

noticeable solubility in dry DMF at room temperature. On warming, a reaction begins at 70 to 80° to give unknown products both in solution and as a precipitate; neither phase then reduces water as does ThI<sub>2</sub>. Satisfactory, alternate explanations for the solid, paramagnetic mono- and diiodide products obtained in the previous study are not apparent. The formation of mono- and diiodides of thorium amides in unknown oxidation states from treatment of the ThI<sub>x</sub> with liquid NH<sub>3</sub> would also allow for the observation that these two products could be reconverted to ThI<sub>4</sub> by excess I<sub>2</sub> at 105°; however, this is not consistent with the (unreported) low nitrogen content.<sup>15</sup> Although the purity of the metal employed earlier was unspecified, it may be significant that the reported susceptibility is 4.7 times that accepted for high quality metal.<sup>11</sup>

Finally, the preparation of ThI<sub>3</sub> and ThCl<sub>3</sub> by thermal decomposition of the respective tetrahalides at 400 to 450° *in vacuo*<sup>6</sup> is very questionable. Since ThI<sub>4</sub> can be readily sublimed at 500–600° without any trace of decomposition and is quite stable in tantalum at lower temperatures, the prior observation to the contrary must instead have been a result of reaction with the oxide containers or with gaseous impurities. The absence of decomposition of ThI<sub>4</sub> in Al<sub>2</sub>O<sub>3</sub> containers at 380–500° also has been established by Scaife and Wylie.<sup>16</sup>

The present ThI<sub>2</sub> example also brings to attention an important consideration involved in the characterization of simple salts in apparent, lower oxidation states. Although the composition ThI<sub>2</sub> suggests a divalent state for the metal, the electrical and magnetic properties indicate that the compound probably should be instead formulated in terms of the normal Th(IV) state with the two electrons necessary for charge conservation delocal-

ized much as in the metal. It therefore seems advisable to include at least a qualitative check for a salt-like resistance in the characterization of any supposed subhalide, particularly an iodide, that shows negligible magnetic evidence for a simple reduced cation before the presence of localized, metal-metal bonding, for example, can be distinguished from the metallic possibility. With lower resistance results, or where magnetic measurements do not clearly distinguish between possible choices of paramagnetic cores, a measurement of the temperature dependence of resistivity would of course be necessary.

With regard to thorium compounds with other anions that are analogous to the diiodide, the refractory sulfides also are so constituted. Eastman, *et al.*,<sup>17</sup> have shown that ThS, and perhaps Th<sub>2</sub>S<sub>3</sub>, are appropriately diamagnetic and have high electronic conductivities. In fact BaS, CeS, US, and ThS, all of which occur in the NaCl structure, apparently have 0, 1, 2, and 2 electrons per metal atom so involved, respectively. It does not seem appropriate to refer to the last three and Th<sub>2</sub>S<sub>3</sub> as examples of lower oxidation states in the specific sense, however, as the electrons in question do not appear to be localized or shielding as would be the case with the reduced cations. In fact, the metal-sulfide distances reported<sup>17</sup> for the above series are in close agreement with the sums of the radii for S<sup>2-</sup> and Ba<sup>2+</sup>, Ce<sup>3+</sup>, U<sup>4+</sup>, or Th<sup>4+</sup>, respectively, the stability in these cases being considerably increased by the extra Madelung energy derived from the higher charged cations.

**Acknowledgments.**—The authors are particularly indebted to Dr. A. H. Daane and his group for continued generosity in the use of their tantalum welding facilities.

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## Complexes in the Rhodium(III)-Chloride System in Acid Solution

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The following species have been isolated and characterized in the rhodium(III)-chloride system in acid solution by means of ion exchange techniques: RhCl<sup>3+</sup> (coordinated water molecules not shown); RhCl<sub>2</sub><sup>+</sup>; *cis*- and *trans*-RhCl<sub>3</sub>; RhCl<sub>4</sub><sup>-</sup>; RhCl<sub>5</sub><sup>2-</sup>; and RhCl<sub>6</sub><sup>3-</sup>. By utilization of the molar absorptivities of these species at appropriate wave lengths, approximate successive formation constants at 120° for the various members of the series have been determined. The constants at an ionic strength of 6.0 *M* are:  $k_1 > 10^3$ ;  $k_2 > 10^3$ ;  $k_3 \sim 10^3$ ;  $k_4 = 250 \pm 120$ ;  $k_5 = 28 \pm 8$ ; and  $k_6 = 0.56 \pm 0.18$ .

The color of aqueous solutions of rhodium(III) chloride varies from yellow to various shades of red depending upon the nature and history of the solution. For example, a solution of hydrous rhodium(III) oxide in dilute hydrochloric acid is yellow; on heating to boiling, the solution becomes cherry-red. Dissolution of

hydrated rhodium(III) chloride in water yields a red-brown solution, which turns yellow on boiling,<sup>1,2</sup> or red if an excess of hydrochloric acid is present during the heating process. These color changes, coupled with

(1) J. Meyer and M. Kawczyk, *Z. anorg. allgem. Chem.*, **228**, 297 (1936).

