tained with a spectrometer[18] equipped with an He–Ne laser source. The instrument was calibrated using helium and argon discharge lines. Small polycrystalline samples were investigated by collecting the light scattered at 90° from the sample held between two thin glass plates. The low solubility of the compounds in available solvents precluded our obtaining Raman spectra in solution.

Acknowledgment.—We are grateful to Professor H. D. Kaesz for helpful discussion of the results of our work.[19]

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[18] R. E. Miller, D. L. Rousseau, and G. E. Leroi, Technical Report No. 22, ONR contract 1858(27), NR 014-203, May 1967 (available from Defense Documentation Center, Cameron Station, Alexandria, Va. 22314).

[19] Since submission of this article, D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Commun.*, 493 (1968), have reported metal–metal stretching frequencies for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ in good agreement with ours. Their estimates of K_{M-M}, using $-M(CO)_4$ as the vibrating units, are nearly twice as large as the values reported here, with $K_{Ru-Ru} > K_{Os-Os}$. It appears that a better approximation for simple calculations of metal–metal force constants in polynuclear carbonyls is to use the metal atom masses alone, neglecting the carbonyl ligands: M. J. Ware, private communication.

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Electron-Transfer Reactions of Ruthenium Ammines

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The rate of self-exchange for the couple $Ru(NH_3)_6^{2+,3+}$ has been measured, taking advantage of the change in absorbance when the deuterated form of one of the oxidation states reacts with the protonated form of the other. At 25° and $\mu = 0.013$ in D_2O as solvent $k = 8.2 \pm 1 \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 10.3 \pm 1.0$ kcal/mol, and $\Delta S^{\ddagger} = -11 \pm 3$ eu. The rate of self-exchange in the $Ru(en)_3^{2+,3+}$ system has been determined less accurately, but it appears certain that at 25° it is slower than that for $Ru(NH_3)_6^{2+,3+}$. The rates of oxidation of $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$ by Fe^{3+} and $FeOH^{2+}$ have been measured, and, in keeping with results for other outer-sphere electron-transfer processes, Fe^{3+} reacts more rapidly than does $FeOH^{2+}$. However, when $Ru(NH_3)_5OH_2^{2+}$ is the reductant, $FeOH^{2+}$ reacts more rapidly than does Fe^{3+}, and the possibility exists that the reaction with $FeOH^{2+}$ proceeds by proton transfer accompanying electron transfer.

Introduction

Endicott and Taube[1,2] have investigated the chemistry of the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5OH_2^{2+}$–$Ru(NH_3)_5OH_2^{3+}$ complexes in aqueous solution, including the rates of oxidation of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$ by a series of cobalt(III)–ammine complexes and the reduction of $Ru(NH_3)_6^{3+}$ by various reductants.[3] They have shown that, under ordinary conditions, $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ are sufficiently inert to substitution in aqueous solution so that their electron-transfer reactions are of the outer-sphere type. Similar behavior is demonstrated in the present study for $Ru(en)_3^{2+}$ and $Ru(en)_3^{3+}$ (en = ethylenediamine).

The simplification arising from the absence of bond rupture in the activated complex for outer-sphere electron-transfer reactions facilitates theoretical calculations[4] of rate constants. Interest in the rates and mechanisms of outer-sphere reactions has been heightened by the possibility of direct comparisons between experimentally determined and theoretically calculated rate constants.

Many of the electron-transfer systems which have been investigated experimentally are between aquo ions, one or both of which are substitution labile compared with the rate of electron transfer.[5] For such systems it is difficult to distinguish between outer- or inner-sphere mechanisms or mechanisms involving net hydrogen atom transfer.

Complexes of back-bonding ligands such as 1,10-phenanthroline and cyanide are generally substitution inert, and their electron-transfer reactions are outer-sphere. However, in a reaction with such complexes involving electron transfer to or from metal t_{2g} orbitals, the exchanging electrons may be spread toward the surface of the complex onto the ligands, and the delocalization of electrons may facilitate electron transfer. Extensive delocalization is known to occur for ferrocyanides. The Mössbauer chemical shifts of ferricyanides and ferrocyanides are almost identical, and a detailed analysis by Shulman and Sugano[6] indicates that the electron added to $Fe(CN)_6^{3-}$, in going to $Fe(CN)_6^{4-}$, resides predominantly on the cyanide ligands and not on the iron. The mechanism of outer-sphere electron transfer for such systems may differ in important respects from that for complexes having only saturated ligands.

The mechanistic ambiguities which apply to aquo ion systems do not apply to the hexaammine and tris(ethylenediamine)ruthenium complexes. Here the mechanisms of electron transfer, at least where the rates of electron transfer are high, must be outer-sphere. The reactions of these ions are also free of the possible special effect associated with back-bonding ligands. Because of their importance in the study of outer-sphere re-

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(1) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).

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

(3) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

(4) For a recent review of chemical electron-transfer theory see R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964), and the references therein.

