sumption of $l_u \rightarrow t_{2g}(\pi)$ transitions, the excited states of bands 1 and 2 must be $^2T_{1u}$ and $^2T_{2u}$, respectively.

From Figure 3 it then follows that l_u can be either $t_{1u}(\sigma^b)$ or $t_{1u}(\pi^b)$ in band 1, while in band 2 it must be $t_{2u}(\pi^b)$. The ambiguity in band 1 cannot be further resolved at this stage since the schemes of Figure 3 are only qualitative and the order of the $t_{1u}(\sigma^b)$ and $t_{1u}(\pi^b)$ levels remains in doubt. Naiman[4] has offered reasons why the l_u in band 1 may be π rather than σ, but these are not conclusive.

No knowledge of the form of the l_u orbitals is required in the calculation of C for $l_u \rightarrow t_{2g}(\pi)$ transitions or is furnished by the observed C values. Some information would be provided by the A terms, but these are not separable in $Fe(CN)_6{}^{3-}$ from the dominating C terms. However, the A terms might be observable in the analogous $^4A_{2g} \rightarrow {}^4T_{2u}$, $l_u \rightarrow t_{2g}(\pi)$ transitions of $Cr(CN)_6{}^{3-}$, where C is zero if spin–orbit coupling is neglected.

In conclusion, on the basis of their MORD curves and of molecular orbital energy level diagrams we assign the 24,100 and 32,900 cm.$^{-1}$ bands of $K_3Fe(CN)_6$ to $t_{1u}(\sigma^b)$ or $t_{1u}(\pi^b) \rightarrow t_{2g}(\pi)$ $(^2T_{2g} \rightarrow {}^2T_{1u})$ and $t_{2u}(\pi^b) \rightarrow t_{2g}(\pi)$ $(^2T_{2g} \rightarrow {}^2T_{2u})$ transitions, respectively.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Hexaaquoruthenium(II)[1]

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The hexaaquoruthenium(II) ion has been separated and characterized in aqueous solution. The ion was formed by electrolytic reduction of ruthenium(III) at a controlled potential of −0.40 v. with respect to a saturated calomel electrode, using a mercury pool cathode. The only anions found which did not interfere with the formation of this ion were tetrafluoroborate and *p*-toluenesulfonate. In the presence of other anions, either oxidation or complexation of the ruthenium was found to take place. The charge on the ion was determined using ion-exchange methods. The oxidation state of the metal was verified by coulometry and titration of the ion with triiodide. The oxidation potential for the half-reaction $Ru^{+2} \rightarrow Ru^{+3} + e^-$ was found to be -0.22 ± 0.03 v. by polarography.

Several previous studies have been made on the aqueous chemistry of ruthenium(II). Most of these studies were made in chloride medium, where the behavior observed is largely that of the chloro complexes. We have found that the properties of the chloro complexes are quite different from those of the aquo complex. The only previous attempts to prepare uncomplexed ruthenium(II) resulted in a variety of uncharacterized products.[2]

Results

(A) Preparation of the Complex.—Our early attempts to prepare the Ru^{+2} ion by chemical reduction were not successful. Most of these failures were due to the particular anions present in solution, usually perchlorate or trifluoroacetate. Later experiments showed that the trifluoroacetate ion forms complexes with ruthenium(II), while the reduction of perchlorate ion is readily accomplished by the Ru^{+2} ion. In other cases reaction with the reducing agent, for example zinc, yielded metallic ruthenium as the principal product. The Ru^{+2} ion was formed most readily by electrolysis, using the following procedure.