(2) J. Meyer and H. Kienitz, *ibid.*, **242**, 281 (1939).

the fact that chloride ion can be precipitated rapidly and completely by silver nitrate only from the yellow solutions, strongly indicate that various chloro-complexes exist in these solutions. Inasmuch as it is necessary to heat the solutions in order to effect the color changes, it is likely that substitution reactions involving at least some of the chloro-complexes take place slowly. The rhodium(III)-chloride system would, therefore, appear to be one well suited to study by the ion exchange method developed by Connick and Cady.<sup>3,4</sup>

The present paper describes the preparation of the various complexes formed between rhodium(III) and chloride ion in dilute hydrochloric acid solution, and the isolation and characterization of these complexes by the ion exchange technique. In addition, the spectra of these complexes in aqueous solution have been determined and utilized for the calculation of successive formation constants.

### Experimental and Results

**Reagents.**—Pure rhodium metal was obtained from Goldsmith Bros. Chemical Company. Hydrated rhodium(III) chloride was purchased from the same source, as well as from the Fielding Chemical Company. The material obtained from Goldsmith Bros. was reported to have a rhodium content of 40%.

Hexa-aquorhodium(III) perchlorate was prepared according to the method of Ayres and Forrester<sup>5</sup> and dried at the temperature of boiling toluene (110°) in an Abderhalden drying apparatus.

Sodium hexachlororhodate(III) was synthesized according to the directions of Ayres<sup>6</sup> by heating rhodium metal with sodium chloride in an atmosphere of chlorine at 750°. The reaction mixture was dissolved in water and the desired compound was precipitated as the 12-hydrate by the addition of ethanol.

*Anal.* Calcd. for  $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ : Rh, 17.1; Cl, 35.4. Found: Rh, 17.0; Cl, 35.4.

Thorium(IV) perchlorate was obtained from the G. Frederick Smith Chemical Company and used without further purification. The perchloric acid employed was Baker Analyzed Reagent.

The ion exchange resins were of analytical grade (Baker Analyzed). Specific resins used were Dowex 50W-X8 (200–400 mesh) and Dowex 1-X8 (200–400 mesh). Before use, they were treated with 6 *M* hydrochloric acid and then washed with demineralized water until chloride-free.

All solutions were prepared with demineralized water obtained from a Crystalab De-Minizer column.

**Analytical Methods.**—Rhodium was determined either gravimetrically as the metal<sup>7</sup> or colorimetrically according to the method of Ayres and Young.<sup>8</sup> In the colorimetric procedure, measurements were made with a Beckman DU spectrophotometer at a wave length of 665  $\mu$  and a slit width of 0.04 mm. Thorium perchlorate solutions were standardized gravimetrically by the oxalate procedure.<sup>9</sup>

The capacities of the cation exchange resin columns were determined by titration of the hydrogen ion set free by displacement with sodium ion from sodium chloride. Measurements of pH were made on either a Beckman Model G pH meter or a Leeds and Northrup pH meter.

Ultraviolet and visible absorption spectra were measured on a

Cary Model 14 recording spectrophotometer. Quartz cells of optical path 1.000 cm. were employed.

**Apparatus.**—For certain of the ion exchange experiments, it was found advantageous to use a "tapered" resin column consisting of three sections of glass tubing of different diameter sealed together in order of decreasing diameter. The lower two sections, of 9 mm. and 7 mm. o.d. tubing, respectively, were each 6 cm. in length; the tubing making up the uppermost section was 13 mm. in o.d. and 38 cm. long. A 2-mm. Teflon stopcock was joined to the bottom of the lowest section. The column has the advantage over a conventional one in that tilted bands of adsorbed complexes tend to straighten themselves out as they move to a section of smaller diameter.

**Ion Exchange Procedures.**—Two types of experiments were performed for the characterization of cationic complexes. The first type of experiment, which permitted the determination of the charge on the species per rhodium(III) atom, was based on the fixed exchange capacity of the cation resin, Dowex 50, in its hydrogen form, measured in equivalents of charge. After the complex species had been adsorbed on the resin column, they were eluted, unless noted otherwise, by means of perchloric acid solutions of  $\text{Th}^{4+}$  ion (in the form of the perchlorate). (A number of equilibration experiments verified the validity of the assumption that each  $\text{Th}^{4+}$  ion displaced four  $\text{H}^+$  ions from Dowex 50 resin in its hydrogen form.) During the course of elution, the various complex species separated into distinct bands which could be collected as they passed from the column. A portion of the eluate containing each band was analyzed for rhodium and free hydrogen ion. From the values for these species and the initial hydrogen ion concentration of the elutriant solution, the charge on the complex species per rhodium(III) atom was calculated according to the method of Connick and Cady.<sup>3,4</sup>