(5) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(6) R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **42**, 39 (1965).

actions, the rates of self-exchange between $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_6{}^{3+}$ and between $Ru(en)_3{}^{2+}$ and $Ru(en)_3{}^{3+}$ and the rates of reaction between Fe(III) and $Ru(NH_3)_6{}^{2+}$ and between $Ru(en)_3{}^{2+}$ and $Ru(NH_3)_5OH_2{}^{2+}$ have been studied in the present work.

Experimental Section[7]

Materials.—Water used for kinetics experiments was deionized and then triply distilled; the first distillation was from alkaline permanganate. Heavy water of deuterium content greater than 99.8 mol % was obtained from Bio-Rad Co. Samples which were initially redistilled from alkaline permanganate gave the same kinetic results as untreated samples. Nitrogen used for deaeration was passed through a series of scrubbing towers containing Cr^{2+} to remove traces of residual oxygen. For experiments in deaerated D_2O solutions, the deoxygenated nitrogen stream was first dried by passing through a calcium sulfate–silica gel column and then saturated with D_2O by passing it through a bubbler containing D_2O.

Solutions of CH_3CO_2D and CF_3CO_2D were prepared by adding the respective anhydrides to D_2O. Deuterioperchloric acid solutions were obtained by diluting Baker and Adamson analyzed perchloric acid with D_2O. At the low concentrations of acid used, the deuterium to hydrogen ratio of the reaction solutions was changed negligibly by the protons introduced with the acid.

Stock solutions of sodium perchlorate were prepared by neutralizing solutions of primary standard sodium carbonate with 70% perchloric acid. Baker and Adamson reagent grade lithium perchlorate, which had been recrystallized several times from water, was used to prepare standard lithium perchlorate solutions. Salt content was determined by analysis for total perchlorate.

Preparation of Ruthenium Complexes. $Ru(NH_3)_6Cl_3$.—The compound was supplied by Johnson, Matthey and Co., Ltd., and recrystallized by dissolving a sample in 1 *M* HCl, filtering, and cooling to 0° to precipitate the pale yellow crystals. The recrystallization procedure was repeated. The crystals were collected, washed with ice-cold 4 *M* HCl, methanol, and ether, and vacuum dried at room temperature.

$Ru(en)_3ZnCl_4$.—An original sample of $Ru(en)_3ZnCl_4$ was kindly provided by Dr. F. M. Lever of Johnson, Matthey and Co., Ltd. Further quantities were prepared as described by Lever and Bradford.[8] *Anal.* Calcd for $Ru(en)_3ZnCl_4$: C, 14.7; H, 4.91; N, 17.2; Cl, 29.1. Found: C, 14.7; H, 4.83; N, 17.3; Cl, 29.4.

$Ru(en)_3ZnBr_4$.—Pure samples of $Ru(en)_3{}^{2+}$ were obtained by preparing the tetrabromozincate salt. A sample of $Ru(en)_3ZnCl_4$ was dissolved in just sufficient deaerated, ice-cold 0.01 *M* HTFA containing a few pieces of zinc–mercury amalgam. The solution was filtered under nitrogen. Deaerated, ice-cold 48% HBr was added dropwise until precipitation appeared complete. The procedure was repeated. The pale yellow solid was collected, washed with ice-cold 4 *M* HBr, methanol, and ether, and dried under vacuum at room temperature. *Anal.* Calcd for $Ru(en)_3ZnBr_4$: C, 10.8; H, 3.61; N, 12.5; Br, 47.7. Found: C, 10.6; H, 3.54; N, 12.5; Br, 47.6.

$Ru(en)_3I_3$.—A sample of $Ru(en)_3ZnCl_4$ was dissolved in 0.01 *M* HTFA with a small amount of precipitate remaining. An acidic medium is necessary because $Ru(en)_3{}^{3+}$ in solution is somewhat air sensitive, the rate of oxygen attack increasing with pH. A solution of iodine in saturated sodium iodide solution was added dropwise with constant stirring. The dropwise addition was continued until a slight excess of triiodide had been added, as indicated by the deepening color of the solution. A few milliliters of ice-cold, saturated sodium iodide solution was added. The dark purple crystals were collected and washed twice with ethanol. The product was purified by dissolving in the minimum amount of HTFA, filtering the solution, and adding ice-cold sodium iodide solution dropwise until crystallization appeared complete. The mixture was cooled in an ice bath and the crystals were collected. The dark purple crystals were washed with ice-cold, saturated sodium iodide, ethanol, and ether and dried under vacuum at room temperature. *Anal.* Calcd for $Ru(en)_3I_3$: C, 10.9; H, 3.65; N, 12.7; I, 57.4. Found: C, 10.8; H, 3.71; N, 12.6; I, 57.2.