A nearly saturated, freshly prepared, aqueous solution of potassium pentachloroaquoruthenate(III) was placed on a cation-exchange column in the hydrogen ion form. By removing the anionic ruthenium complexes from the column with water, the potassium ions in solution were replaced by hydrogen ions. Sufficient tetrafluoroboric acid was added to give a solution which was about 1 M in hydrogen ion and 10^{-2} M in ruthenium(III). A 0.5 M silver tetrafluoroborate solution was added dropwise, until no more silver chloride formed. The solution was allowed to stand at room temperature for 3–4 days, giving a solution containing mostly the mono- and dichloro complexes of ruthenium(III), as indicated by the ultraviolet spectra of the solutions.[3] The absence of silver ion in solution was proven by adding a few drops of the solution to 1 ml. of 1 M hydrochloric acid. The ruthenium in about 5 ml. of this solution was reduced at a mercury cathode, the potential of which was controlled at −0.40 v. with respect to a saturated calomel electrode.[4] The electrolysis was continued at room temperature

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(1) (a) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965. (b) This work was supported by the National Science Foundation on Grant No. GP-1584.

(2) H. H. Cady, Ph.D. Thesis, University of California, Berkeley, 1957 (AEC-UCRL-3757).

(3) H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

(4) G. A. Rechnitz, *Inorg Chem.*, **1**, 953 (1962).

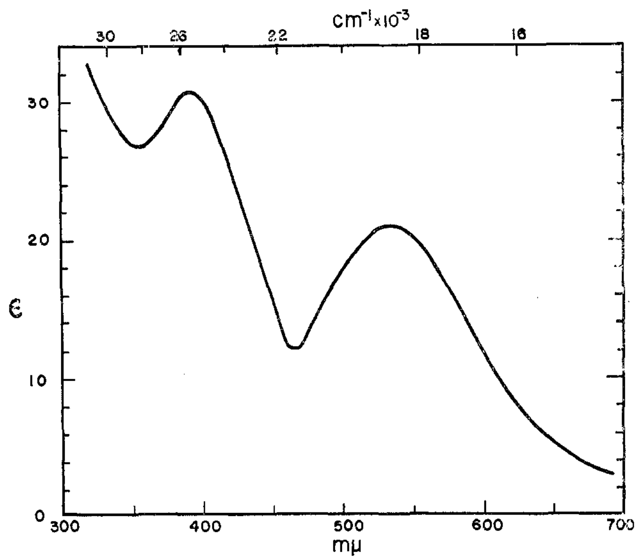

Figure 1.—Molar extinction coefficients of $Ru(H_2O)_6^{+2}$ in 0.01 M tetrafluoroboric acid at 25°.

until the current dropped to about 1% of the initial current. The final current was usually about 0.05 ma. The reduced solutions contained the deep blue chloro complexes of ruthenium(II) and the uncomplexed ion. Usually about 60% of the ruthenium(II) was present as the uncomplexed ion, but this varied considerably depending upon prior treatment. The solution was then placed on a cation-exchange column in the hydrogen form, which was thermostated at 0°. The chloro complexes of ruthenium(II) were washed from the column with 0.1 M tetrafluoroboric acid. During this elution the aquo complex remained on the resin as a narrow, dark band at the top of the column. This band was eluted from the column with a solution of 0.01 M barium tetrafluoroborate, which was also 0.01 M in hydrogen ion.

The same procedure was used to prepare the complex in p-toluenesulfonate solution, except lanthanum ion was used in the elution in place of the barium ion.

The Ru^{+2} ion was produced only when the anion present in solution was either tetrafluoroborate or p-toluenesulfonate. The visible spectra of the solutions were identical above 350 mμ in the presence of both of these ions. The strong absorption of light by p-toluenesulfonate below this wave length prohibited any comparison of the spectra. The spectrum in tetrafluoroboric acid solution is shown in Figure 1. Beer's law was obeyed in the tetrafluoroborate solution from 6.0×10^{-3} to 2.6×10^{-2} M. There was no spectral evidence of complexing by the p-toluenesulfonate up to a concentration of 0.1 M p-toluenesulfonic acid.