The charge per complex species was determined in the second type of experiment. A fraction of eluate containing a pure complex species, whose charge per rhodium atom had been found, was diluted with a known volume of standardized perchloric acid. The resulting solution was equilibrated with a weighed quantity of Dowex 50 resin in hydrogen form whose capacity was known. A sample of solution then was removed and analyzed for rhodium. A definite volume of water was now added to the resin and remaining solution, and equilibration was repeated, following which an aliquot of solution again was removed for rhodium analysis. From a knowledge of the resin capacity, the rhodium content in the initial solution and in solution after each equilibration, and from the initial hydrogen ion concentration of each solution, the charge per complex species can be calculated.<sup>4</sup>

Ion exchange experiments with all the complexes, both cationic and anionic, were carried out in solutions which were sufficiently acidic to preclude the formation of hydroxo-complexes.

**The Rhodium(III) Species in Solutions of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in Perchloric Acid.**—In ion exchange experiments designed to determine the nature of the cation in solutions of  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in perchloric acid, the hydrogen ion concentration was maintained at values of 0.1 *M* or greater to prevent the formation of hydroxo-complexes encountered in less acidic solutions by other investigators.<sup>10–13</sup>

In a typical experiment, 8 to 10 g. of Dowex 50 W-X8 resin in the hydrogen form was stirred with 150 ml. of 0.001 *M*  $\text{Rh}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  in 0.1 *M* perchloric acid and the mixture was added as a slurry to an ion exchange column which already contained 2 g. of resin in the lower, narrower sections. Sufficient additional resin then was added to the column to give a layer 1 in. in height above the section of the resin bed containing adsorbed rhodium(III). The extra resin served to prevent mixing of the resin in the center section of the column as the initial eluting solution was added. Elution of the adsorbed rhodium, present as a yellow band, was effected with 0.01–0.02 *M* thorium(IV) perchlorate in

(3) R. E. Connick and H. H. Cady, *J. Am. Chem. Soc.*, **79**, 4242 (1957).

(4) H. H. Cady and R. E. Connick, *ibid.*, **80**, 2646 (1958).

(5) G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

(6) G. H. Ayres, *Anal. Chem.*, **25**, 1622 (1953).

(7) W. C. Hillebrand, G. E. Lundell, H. A. Bright, and J. J. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 380.

(8) G. H. Ayres and F. Young, *Anal. Chem.*, **24**, 165 (1952).

(9) Reference 7, p. 542.

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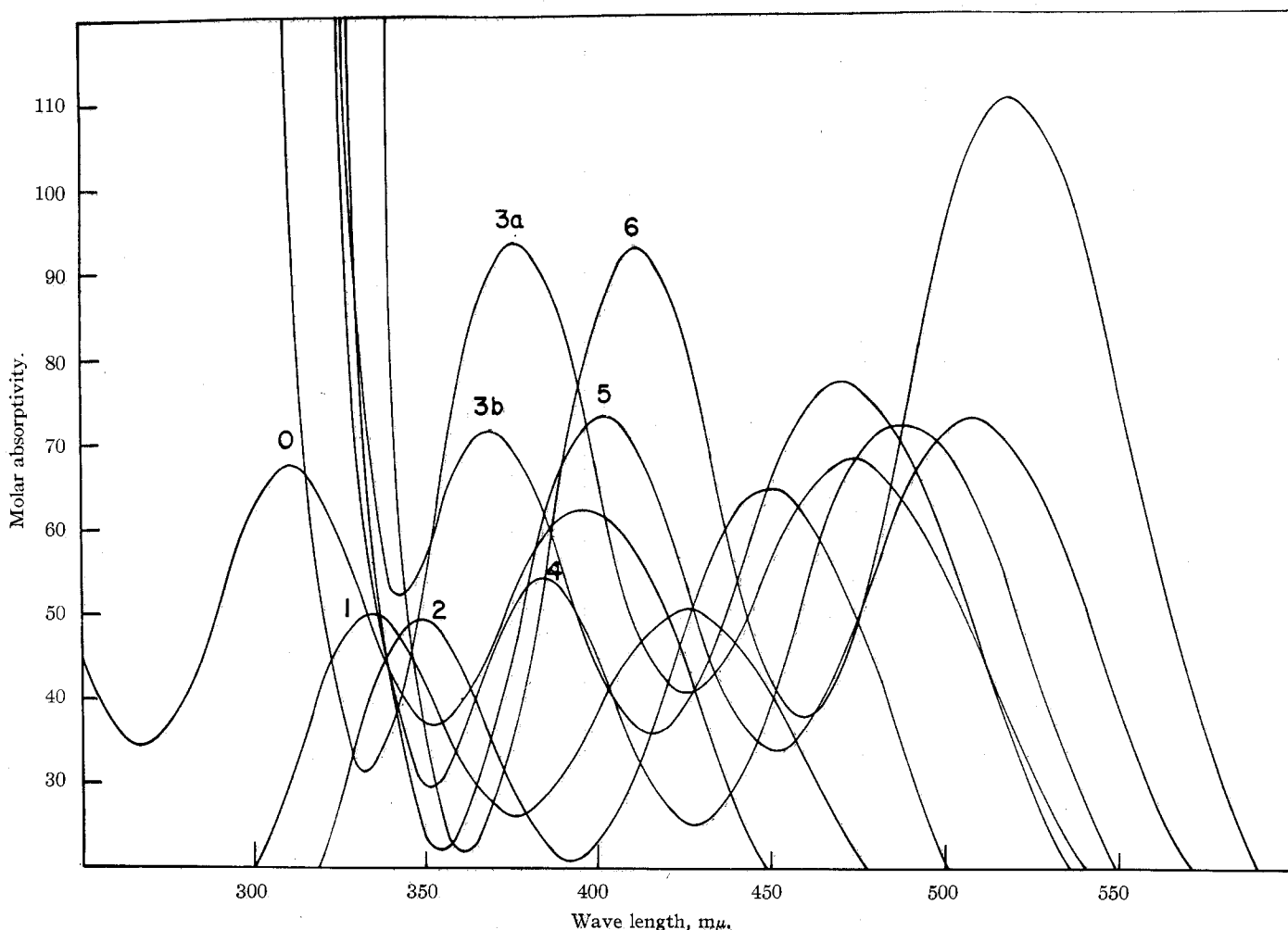