$Ru(en)Br_3$.—A sample of $Ru(en)_3I_3$ was dissolved in the minimum volume of 0.01 *M* HTFA and the solution was filtered. Ice-cold 48% HBr was added dropwise and the solution was cooled in an ice bath until crystallization was complete. The orange solid was redissolved and cold, concentrated HBr was added until crystallization had just begun. Precipitation was completed by cooling at 0°. The bright orange crystals were collected, washed with cold 4 *M* HBr, ethanol, and ether, and vacuum dried at room temperature. The complex is very hygroscopic. *Anal.* Calcd for $Ru(en)Br_3$: C, 13.8; H, 4.64; N, 16.1; Br, 46.0. Found: C, 13.82; H, 4.60; N, 16.4; Br, 45.9.

$[Ru(NH_3)_5Cl]Cl_2$.—The compound was prepared as previously described[9] and recrystallized from hot 0.1 *M* HCl.

The analyses described for carbon, hydrogen, nitrogen, and halogen were performed by the Stanford University Microanalytical Laboratory.

Preparation of Reactant Solutions Fe(II) and Fe(III).—Baker and Adamson 99.8% iron wire for standardization was added to a flask containing diluted perchloric acid in slight excess. The solution was boiled until the iron wire was completely dissolved, filtered to remove any traces of undissolved iron oxide, and diluted to the proper volume. Because ferrous ion oxidizes slowly in air, the solutions were analyzed for both Fe(II) and Fe(III) before use. To prepare Fe(III) solutions, Fe(II) solutions were oxidized by adding hydrogen peroxide dropwise until the addition of more peroxide resulted in the evolution of oxygen. The solution was stirred for a few hours during which time excess hydrogen peroxide decomposed. The absence of the characteristic blue color when a drop of the final solution was added to a ferricyanide solution indicated that Fe(II) had been completely consumed.

Solutions containing Fe(II) were analyzed by adding 1,10-phenanthroline to acetate-buffered solutions and determining the resulting phenanthroline complex spectrophotometrically at 510 mμ, using ϵ 11,100 M^{-1} cm^{-1}.[10] Spectral interference from iron(III)–phenanthroline species was negligible for the conditions used. Solutions of Fe(III) were analyzed similarly but after first reducing Fe(III) to Fe(II) with excess hydroxylamine hydrochloride.[10] The results from the phenanthroline method agreed well with determinations at 240 mμ (ϵ 4160) for Fe(III) solutions acidified with perchloric acid.[11]

$Ru(NH_3)_6{}^{2+}$, $Ru(en)_3{}^{2+}$, and $Ru(NH_3)_5OH_2{}^{2+}$.—Solutions of $Ru(NH_3)_6{}^{2+}$ were prepared by the zinc–mercury amalgam reduction of $Ru(NH_3)_6{}^{3+}$. In the same way, the reduction of solutions of $Ru(en)_3Br_3$ or $Ru(en)_3I_3$ gave $Ru(en)_3{}^{2+}$. The latter complex was also prepared by dissolving either the tetrabromozincate or tetrachlorozincate salt of $Ru(en)_3{}^{2+}$ in a deaerated solution.

The times for complete reduction of the +3 complexes to the +2 by a large excess of zinc–mercury amalgam were shown to be less than 5 min for a $\sim 1 \times 10^{-3}$ *M* solution of $Ru(NH_3)_6{}^{3+}$ and less than 20 min for a $\sim 1 \times 10^{-3}$ *M* solution of $Ru(en)_3{}^{3+}$ at 25° in 0.01 *M* HTFA. The times of reduction and the total reducing powers of the solutions were obtained by adding excess Fe(III) and determining the Fe(II) produced spectrophotometrically as the 1,10-phenanthroline complex. It was shown by the same method that solutions of $Ru(en)_3{}^{2+}$ retained their total reducing power (and constant ultraviolet spectra) for at least 1 hr. The reduction of solutions of $Ru(en)_3{}^{3+}$ to $Ru(en)_3{}^{2+}$, followed by reoxidation with the stoichiometric amount of Fe-

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[7] The abbreviations used in this paper are: en = ethylenediamine; TFA^- = trifluoroacetate; OAc^- = acetate; enD = $D_2NCH_2CH_2ND_2$.

[8] F. M. Lever and R. Bradford, *Platinum Metals Rev.*, 106 (1964).

[9] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

[10] W. B. Fortune and M. G. Mellor, *Ind. Eng. Chem., Anal. Ed.*, **10**, 60 (1938).

[11] R. Bostian, R. Weberling, and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

(III), exactly reproduced the spectrum of the initial $Ru(en)_3^{2+}$ solutions.

Preparations of the $Ru(en)_3ZnCl_4$ compound contained an impurity which absorbs strongly in solution at about 370 mμ. Repeated purification of the complex as the tetrabromozincate salt decreased the extinction coefficient for the maximum at 370 mμ from 350–500 M^{-1} cm^{-1} to a constant value of 120 ± 10 and slightly increased the extinction coefficient of the absorption maximum at 302 mμ. The extinction coefficient values for solutions of the recrystallized salt agreed well with values obtained by reduction of solutions of $Ru(en)_3Br_3$ and $Ru(en)_3I_3$. Reduction by zinc–mercury amalgam of solutions of $Ru(NH_3)_5Cl^{2+}$ gave $Ru(NH_3)_5OH_2^{2+}$ since the ion $Ru(NH_3)_5Cl^{+}$, which is presumably formed initially, is rapidly aquated.[1] Aqueous solutions of the ruthenium(II)–ammine complexes are oxygen-sensitive, and all operations involving them were carried out under nitrogen.