(B) Characterization of the $Ru(H_2O)_6^{+2}$ Ion.—The identity of the uncomplexed ruthenium(II) was proven by determining the charge per atom and the charge per ion by the method of Cady and Connick.[3] To determine the charge per ruthenium atom the complex ion was absorbed on a cation-exchange column in the hydrogen ion form and was eluted with a solution of lanthanum p-toluenesulfonate in dilute p-toluenesulfonic acid of known concentration. Since the lanthanum ion is absorbed by the resin much more strongly than the ruthenium ion, which was in turn held more tightly than hydrogen ion, the ruthenium essentially saturated the resin in a band preceding the lanthanum. As the band emerged from the column, several successive fractions were analyzed for ruthenium and hydrogen ion. Lanthanum ion was absent from all fractions used, and the hydrogen ion concentrations in the lanthanum and ruthenium solutions were the same, so a charge balance across the column gives the equation

$$\text{charge/Ru atom} = 3[La^{+3}]/[Ru]$$

The results of these experiments are summarized in Table I.

TABLE I

CHARGE PER RUTHENIUM ATOM[a]

	Composition of fractions	
pH	(g.-atoms of Ru/l.) × 10²	Charge/atom
1.97	2.59	2.15
2.07	2.87	2.04
2.07	2.92	2.00

[a] All elutions were made with a solution of pH 2.08, $[La^{+3}] = 1.95 \times 10^{-3}$ M.

The charge per ion was determined by equilibration of acidic aqueous solutions of the complex with cation-exchange resin in the hydrogen ion form.[3] At equilibrium

$$\log D_{Ru} = \log K + n \log D_H$$

assuming activity coefficients do not change. D_{Ru} and D_H are the ratios of the concentration of the respective ions in the resin (in moles/kg. of resin) to the molar concentration of the ion in the aqueous phase, K is a concentration equilibrium constant, and n is the charge on the ruthenium ion absorbed.

In a typical experiment 6 ml. of a solution 1.5×10^{-2} M in ruthenium in 0.5 M p-toluenesulfonic acid was equilibrated with 0.1 g. of resin. Three ml. of the solution was removed for analysis and replaced with an equal volume of distilled water. After a second equilibration this same procedure was repeated. Three or four equilibrations, at different hydrogen ion concentrations, were made in each experiment. The number of millimoles of ruthenium in the resin phase was calculated from the ruthenium analysis of the aqueous phase before and after the equilibration. Since a significant fraction of the resin sites were occupied by the metal ion, the concentration of hydrogen ion in the resin phase was calculated by subtracting twice the resin phase concentration of the ruthenium from the capacity of the resin.

The cation-exchange resin was stored in a constant humidity atmosphere, provided by a saturated lead nitrate solution,[5] to ensure a constant weight capacity of the resin. The capacity of the resin was determined by stirring a weighed sample of the resin with an excess of standard sodium hydroxide, separating the

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(5) L. A. Blatz, *J. Phys. Chem.*, **66**, 160 (1962).

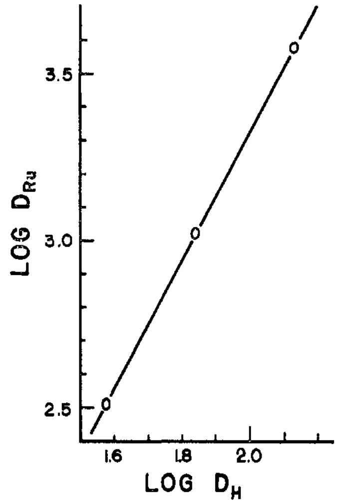

Figure 2.—The equilibrium distribution of $Ru(H_2O)_6^{+2}$ between aqueous acid solutions and Dowex 50X8 cation-exchange resin at room temperature, approximately 22°. $D_X \equiv [X]_{resin}/[X]_{aq}$.

resin by filtration, and titrating the excess base with standard hydrochloric acid.

The equilibrium distribution of the ruthenium ion between ion-exchange resin and aqueous solutions of different hydrogen ion concentrations is presented graphically in Figure 2. The slope of the line was found to be 1.96 and may be set equal to the charge per ion. Since both the charge per atom and charge per ion are the same within experimental error, the ruthenium is present as a monomeric ion having a charge of +2.