Fig. 1.—Molar absorptivities of rhodium(III)-chloride species in 6 *M* acid ( $\text{HCl} + \text{HClO}_4$ ): 0,  $\text{Rh}(\text{aquated})^{3+}$ ; 1,  $\text{RhCl}_2^{2+}$ ; 2,  $\text{RhCl}_2^+$ ; 3a, *cis*- $\text{RhCl}_3$ ; 3b, *trans*- $\text{RhCl}_3$ ; 4,  $\text{RhCl}_4^-$ ; 5,  $\text{RhCl}_5^{2-}$ ; 6,  $\text{RhCl}_6^{3-}$ .

0.1 *M* perchloric acid. Five-ml. fractions were collected as they came off the column and were analyzed for rhodium and hydrogen ion content. Calculation of the charge on the species per metal atom gave values of 3.1, 3.0, and 3.1 for three separate fractions. The spectra<sup>14</sup> of successive fractions were identical, having maxima at 311  $m\mu$  ( $\epsilon$  67.4) and 396  $m\mu$  ( $\epsilon$  62.0) as shown in Fig. 1.

Charge per species determinations also were carried out on fractions collected from the column runs. In a typical experiment 1 ml. of a given fraction was mixed with 15 ml. of 1 *M* perchloric acid and the pH determined. To this solution there was added a weighed quantity (*ca.* 0.2 g.) of Dowex 50 resin in the hydrogen form, the capacity of which had been determined previously. After the mixture had been stirred for 4–6 hr., 5 ml. of solution was withdrawn and analyzed for rhodium. To the remaining mixture, 10 ml. of water was added and the pH determined. The mixture again was stirred for 4–6 hr., and 10 ml. of solution was withdrawn for rhodium analysis. Charge per species values of 3.0 and 3.2 were found in two separate experiments.

The values of charge per species and charge per species per rhodium atom demonstrated unequivocally that the rhodium was present as the simple (aquated)  $\text{Rh}^{3+}$  ion.

**Preparation and Characterization of  $\text{RhCl}_2^{2+}$ .**—In order to substitute chloride ion for water in the coordination sphere of the aquated rhodium(III) ion, it was necessary to heat solutions of the perchlorate in hydrochloric acid. Preliminary ion exchange

experiments showed that optimum amounts of the  $\text{RhCl}_2^{2+}$  species were produced by boiling a 0.001 *M* solution of rhodium(III) perchlorate in 0.1 *M* hydrochloric acid for 5 min. On a column of Dowex 50, this species was separated as a compact, dark yellow band, below a lighter band which was shown to contain the aquated  $\text{Rh}^{3+}$  ion. Elution of the dark yellow band and analysis gave in separate experiments values of 1.9, 1.8, and 2.2 for the charge on the species per rhodium atom and 1.8 and 1.7 for the charge per species. Absorption maxima for the species were found at 335  $m\mu$  ( $\epsilon$  50.0) and 426  $m\mu$  ( $\epsilon$  50.4) (Fig. 1).