It has recently been shown[12] that N_2 reacts spontaneously with $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$ at room temperature. The reaction with the hexaammine is so slow that, under the conditions of the experiments in the limited time of contact with N_2, very little conversion to N_2-containing products could have occurred. Though the reaction of N_2 with $Ru(NH_3)_5OH_2^{2+}$ is more rapid than with $Ru(NH_3)_6^{2+}$, even for the aquo complex little formation of $Ru(NH_3)_5N_2^{2+}$ took place. The ion $Ru(NH_3)_5OH_2^{2+}$ was in contact with N_2 for *ca.* 20 min in preparation for the experiment with Fe^{3+} as oxidant. At 10°, the temperature of the experiments, $t_{1/2}$ for the conversion of $Ru(NH_3)_5OH_2^{2+}$ to $Ru(NH_3)_5N_2^{2+}$ appears to be much longer than this,[13] at least at low concentrations of Ru(II).

$Ru(en)_3^{3+}$.—Aqueous solutions of $Ru(en)_3^{3+}$ in contrast to solutions of $Ru(NH_3)_6^{3+}$ are air sensitive. The rate of air oxidation increases with increasing pH. At a pH less than 2, the solutions are stable for hours, and so experiments using $Ru(en)_3^{3+}$ were carried out in fairly acidic media.

Deuterated Ruthenium–Ammine Complexes.—Deuterated ruthenium(III)–ammine complexes in solution were prepared by dissolving the protonated salts in neutral D_2O in which deuterium exchange for hydrogen is complete in less than 10 sec. The proper amount of deuterated acid was added after complete exchange. Reduction over zinc–mercury amalgam gave solutions of the deuterated ruthenium(II)–ammine complexes. Solutions of the Ru(III) protonated complexes were obtained by dissolving the protonated salts in fairly acidic D_2O solutions (at 0.01 *M* acid the half-time for deuterium exchange in $Ru(NH_3)_6^{3+}$ is about 30 min). Zinc–mercury amalgam reduction produced the Ru(II) complexes; these undergo deuterium exchange for hydrogen about 100 times more slowly than the Ru(III) complexes.

The Solution Spectra of the Ruthenium–Ammine Complexes.—The visible and ultraviolet spectra of solutions of $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_6^{3+}$, $Ru(en)_3^{2+}$, and $Ru(en)_3^{3+}$ were recorded on a Cary Model 14 spectrophotometer. Calculated extinction coefficients for the observed absorption maxima are given in Table I, where the error limits quoted represent the range of values obtained for from five to eight determinations. The maxima are not peaks but, rather, well-defined shoulders.

The higher energy absorptions arise from charge-transfer transitions which are characteristic of ruthenium(III)–ammine complexes in this spectral region[14] and which effectively mask most of the ligand field transitions. The calculated extinction values for the maxima at 275 mμ for both $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ vary with the nature and concentration of the supporting electrolyte. The observed spectral effects are different for the two complexes. Experiments using the spectra of the various complexes were carried out in media for which the extinction coefficients were known.

TABLE I

EXTINCTION COEFFICIENTS FOR THE ABSORPTION MAXIMA IN THE SPECTRA OF HEXAAMMINERUTHENIUM(II) AND -(III) AND TRIS(ETHYLENEDIAMINE)RUTHENIUM(II) AND -(III)

Complex	Medium	λ_1, mμ	ϵ_1^a	λ_2, mμ	ϵ_2^a
$Ru(NH_3)_6^{2+}$	0.1 *M* $NaClO_4$	~400	~30	275	624 ± 10
$Ru(NH_3)_6^{3+}$	0.1 *M* $NaClO_4$	~320	~100	275	475 ± 10
$Ru(en)_3^{2+}$	0.01*M* HTFA	370	120 ± 10	302	1020 ± 60
$Ru(en)_3^{3+}$	0.01*M* HTFA	...	...	310	360 ± 25

[a] ε values are given in units of M^{-1} cm^{-1}.

Apparatus and Techniques.—All operations with air-sensitive reagents were carried out under nitrogen. Syringe techniques were used for the transfer of air-sensitive solutions. The ammine-ruthenium self-exchange reactions were carried out in D_2O, and a dry stream of nitrogen which had been bubbled through D_2O was used for deaeration.

Rate studies of the reactions of the ruthenium complexes were made spectrophotometrically, largely in the very near-infrared spectral region. A Cary Model 14 spectrophotometer fitted with a thermostated cell compartment was used. Changes in N–H and O–H overtone stretching absorptions were observed using a 0.0–0.1 expanded-scale slidewire and 2-, 5-, and 10-cm spectrophotometric cells. Total optical density changes of about 0.01–0.10 were observed, depending on the cell path lengths and reactant concentrations.

