of the determinations are given in Table I. They indicate that both species are monomers, i.e., there is one ruthenium atom per species. Although the accuracy of the determinations with the Beckman thermometer is not great, it is sufficient to distinguish between a monomer and a dimer or higher polymer.

Determination of Chlorides per Ruthenium.— The total chloride content of solutions of the pure species was determined as described under Analysis. The chloride bound to ruthenium was calculated as the difference between the total chloride and the free chloride content of the solutions. The free chloride concentration was taken to be equal to the hydrogen ion concentration, which was determined by pH measurement. Ruthenium analyses of the solutions enabled the number of bound chlorides per ruthenium atom to be calculated. The results are given in Table II. They indicate that both species have three chlorides bound to each ruthenium.

TABLE II
Chloride per Ruthenium Determinations

AgCl wt., g.	Total chloride, meq.	Free chloride, meq.	Ru mg.-atoms	Chlorides per Ru
		Species A		
0.0328	0.229	0.111	0.0401	2.95
.0328	.229	.111	.0401	2.95
.0735	.514	.120	.123	3.16
.0347	.242	.060	.0615	2.98
.0356	.248	.060	.0615	3.07
.0342	.239	.060	.0615	2.93
.1039	.728	.252	.153	3.10
.1023	.716	.252	.153	3.04
		Species B		
0.0283	0.198	0.015	0.0588	3.12
.0174	.122	.021	.0319	3.16
.0179	.125	.021	.0319	3.26
.0261	.182	.009	.0544	3.19

The formula of an uncharged monomeric Ru(III) chloride complex ought to be $RuCl_3$, since chloride is the only complexing anion present. The chloride per ruthenium analyses confirm this formula. Since both species have the formula $RuCl_3$, they are presumed to be the two isomers of the octahedral complex $Ru(H_2O)_3Cl_3$.

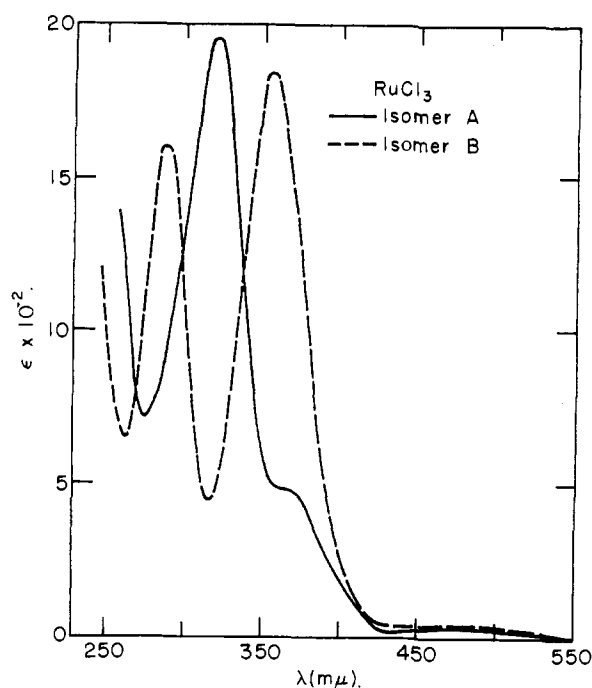**Spectra.**—The molar extinction coefficients of the two species are plotted in Fig. 1 as a function

Fig. 1.—Molar extinction coefficients of RuCl₃ species: dotted line, isomer B; solid line, isomer A.

of wave length. Solutions of the species are deep orange in color. Rehn and Wilson[4] presented a spectrum which they labeled "RuCl₃ and/or RuCl₄⁻." This spectrum shows similarities to that of RuCl₃(B). Both spectra have peaks at ca. 288 and 357 mμ and a minimum at 316–320 mμ. Rehn and Wilson's curve, however, has ϵ's at 288 and 357 mμ which are ca. 20 and 35% lower, respectively, than the ϵ's of RuCl₃(B) at these wave lengths; the ϵ of their minimum at 316 mμ is ca. 100% higher than the ϵ of the minimum of RuCl₃(B). Rehn and Wilson obtained their spectrum by dissolving K₂RuCl₅·H₂O in 1 M trifluoroacetic acid and allowing the solution to stand 6 days; the differences between their spectrum and that of RuCl₃(B) may be due to the presence of other ruthenium species in their solution. A mixture of RuCl₃(B) and RuCl₃(A) would not explain the differences, as the ϵ's of such a mixture would be higher throughout most of the wave length range than those of Rehn and Wilson; the presence of some RuCl₂⁺ would, however, lower the ϵ's.