**Preparation and Characterization of  $\text{RhCl}_2^+$ .**—Maximum yields of the dichlororhodium(III) species were obtained by dissolving 2 g. of the perchlorate 6-hydrate in 0.5 *M* hydrochloric acid and refluxing for 3 hr. After this treatment, the solution was placed on a column filled with Dowex 50 to a height of 22 cm. Neutral and anionic species then were removed by washing the resin column with water. The  $\text{RhCl}_2^+$  complex was found to be adsorbed rather diffusely below a compact band of the  $\text{RhCl}_2^{2+}$  species. The former complex was not eluted in a compact band by means of thorium(IV) in perchloric acid, but moved down the column spread over a wide region. Elution of the complex could, however, be effected successfully with standard 0.1 *M* perchloric acid; the eluting agent did not affect the band containing the  $\text{RhCl}_2^{2+}$  complex. Fractions of eluate containing the desired complex were collected and analyzed for rhodium. From a knowledge of this analysis and the hydrogen ion concentrations of elutriant and eluate, the charge on the complex species per metal atom were determined. Values of 0.8, 0.9, and 1.0 were obtained in three experiments.

(14) All spectra were taken on solutions to which had been added sufficient perchloric acid to bring the ionic strength to 6 *M*.

Charge per species equilibration experiments were performed as described previously, except that it was necessary to employ low concentrations (*ca.* 0.01 *M*) of perchloric acid in order to obtain appreciable adsorption of the complex on the resin. Charge per species values of 1.0 and 1.3 were found in two experiments.

The various fractions collected in the column experiments had identical spectra, with maxima of 349  $m\mu$  ( $\epsilon$  49.5) and 450  $m\mu$  ( $\epsilon$  64.9), as shown in Fig. 1.

**Preparation and Isolation of  $RhCl_3$  Isomers.**—A solution of 2 g. of rhodium(III) perchlorate 6-hydrate in 20 ml. of 0.5 *M* hydrochloric acid was refluxed for 6 hr. and then passed through a Dowex 1 resin column to remove anionic rhodium complexes. A deep red anion band was observed at the top of the column, and below this band there was a wide light red band. Upon washing with water, the light red band moved slowly down the column and finally was collected. The aqueous solution containing this band then was passed through a column containing Dowex 50 resin to remove cationic complexes. Spectra of successive fractions of solution which came through the cation exchange column were taken and showed the absence of cationic rhodium species. Successive early fractions had identical spectra, different from the spectra of the later fractions, which also were identical. These spectra indicated the presence of two different neutral rhodium(III) chloride species. The spectrum of the early fractions exhibited absorption maxima at 370  $m\mu$  ( $\epsilon$  71.6) and 471  $m\mu$  ( $\epsilon$  77.1), whereas the absorption maxima of the species in the later fractions occurred at 376  $m\mu$  ( $\epsilon$  93.5) and 474  $m\mu$  ( $\epsilon$  68.3). The molar absorptivities were calculated on the assumption that both species had the formula  $RhCl_3$  (see below).

That these neutral species were indeed monomeric  $RhCl_3$  was confirmed by freezing point studies. For these experiments, a conventional apparatus was employed, consisting of a jacketed test tube fitted with a stopper with holes for a Beckmann thermometer and a glass stirring rod. The complete assembly was immersed in an ice-salt bath in a dewar flask. Since solutions of the neutral rhodium(III) chloride species contained some hydrochloric acid, the freezing point lowering due solely to the rhodium compound in a particular experiment was taken as the difference between the freezing point lowering of the solution and that of a hydrochloric acid solution of the same pH. The results of the freezing point experiments are given in Table I.

**Characterization of  $RhCl_4^-$  and  $RhCl_5^{2-}$  Complexes.**—These complexes were not characterized as unequivocally as were the cationic and neutral species, because the anionic complexes were found to be much more labile than the others.

When a solution of rhodium(III) perchlorate in 2 *M* hydrochloric acid was heated to boiling for 3 hr. and passed through a column of Dowex 1, a dark red band was adsorbed at the top of the column. Elution with 2 *M* hydrochloric acid moved most of the rhodium down the column as a wide red band, leaving a

small amount adsorbed at the top in a brown band. The column runs were carried out with a condenser-type jacket surrounding the column, with ice water being circulated through the jacket to minimize changes in the nature of the adsorbed species.

The spectra of fractions of the wide red band indicated that two species were present. The early fractions had identical spectra with maxima occurring at 385  $m\mu$  ( $\epsilon$  54.1) and 488  $m\mu$  ( $\epsilon$  72.0), and the later fractions also had identical spectra with maxima at 402  $m\mu$  ( $\epsilon$  73.4) and 507  $m\mu$  ( $\epsilon$  72.8) (Fig. 1). No change occurred in the spectra of these species provided the solutions were maintained at temperatures near 0°; however, if the solutions were permitted to stand at room temperature, the spectra changed significantly within 24 hr.

The first species to come off the column was assumed to be  $RhCl_4^-$ , and the second  $RhCl_5^{2-}$ . Reasons for these formulations are given in the Discussion section.