Reactions were initiated by the injection of a small volume of one reactant into the bulk of the reaction volume which was in a cylindrical spectrophotometric cell. The cell was stoppered with a serum cap. Under optimal conditions, the injection procedure and subsequent mixing were completed and the spectrophotometer turned on in 5–7 sec.

Very rapid reactions were followed with a stopped-flow apparatus. The apparatus was constructed by Stritar[15] and was designed essentially as described by Dulz.[16]

Electrochemical measurements were carried out under nitrogen and were made with a Beckman 39186 Pt–Ag|AgCl, KCl (saturated) combination electrode attached to a Beckman Expandomatic pH meter. The Ag|AgCl reference electrode was checked against an external saturated calomel electrode. Measurements were made at constant temperature by immersion of the electrode apparatus in a constant-temperature bath. The supporting electrolyte was sodium perchlorate–perchloric acid.

Measured emf values for deaerated solutions containing both oxidation states of the hexaammine, trisethylenediamine, and aquopentaammineruthenium complexes included contributions from liquid junction effects. Measurements of emf for the Fe(II)–Fe(III) couple were made in the same media with the same electrode. The external potentials for the electrode in a given ionic medium were calculated by comparing the observed emf values of the Fe(II)–Fe(III) couple with values for the same couple in the same medium, measured in a cell with no liquid junction potentials.[17]

Corrections for the hydrolysis of Fe(III) were calculated from the data of Milburn and Vosburg.[18] The measured emf values for solutions containing equal concentrations of the two oxidation states at various ionic strengths were then corrected, using the calculated liquid junction effects at the given ionic strength.

Results

Standard Oxidation Potentials.—Solutions of the ruthenium complexes in the two oxidation states were mixed under nitrogen in the electrode apparatus. The emf values became stable shortly after mixing and remained stable for at least 10–15 min. Measurements for the $Ru(NH_3)_5OH_2^{2+,3+}$ couple drifted steadily to more negative values, in part, at least, because of the fairly rapid perchlorate ion oxidation of $Ru(NH_3)_5$-

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(12) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

(13) D. E. Harrison, *et al.*, work in progress.

(14) H. Hartmann and C. Buschbeck, *Z. Physik. Chem.*, **11**, 120 (1957).

(15) J. A. Stritar, Ph.D. Thesis, Stanford University, 1967.

(16) G. Dulz, Ph.D. Thesis, Columbia University, New York, N. Y., 1962.

(17) W. C. Schumb, M. S. Sherrill, and S. B. Sweetser, *J. Am. Chem. Soc.*, **59**, 2360 (1937).

(18) R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

OH_2^{2+}.[2] The initial potentiometer reading was used for this couple.

In Table II the data for the three couples at various ionic strengths are summarized.

To obtain standard oxidation potentials for the hexaammine and trisethylenediamine couples at infinite dilution, the variation of the measured oxidation potentials with ionic strength was assumed to be of the form

$$E = E^\circ - a\mu + 2.02(0.592)\frac{\mu^{1/2}}{1 + \mu^{1/2}} \qquad (1)$$

by analogy with the Fe(II)–Fe(III) couple.[17] Values for a were chosen to make E° constant as calculated from the above equation, using values of E and μ from Table II. The best fits were obtained for $a = 0.01$ for the ethylenediamine couple and $a = 0.05$ for the hexaammine couple. The E° value for the aquopentaammine couple was estimated using the ionic strength extrapolation for the hexaammine couple. Plots of E *vs.* $[-a\mu + 0.1195\mu^{1/2}/(1 + \mu^{1/2})]$ are given in Figure 1, and the E° values for the three couples are given in Table II.

Table II

Oxidation Potentials for the Hexaammine-, Aquopentaammine-, and Tris(ethylenediamine)-ruthenium (II, III) Couples at 25.0 ± 0.2°[a]

Couple	μ	$-E_{\text{measd}}$,[b] V	ΔE,[c] V	$-E$,[d,e] V	$-E^\circ$, V[f]
$Ru(NH_3)_6^{2+,3+}$	0.21	0.088	0.015	0.073	0.10 ± 0.01
$Ru(NH_3)_6^{2+,3+}$	0.061	0.092	0.012	0.080	...
$Ru(NH_3)_6^{2+,3+}$	0.011	0.099	0.009	0.090	...
$Ru(en)_3^{2+,3+}$	0.21	0.187	0.015	0.172	0.21 ± 0.01
$Ru(en)_3^{2+,3+}$	0.061	0.196	0.012	0.184	...
$Ru(en)_3^{2+,3+}$	0.011	0.206	0.009	0.197	...
$Ru(NH_3)_5OH_2^{2+,3+}$	0.011	0.16	0.01	0.15 ± 0.01	0.16