In all experiments it was necessary to remove all dissolved oxygen from the solutions and protect them with an atmosphere of nitrogen, to prevent the oxidation of the metal to the +3 oxidation state. When the solutions in tetrafluoroboric acid were allowed to air oxidize, the spectrum of the solution agreed with that reported by Cady and Connick[3] for the hexaaquoruthenium(III) ion in perchloric acid. Solutions of Ru^{+3}, produced by this air oxidation, were reduced by quantitative electrolysis to the Ru^{+2} ion. A second method used to verify the oxidation state of the metal ion in solution involved the oxidation of the metal to ruthenium(III) by a standard triiodide solution. It has been shown by Wehner and Hindman[6] that the higher oxidation states of ruthenium may be reduced to ruthenium(III) using iodide as the reducing agent in acid solution, the reaction products being iodine and a green ruthenium(III) solution, probably containing iodide complexes. We have found that the same oxidation-reduction couple will oxidize ruthenium(II) to the same green solution.

The Ru^{+2} was titrated directly with standard triiodide solution, using starch as an indicator. The results of the oxidation state determinations are summarized in Table II.

(C) **Some Properties of Ru(II).**—Polarograms were obtained on solutions containing both the Ru^{+2} and Ru^{+3} ions in *p*-toluenesulfonic acid. In the curves obtained the oxidation and reduction occurred in a single wave, which corresponded to a one-electron reaction, with $E_{1/2} = -0.02$ v. *vs.* a saturated calomel electrode.

Table II

Oxidation State Determination

Method[a]	mmoles of Ru	mequiv. of Ru
Coulometric reduction	8.74×10^{-3}	8.68×10^{-3}
Titration with I_3^-	2.17×10^{-2}	2.22×10^{-2}
Titration with I_3^-	2.41×10^{-2}	2.47×10^{-2}

[a] In both methods ruthenium(III) was known to be the initial or final oxidation state of the metal.

When the electrolytic reductions were carried out in perchlorate solution, the color of the solution changed from a yellow to a brown, and a large quantity of chloride ion was produced. The current did not decrease upon prolonged electrolysis, indicating that the chloride in solution came from the reduction of the perchlorate present. Electrolysis of solutions containing 0.1 *M* trifluoroacetate ion produced yellow solutions. If solutions containing the blue chloro complexes of ruthenium(II) were treated with trifluoroacetic acid, the same yellow color could be produced. By raising the chloride ion concentration, the blue color was regenerated. The color changes observed were not instantaneous, but no quantitative measure of the rates was made. When the concentration of the complexing agent was about 0.5 *M*, the change in color was noticeable in less than 5 min. These qualitative experiments showed that ruthenium(II) forms trifluoroacetate complexes quite readily.

Experimental

Analysis.—Ruthenium was determined spectrophotometrically by one of two methods. The first method is essentially that used by Gortsema.[7] The ruthenium was oxidized to the tetroxide using periodic acid, and the concentration was determined from the absorbance at 385 mμ, using a molar extinction coefficient of 930. The second method used is a modification of that reported by Woodhead and Fletcher.[8] An aliquot of the solution was made basic with sodium hydroxide solution, so that the final hydroxide concentration would be 0.2–0.4 *M*. Bromine water was added dropwise until the green color of perruthenate ion persisted, then the solution was diluted to the mark in a volumetric flask. Large excesses of the oxidizing agent were avoided. The spectrum of the solution was recorded from 500 to 350 mμ. A small crystal of sodium iodide was added to reduce part of the perruthenate to ruthenate, and the spectrum was recorded again. The absorbance at the isosbestic point at 415 mμ, molar extinction coefficient 1045, was used to calculate the concentration of the ruthenium.

Lanthanum concentrations were determined gravimetrically by precipitating the oxalate, which was ignited to give the oxide. Barium was assayed by a gravimetric determination as barium sulfate.

Reagents.—The ruthenium was obtained as ruthenium chloride (38.4% Ru) from Engelhard Industries. Potassium pentachloroaquoruthenate(III) was prepared as follows. Ruthenium chloride was dissolved in 12 *M* hydrochloric acid and boiled for several hours. A stoichiometric amount of potassium chloride was added, and the solution was stirred with mercury until the solution became green, indicating the formation of some ruthenium(II). Mercurous chloride was removed by filtration, and the

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(6) P. Wehner and J. C. Hindman, *J. Am. Chem. Soc.*, **72**, 3911 (1950).