Attempts to characterize these species more conclusively were unsuccessful. Theoretically, it should be possible to carry out charge per metal atom experiments in a manner analogous to that described for the cationic complexes. Inconclusive results were obtained in attempts to determine the charge per metal atom from the free chloride ion concentration in elutriant and eluate and the rhodium concentration in the eluate. One of the reasons for failure was the very low rhodium concentration in the eluate.

The brown band remaining on the top of the column after elution with 2 *M* hydrochloric acid was eluted by means of more concentrated acid. The spectrum of the eluate was identical with that of a freshly prepared solution of  $Na_3RhCl_6$  (Fig. 1), with maxima at 411  $m\mu$  ( $\epsilon$  93.8) and 518  $m\mu$  ( $\epsilon$  111.5).

**Determination of Formation Constants.**—For the determination of the formation constants of the complexes in the rhodium(III)-chloride system, 40 solutions were prepared which were 0.0100 *M* in rhodium(III) perchlorate and contained sufficient hydrochloric acid and perchloric acid to give a total ionic strength of 6.0 *M*. In these solutions the chloride ion content varied from 0.002 to 6.0 *M*. The solutions were made up in Pyrex tubes, which subsequently were sealed and placed in an oven at 120° for 2 weeks. Preliminary experiments had showed that this period of time was necessary for the attainment of equilibrium among the complex species, the criterion for equilibrium in any one solution being identical spectra in successive measurements made at a 1-week interval.

The spectra of the solutions showed shifts of the absorption maxima toward longer wave lengths with increasing chloride concentration. The chloride (*i.e.*, hydrochloric acid) concentrations of the solutions whose spectra at equilibrium corresponded most closely to those of the various complexes isolated in the course of this investigation are shown in Table II.

TABLE I  
MOLECULAR COMPLEXITY OF NEUTRAL RHODIUM(III) CHLORIDE SPECIES

Rh concn., <i>M</i>	pH of Rh and HCl soln.	Diff. in f.p. lowering of HCl and Rh soln., °C.	Theoretical lowering, °C.	
			Monomer	Dimer
Early fractions <sup>a</sup>				
0.025	1.05	0.054	0.047	0.023
.024	1.12	.050	.045	.022
.040	0.098	.078	.074	.037
Later fractions <sup>a</sup>				
0.017	2.95	0.032	0.032	0.016
.020	3.10	.040	.037	.018
.020	2.83	.036	.037	.18

<sup>a</sup> The  $RhCl_3$  species coming off the column in the early fractions was assigned the *trans* configuration, and that coming off in later fractions the *cis* configuration. An explanation for these assignments is given in the Discussion section.

TABLE II

HCl concn., <i>M</i>	Complex species
0.010	$RhCl_2^+$
.020	$RhCl_3^+$
.035	$RhCl_3$
.070	$RhCl_4^-$
.20	$RhCl_5^{2-}$
2.00	$RhCl_6^{3-}$

The spectral data were treated by an adaptation of the method of Sternberg, Stillo, and Schwendeman.<sup>15</sup> This method, which has not been utilized previously for the calculation of formation constants, is an analytical curve-fitting technique employing the least squares method in matrix form. All matrix calculations were carried out on an I.B.M. 650 computer.

The method involves setting up a matrix *A* of dimension *m* × *n* in which the elements are the molar absorptivities of the *n* chloro-complexes of rhodium(III) assumed to be present in a given solution at *m* evenly spaced wave lengths. Matrix *A* then is premultiplied by its transpose  $\bar{A}$ . The inverse of this

(15) J. C. Sternberg, H. S. Stillo, and R. H. Schwendeman, *Anal. Chem.*, **32**, 84 (1960).

new matrix  $(\bar{A}\bar{A})^{-1}$  then is postmultiplied by the transpose of the original matrix to give  $(\bar{A}\bar{A})^{-1}\bar{A}$ . This final matrix then is multiplied by a column matrix in which the elements are the absorptivities of an equilibrium solution of rhodium(III) perchlorate in hydrochloric acid at the  $m$  evenly spaced wave lengths. The individual concentrations of the  $n$  chloro-complexes of rhodium(III) which were assumed to be present are obtained as a result of these matrix multiplications. By subtracting the calculated bound chloride from the total chloride concentration, the free, or uncomplexed, chloride concentration can be determined. The successive formation constants can be evaluated readily by substitution of the necessary concentration data into the equation

$$k_n = \frac{(\text{RhCl}_n^{3-n})}{(\text{RhCl}_{n-1}^{3-1-n})(\text{Cl}^-)}$$

Two basic approaches were made in using the matrix method. In the first, it was assumed that each solution contained three chloro-complexes of rhodium(III). The choice of particular species assumed to be present was based on the data cited above, in which hydrochloric acid concentration is related to principal complex formed. In the concentration region where a given complex was the most abundant, it was assumed that two other chloro-complexes (usually with one less and one more chloride) also were present. In the second approach, the assumption was made that six rhodium(III) species were present in all solutions. In order to obtain the best results in the concentration regions in which geometrical isomers are possible, *i.e.*, where  $\text{RhCl}_2^+$ ,  $\text{RhCl}_3$ , and  $\text{RhCl}_4^-$  are present, three sets of molar absorptivity data for the  $\text{RhCl}_3$  species were used. These three sets were the molar absorptivity of the *trans* isomer (see footnote to Table 1 and also Discussion), the absorptivity of the *cis* isomer, and an average of the molar absorptivities of the two isomers on the assumption that the isomeric ratio was 1.0.