[a] [Ru(II)] = [Ru[III)] and is 1.00×10^{-4}, 0.96×10^{-4}, and 1.02×10^{-4} *M* for the hexaammine, tris-en, and aquopentaammine couples; $[HClO_4] = 1.00 \times 10^{-2}$ *M*. [b] $E_{\text{measd}} = -0.199$ V − emf reading and is uncorrected for junction potentials. [c] ΔE is the external potential for a given ionic strength calculated from measurements on the Fe(II)–(Fe(III) couple as described in the previous section. [d] E is the oxidation potential corrected for the junction potential by $E = E_{\text{measd}} + \Delta E$. [e] The estimated error limits are ±0.002, except where otherwise noted. [f] Because there are discrepancies between the values of E° reported here and those reported earlier, it was considered worthwhile to check at least one of the values in the table. Dr. J. R. Kuempel has made measurements in the cell

$$Hg|RuA_6^{3+}, RuA_6^{2+}, KCl\ (a = 1\ M)|KCl\ (a = 1\ M), AgCl(s)|Ag$$

and has obtained the value 0.095 ± 0.004 V as E° for the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ half-reaction.

The Direct Determination of the $Ru(NH_3)_6^{2+}$–$Ru(ND_3)_6^{3+}$ and $Ru(en)_3^{2+}$–$Ru(enD)_3^{3+}$ Self-Exchange Reactions.—The rates of self-exchange reactions have most often been studied by using radioactive-tracer techniques, but in some cases nmr and epr line-broadening methods have also been successful. The exchange reactions studied here were so rapid that the radioactive tracer method was deemed to be of marginal utility. In attempts to observe the epr spectrum of paramagnetic $Ru(NH_3)_6^{3+}$ in aqueous solution, no signal was observed. The nmr method based on observing the proton magnetic resonances of the coordinated ligands, although in principle applicable, proved to be experimentally unfeasible because $Ru(NH_3)_6^{2+}$ at the high concentrations called for proved to be unstable. The slight differences in the changes in shape of the ultraviolet charge-transfer bands of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$, upon deuteration of the complexes, also seemed to provide a means for studying the reactions. After some trials, this technique was abandoned, partly because of the experimental difficulties encountered, because of the small differences in absorption, but mainly because of the success promised by the infrared techniques described below.

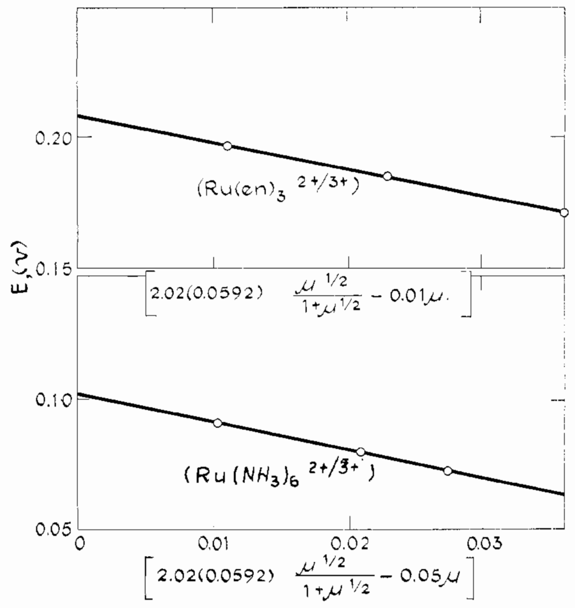

Figure 1.—The variation of E *vs.* ionic strength for the $Ru(NH_3)_6^{2+,3+}$ and $Ru(en)_3^{2+,3+}$ couples.

The ir spectra of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ in 0.1 *M* DTFA from 1.3 to 1.8 μ are given in Figure 2. The spectra are qualitatively similar to the spectrum of $Co(NH_3)_6^{3+}$.[19] The maxima at 1.5 μ are overtone N–H stretching absorptions. The spectral differences between the protonated $Ru(en)_3^{2+}$ and $Ru(en)_3^{3+}$ complexes are qualitatively the same, but the maximum difference in optical density occurs at about 1.57 μ. The deuterated complexes do not absorb appreciably in this region.

The differences in the spectra of the two oxidation states when protonated make it possible to follow the rate of the reaction

$$Ru(NH_3)_6^{2+} + Ru(ND_3)_6^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ru(ND_3)_6^{2+} + Ru(NH_3)_6^{3+} \qquad (2)$$

directly by observing the change in optical density with time near 1.55 μ (1.57 μ for the ethylenediamine complexes). In fairly acidic media, deuterium–hydrogen exchange between the complexes and solvent is negligibly slow.