The spectra presented here do not agree at all with the spectrum of the "neutral species" presented previously.[1] This species has been encountered in both acid and water elutions of anion columns charged with certain stock solutions. The peak at 285–290 mμ characteristic of this species is absent from most of the stock solutions; it never has been observed in solutions of K₂RuCl₅·H₂O, whereas RuCl₃(A) and RuCl₃(B) have both been observed in solutions of this salt. Possibilities as to the origin and nature of the species are impurities in particular stock solutions, an oxidation state of ruthenium other than + 3, or a polymeric

(4) I. M. Rehn and A. S. Wilson, "Ruthenium (III) Chloride Complexes in Trifluoroacetic Acid Solution," Hanford Atomic Works, Richland, Washington.

or hydrolyzed species formed only under a peculiar set of conditions.

Isomerization.—Examination of the neutral species present in ruthenium solutions at equilibrium has yielded information regarding the isomerization of RuCl₃. The RuCl₃ was separated from the ionic ruthenium components of the solutions by water elution of ion exchange columns charged with the solutions. Nine solutions were treated in this way. Five of the solutions were solutions of K₂RuCl₅·H₂O in 0.75–3 M HCl. The salt was synthesized according to the method of Charonnat.[5] Four solutions were solutions of RuCl₃(A) or RuCl₃(B) obtained from columns and allowed to stand. About 2 weeks were required for the attainment of equilibrium. Constancy of absorption spectrum was used as the criterion for equilibrium. The isomeric composition of the RuCl₃ separated from the solutions by elution of columns was calculated from absorption spectra. This was done by comparing the ratio of the absorbances at 320 and 290 mμ with the ratios of the molar extinction coefficients at these wave lengths calculated for mixtures of the two isomers. The ratio varies from 0.305 for pure RuCl₃(B) to 1.96 for pure RuCl₃(A). The average composition was found to be approximately 75% RuCl₃(A) and 25% RuCl₃(B) at room temperature.

Equilibrium with Lower Complexes.—Some information regarding equilibria between RuCl₃, RuCl₂⁺ and RuCl⁺⁺ was obtained from two solutions of K₂RuCl₅·H₂O; the salt was ca. 10⁻⁴ M and the HCl was 0.10 and 0.05 M. The solutions were kept in a 25° bath for 74 and 67 days, respectively. At the end of these periods, the spectra of the solutions appeared to be constant. The solutions then were placed on cation exchange columns. The RuCl₃, RuCl₂⁺ and RuCl⁺⁺ present in the solutions were eluted from the column with water, 0.1 M HCl and 1 M HCl, respectively. Concentrations of the species in the eluted samples were calculated from their spectra, using the molar extinction coefficients previously determined for these species.[1,2] The solution in 0.10 M HCl was found to be 16% RuCl₃, 61% RuCl₂⁺ and 23% RuCl⁺⁺. The solution in 0.05 M HCl was found to be 8% RuCl₃, 57% RuCl₂⁺ and 35% RuCl⁺⁺. These results yield values of 0.038 and 0.031 for $Q_{12} = (RuCl^{++})(Cl^-)/(RuCl_2^+)$. The parentheses stand for concentrations in moles per liter. The values obtained for $Q_{23} = (RuCl_2^+)(Cl^-)/(RuCl_3)$ are 0.38 and 0.36. The only value available for comparison is Rehn and Wilson's value of 0.029 for Q_{12} at 64° and 0.07 M chloride in 1.0 M HTFA.[4]

Note Added in Proof.—More recent experiments by Dr. Edward E. Mercer in this laboratory have shown that the separation of species A and B in the experiments of Tables I and II was not complete, there having been approximately 3% of B in the samples of A and 20% A in the samples of B. We are indebted to Dr. Mercer for the corrected spectra shown in Fig. 1. The discussion elsewhere has been corrected on the basis of the new molar extinction coefficients.

(5) R. Charonnat, Ann. Chim., (10) 16, 52 (1931).