The results obtained from these calculations are shown in Table III. In this table the integers (second column) indicate the rhodium species assumed to be present in the concentration region for which a given formation constant was evaluated. These numbers represent the number of coordinated chlorides per rhodium atom. Thus, 3-5 indicates that  $\text{RhCl}_3$ ,  $\text{RhCl}_4^-$ , and  $\text{RhCl}_5^{2-}$  were assumed to be present. The *cis* or *trans* in paren-

theses designates which set of molar absorptivities for  $\text{RhCl}_3$  was employed; the symbolism *cis* and *trans* indicates that an average of the molar absorptivities of the two isomers was used.

### Discussion of Results

The spectra of the chloro-complexes of rhodium(III) isolated in this investigation all have two maxima (Fig. 1). This is in accord with Jørgensen's<sup>11</sup> ligand field predictions that these complexes should exhibit transitions to two singlet and two triplet levels. For  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$  and  $\text{RhCl}_6^{3-}$  Jørgensen attributed the two strong bands as being due to transitions to the triplet levels. The absorption maxima of the chloro-complexes show a shift toward longer wave lengths with increasing number of chloride ligands, a situation analogous to that encountered by Newman and Hume<sup>16</sup> in the bismuth(III)-chloride system.

A number of workers<sup>10-13,17</sup> have reported the absorption spectrum of rhodium(III) in perchloric acid where the species present is presumably  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ . In solutions which contained sufficient acid to prevent the formation of hydroxo-complexes, absorption maxima were reported in the regions 300-310 and 393-396  $m\mu$  with respective molar absorptivities ranging from 55 to 69 and 47 to 62. Our values for the absorption maxima of completely aquated species are 311  $m\mu$  ( $\epsilon$  67.4) and 396  $m\mu$  ( $\epsilon$  62.0).

The values of 411  $m\mu$  ( $\epsilon$  93.8) and 518  $m\mu$  ( $\epsilon$  111.5) found in this investigation for the absorption maxima for the  $\text{RhCl}_6^{3-}$  complex are also in good agreement with those observed by other investigators.<sup>11,18-20</sup>

The results obtained in charge on species per metal atom and charge per species demonstrate the monomeric character of the  $\text{RhCl}^+$  and  $\text{RhCl}_2^+$  complexes isolated. Analogous species in the ruthenium(III)-chloride system<sup>4,21,22</sup> also have been shown to be monomeric. In contrast to the characterization of geometrical isomers for  $\text{RuCl}_2^+$ ,<sup>21,22</sup> no evidence was obtained for such isomers for  $\text{RhCl}_2^+$ .

The two uncharged species of  $\text{RhCl}_3$  which were isolated would appear to be *cis* and *trans* isomers. King and co-workers<sup>23-25</sup> have shown that it is possible to separate *cis* and *trans* isomers of complexes by ion exchange chromatography. Since the *trans* isomer has a lower dipole moment than the *cis* and is held on a resin column less tightly, the species coming off the column first is assigned the *trans* configuration and that coming off later the *cis* configuration. This was the basis for our assignment of configuration. The ratio of *trans* to *cis* isomer found in our experiments was roughly 3 to 1. It is interesting to note that the shifts in the positions of

TABLE III  
SUCCESSIVE FORMATION CONSTANTS AT 120° FOR THE COMPLEXES  
IN THE RHODIUM(III)-CHLORIDE SYSTEM

Constants	Number of bound chlorides in species present
$k_1 > 10^3$	
$k_2 > 10^3$	
$k_3 \sim 10^3$	
$k_4$ 360 ± 200	0-5 ( <i>trans</i> )
280 ± 230	0-5 ( <i>cis</i> )
260 ± 140	1-6 ( <i>cis</i> and <i>trans</i> )
450 ± 140	1-6 ( <i>cis</i> )
120 ± 30	3-5 ( <i>cis</i> )
160 ± 90	3-5 ( <i>trans</i> )
180 ± 110	3-5 ( <i>cis</i> and <i>trans</i> )
260 ± 80	0-5 ( <i>trans</i> )
Av. = 250 ± 120	
$k_5$ 24 ± 8	1-6 ( <i>cis</i> )
20 ± 12	1-6 ( <i>trans</i> )
30 ± 17	1-6 ( <i>cis</i> and <i>trans</i> )
22 ± 6	3-5 ( <i>cis</i> )
25 ± 11	3-5 ( <i>trans</i> )
31 ± 6	4-6
22 ± 5	3-5 ( <i>cis</i> and <i>trans</i> )
Av. = 25 ± 8	
$k_6$ 0.53 ± 0.26	1-6 ( <i>cis</i> )
0.34 ± 0.07	4-6
0.82 ± 0.21	1-6 ( <i>trans</i> )
Av. = 0.56 ± 0.18	