For the self-exchange reactions, the spectral changes

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(19) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

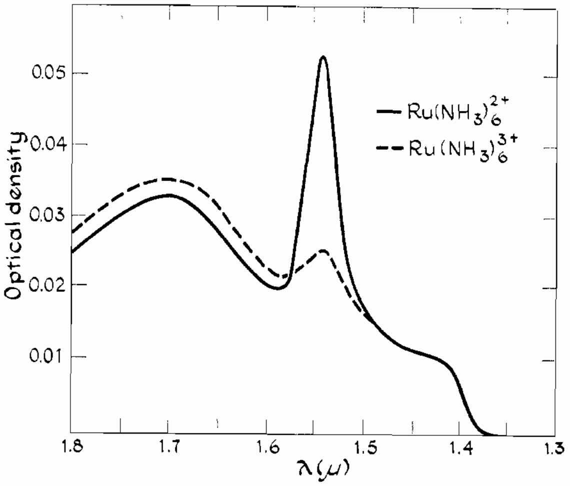

Figure 2.—The near-infrared spectra of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ in D_2O.

with time refer to the rate of isotopic equilibration of deuterium and hydrogen between the Ru(II) and Ru(III) complexes. The rate of isotopic exchange is related to the rate of chemical reaction carrying the exchange by the McKay equation

$$Rt = \frac{AB}{A + B}\ln(1 - F) \tag{3}$$

where F is the fraction of exchange at time t. If A and B are in gram-atoms per liter of exchanging atoms, R is expressed in gram-atoms per liter per unit time. Rearranging eq 3 and relating $1 - F$ to the observed optical density changes gives

$$\frac{A + B}{2.3AB}Rt + \log(A_\infty - A_0) = \log(A_\infty - A_t) \tag{4}$$

where A_0, A_t, and A_∞ are the optical densities at times 0, t, and ∞, respectively. From a plot of $\log(A_\infty - A_t)$ *vs.* t, k_{ex} was evaluated where

$$k_{ex} = \frac{A + B}{2.3AB}R \qquad R = \frac{k_{ex}AB}{A + B} \tag{5}$$

If the reaction carrying the exchange is first order in each of the complexes, then $R/18 = k_1[\mathrm{Ru(III)}][\mathrm{Ru(II)}]$ where the quantities in brackets denote the molar concentrations of the complexes; k_1 will have the dimensions of $M^{-1}\ sec^{-1}$, and

$$k_1 = \frac{k_{ex}}{[\mathrm{Ru(II)}](\mathrm{Ru(III)}]} \tag{6}$$

Note each mole of complex contains 18 g-atoms of hydrogen.

The reactions were initiated by adding aliquots of solutions of $Ru(NH_3)_6^{2+}$ (or $Ru(en)_3^{2+}$) in 0.01 M DTFA or $DClO_4$ to the bulk of solution in 5- or 10-cm cylindrical cells which contained $Ru(ND_3)_6^{3+}$ (or $Ru(enD)_3^{3+}$) in the same medium. The short half-lives for the reactions, the uncertainties in the volumetric procedure, and the small optical density changes combined to limit the reproducibilities of the rate constants to about ±15%.

Summaries of the kinetic data for the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ self-exchange reactions are given in Table III. Activation parameters for the $Ru(NH_3)_6^{2+,3+}$ self-exchange reaction were evaluated from plots of $\log(k_1/T)$ *vs.* $1/T$, using the reaction rate theory expression

$$\ln(k/T) = \ln(k_B/h) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \tag{7}$$

where k_B is Boltzmann's constant, h is Planck's constant, and $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the enthalpies and entropies of activation, respectively. When a plot is made from the results of the first 12 experiments of Table III, the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for self-exchange in the $Ru(NH_3)_6^{2+,3+}$ reaction are found to be 10.3 ± 1.0 kcal/mol and −11 ± 3 eu.

TABLE III

THE ELECTRON-EXCHANGE REACTION BETWEEN HEXAAMMINERUTHENIUM(II) AND HEXAMMINERUTHENIUM(III) AT $\mu = 0.013^a$ IN D_2O

$10^4[Ru(NH_3)_6^{2+}]$, M	$10^4[Ru(ND_3)_6^{3+}]$, M	10^2k_{ex}, sec^{-1}	$10^{-1}k_1$, $M^{-1}\ sec^{-1}$	Temp,[b] °C
6.4	6.4	23	18	1.2
6.4	6.4	19	15	0.8
3.2	3.2	19	29	8.0
3.2	3.2	16	25	8.0
2.13	2.15	15	36	15.0
2.13	1.15	16	39	15.0
1.07	1.07	15	74	25.0
1.07	1.07	18	89	25.0
1.07	1.07	19	92	25.0
2.15	2.15	19	45	15.0
3.2	3.2	10	16	1.0
1.07	1.07	17	82	25.0
1.55	2.58	20	48	15.0
1.81	2.60	24	51	15.0
1.46	2.32	16	43[c]	15.0

[a] The electrolyte was 0.01 M DTFA. [b] All temperature values are quoted to ±0.1°. [c] In 0.01 M $DClO_4$.

Later attempts to reproduce the rate constants for the hexaammine self-exchange reaction gave values consistently greater, by as much as a factor of 2 or 3, than the earlier results which are recorded in Table III. By repeated purification of the starting material, it was found possible to reproduce the initial values, and we have some confidence, therefore, that the results presented describe the intrinsic rate of self-exchange for the hexaammine system.