(7) F. P. Gortsema, Ph.D. Thesis, Purdue University, 1960.

(8) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

solution was evaporated to a small volume and cooled. The resulting red crystals were separated by filtering, washed with ethanol, and recrystallized from 6 *M* hydrochloric acid.

The lanthanum solutions were prepared by dissolving lanthanum oxide (99.9%), obtained from Matheson Coleman and Bell, in *p*-toluenesulfonic acid. Barium solutions were prepared in the same manner from barium hydroxide.

The *p*-toluenesulfonic acid was obtained from Columbia Organic Chemicals Co. and purified by recrystallization from anhydrous diethyl ether.

The ion-exchange resin was Bio-Rad Laboratories AG50WX 8, 200–400 mesh, and was used without further purification.

All other chemicals used were reagent grade.

Equipment.—Spectra were recorded on a Cary Model 14 spectrophotometer, using 1 or 0.1 cm. quartz cells. The reductions and coulometric determinations were carried out using a controlled potential coulometer with transistorized power amplifiers, designed by Propst.[9] All pH measurements were made with a Beckman Model G pH meter. Polarograms were recorded on a Sargent Model XV polarograph with a dropping mercury electrode, using a saturated calomel electrode as a reference.

Discussion

The agreement of the charge per ion determination with the true value of 2.00 is far better than the results obtained by others using the same methods and also is much better than can be expected. The main difference between our measurements and others using this technique was the much heavier loading of the resin with the metal ion, which occupied about 20% of the ionic sites in the resin phase. It is possible that there was an accidental cancellation of activity coefficients under these circumstances, leading to fortuitously good agreement.

By assuming that the diffusion coefficients of the Ru^{+2} and Ru^{+3} ions are not too different an approximate oxidation potential for the half-reaction

$$Ru(H_2O)_6^{+2} \longrightarrow Ru(H_2O)_6^{+3} + e^-$$

is calculated to be −0.22 ± 0.03 v. This value is the same within experimental error as that found by Endicott and Taube[10] for the couple involving the hexaammine complexes of ruthenium(II) and -(III). From the similarity of these potentials we conclude that the stability constants for both the hexaammineruthenium(II) and -ruthenium(III) complexes are very nearly equal to each other.

These data also indicate that neither hexaammineruthenium(II) nor hexaaquoruthenium(II) is capable of reducing water in acidic solution. This is in direct contrast to the behavior of ruthenium(II) in acidic chloride medium.[11,12]

The intensities of the two bands observed in the spectrum of the $Ru(H_2O)_6^{+2}$ ion indicate that these are crystal field bands, and we have assigned the band at 25,640 cm.$^{-1}$ to the $^1T_2 \leftarrow {}^1A_1$ transition and that at 18,870 cm.$^{-1}$ to $^1T_1 \leftarrow {}^1A_1$. From these assignments and using the approximations of Tanabe and Sugano[13] we calculate $Dq = 2100$ cm.$^{-1}$, $B = 423$ cm.$^{-1}$. The location of the crystal field bands and the value calculated for Dq are nearly identical with those given by Jørgenson[14] for the isoelectronic $RhCl_6^{-3}$ complex. Apparently the decrease in Dq caused by the lower charge on the central ion is just compensated by the increase expected by using water as a ligand in place of chloride ion.

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[9] R. C. Propst, U. S. Atomic Energy Commission Report DP-798, May 1963.

[10] J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

[11] J. R. Backhouse and F. P. Dwyer, *Proc. Roy. Soc. N. S. Wales*, **83**, 138 (1949).

[12] G. A. Rechnitz and H. C. Catherino, *Inorg. Chem.*, **4**, 112 (1965).

[13] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[14] C. K. Jørgenson, *Acta Chem. Scand.*, **10**, 500 (1956).