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the absorption maxima from *trans* to *cis* isomer were only a few millimicrons; these shifts are in accord with the very small one found in the absorption maximum of the isomeric forms of  $\text{RuCl}_2^+$ .<sup>21</sup>

A word is in order regarding the assignment of formulas to the species designated as  $\text{RhCl}_4^-$  and  $\text{RhCl}_5^{2-}$ . There is no question from the ion exchange experiments that the species given these formulations are anionic in character, and the absorption spectra (see Experimental) definitely eliminate the possibility that either is the  $\text{RhCl}_6^{3-}$  complex. Both the order of elution and the positions of the absorption maxima argue for our assignment. On the basis that an anion of charge  $-1$  would be held less tightly than one of  $-2$  charge, the species coming off the anion resin column first was given the formula  $\text{RhCl}_4^-$ . Moreover, the assignment is consistent with the fact that the absorption maxima for this species occur at shorter wave lengths than do those of the second species off the column, to which the formula  $\text{RhCl}_5^{2-}$  was given.

It should be mentioned that these two anionic complexes differ in spectra from those to which Kristjanson and Lederer<sup>20</sup> gave the same formulas. These investigators isolated their complexes by boiling a solution of rhodium(III) hydroxide in 6 *M* hydrochloric acid, passing the solution through a Dowex 2 (anion) resin, and eluting with hydrochloric acid. The " $\text{RhCl}_4^-$ " species was reported to move with the eluting solvent as a yellow band and the " $\text{RhCl}_5^{2-}$ " complex was described as being present on the resin as a very fast-moving orange-tan band. The spectra for these complexes reported by Kristjanson and Lederer correspond roughly to those attributed by us to  $\text{RhCl}_2^+$  and  $\text{RhCl}_3$ . It is conceivable that the former workers failed to wash their resin column with water to remove positively charged and neutral species prior to elution with hydrochloric acid.

The various rhodium(III)-chloride species isolated in the investigation herein reported would appear to correspond to those separated by Lederer<sup>26,27</sup> in his study of the same system by paper chromatography, paper electrophoresis, and paper ion exchange chromatography. In his work, assignment of charge was based on comparisons of migration rates with those of similar ions of known charge.

The best values of formation constants were obtained for  $k_4$ ,  $k_5$ , and  $k_6$  (Table III). The few values which were determined for  $k_1$ ,  $k_2$ , and  $k_3$  would indicate that these constants are all of the same order of magnitude,  $10^3$ , although it is probable that this value is a lower limit for  $k_1$  and  $k_2$ . In many instances no values could be obtained for  $k_1$ ,  $k_2$ , and  $k_3$  because the calculated bound chloride concentrations were evaluated to be slightly greater than the total chloride concentrations. Frequently, the concentrations of a given chloro-complex came out to have negative values, which precluded calculation of meaningful formation constants.

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## Rate Constants for the Formation and Aquation of *cis*- and *trans*- $\text{CrCl}_2^{+1}$

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The pseudo first order rate constants for the reactions  $\text{trans-CrCl}_2^+ = \text{CrCl}^{+2} + \text{Cl}^-$  (1) and  $\text{cis-CrCl}_2^+ = \text{CrCl}^{+2} + \text{Cl}^-$  (2) were determined at 25.0° in 1.0 *M* hydrochloric acid solutions and found to be  $8.23 \times 10^{-5} \text{ sec.}^{-1}$  and  $4.25 \times 10^{-5} \text{ sec.}^{-1}$ , respectively. The activation energy for reaction 1 is 26.5 kcal./mole. Extinction coefficients for *trans*- $\text{CrCl}_2^+$ , *cis*- $\text{CrCl}_2^+$ , and  $\text{CrCl}^{+2}$  in 1 *M* hydrochloric acid were determined at 450 and 635  $\mu$ . In the presence of  $\text{Cr}^{+2}$  reaction 2 was observed to be very fast.

The rate of conversion of  $\text{CrCl}_2^+$  to  $\text{CrCl}^{+2}$  and  $\text{Cl}^-$  has been studied by a number of investigators<sup>2–6</sup> em-

ploying different methods. Recently, the *cis*- and *trans*- $\text{CrCl}_2^+$  isomers were separated and their spectra published.<sup>7</sup> It was shown that only the *trans*- $\text{CrCl}_2^+$

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