The situation with respect to the ethylenediamine complexes is much less clear, however. Here, as in the work with the hexaammine species, at a certain stage the rates unexplainedly increased, but in this case we were unable, even after using different sources (that is, the $ZnCl_4^{2-}$, $ZnBr_4^{2-}$, or Br^- salts) and methods of purification of the complexes, to reproduce the earlier slower rates.

For a large number of experiments, the specific rates, k, measured for the $Ru(en)_3^{2+,3+}$ exchanges at 25° and $\mu = 0.013$ (concentrations covering the range 1×10^{-4}–6×10^{-4} M) were less than 2.4×10^2, with a large number of values clustering about 2×10^2. Relying on the principle that reaction by an intrinsic path cannot be inhibited but a new reaction path can always be encountered, we feel confident that 2×10^2 M^{-1} sec^{-1} represents an upper limit on the specific rate of self-exchange in the $Ru(en)_3^{2+,3+}$ system under our experimental conditions.

Because of experimental difficulties, the net chemical reaction between $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{3+}$ was not studied very extensively. However, by using the ir technique just described, cursory experiments indicated that the rate constant for the reaction between $Ru(NH_3)_6^{2+}$ and $Ru(enD)_3^{3+}$ in 0.01 M DTFA or $DClO_4$ is 500–600 M^{-1} sec^{-1} at 15°.

Attempted Indirect Determination of the $Ru(NH_3)_6^{3+}$–$Ru(ND_3)_6^{3+}$– Self-Exchange Reaction.—Basolo, Palmer, and Pearson[20] and Palmer and Basolo[21] have determined the rates of deuterium exchange for hydrogen in a series of metal–ammine complexes in D_2O. Their techniques were used to study the rates of deuterium exchange for hydrogen in $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_6^{3+}$, $Ru(en)_3^{2+}$, and $Ru(en)_3^{3+}$. Reactions involving the Ru(II) complexes were carried out under nitrogen, by syringing an aliquot of an acidic, deaerated solution of Ru(II) into a cylindrical spectrophotometric cell which contained a deaerated buffer solution. The reactions were followed spectrophotometrically by observing the rate of decrease of the N–H band at 1.55 μ or the rate of increase of the solvent O–H band at 1.65 μ, as described in ref 19.

The rates of deuterium exchange for hydrogen are first-order in $[OD^-]$ and first-order in the concentration of exchanging hydrogens in gram-atoms per liter. The concentration of OD^- was held constant during a reaction by using solutions buffered with NaOAc–DOAc. By varying the buffer ratio, $[OD^-]$ was varied for different runs; its concentration was calculated using $pK_a = 5.26$ for deuterioacetic acid at 25°,[22] and $K_{D_2O} = 0.15 \times 10^{-14}$ at 25°.[23]

The reactions were carried out in D_2O of high percentage deuterium and at low complex concentration. Under these conditions the net chemical reaction is

$$H_{Ru} + D_2O \rightleftharpoons D_{Ru} + HDO \qquad (8)$$

where the equilibrium isotopic distribution is approached from far to the left. The rate of isotopic equilibration can be followed spectrophotometrically. For the first several half-lives, only the reaction from the left in eq 8 is important, and, at equilibrium, the complex is nearly completely deuterated. Since only the forward rate is observed for the first several half-lives

$$Rt = -H_a \ln (1 - F) = -H_a \ln \left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) \qquad (9)$$

R is the net rate of isotopic exchange in gram-atoms per liter per second, H_a is the sum of deuterium and hydrogen in the complex, and the fraction of exchange has been expressed in terms of the observed changes in optical density. From plots of log $(A_t - A_\infty)$ *vs.* t

$$R = k_{ex}H_a = k[OD^-]H_a \qquad (10)$$

The values of k found for the four complexes are given in Table IV.

TABLE IV

THE RATES OF HYDROGEN–DEUTERIUM EXCHANGE FOR SOME RUTHENIUM–AMMINE COMPLEXES IN D_2O AT 25.0 ± 0.1°

Complex	10^4[Ru], M	10^{10} [OD$^-$], M	[OAc$^-$],^{a} M	[DOAc], M	10^3k_{ex}, sec^{-1}	$10^{-7}k$, l. g-atom^{-1} sec^{-1}
$Ru(NH_3)_6^{2+}$	3.3	3.8	0.125	0.075	4.3	1.1
$Ru(NH_3)_6^{2+}$	3.29	1.9	0.185	0.015	2.4	1.2
$Ru(NH_3)_6^{2+}$	3.7	3.8	0.125	0.075	7.0	1.7
$Ru(NH_3)_6^{2+}$	3.26	6.5	0.150	0.050	9.5	1.5
$Ru(NH_3)_6^{2+}$	3.4	2.2	0.100	0.100	2.8	1.3
$Ru(en)_3^{2+}$	4.5	3.8	0.125	0.075	1.9	0.50
$Ru(en)_3^{2+}$	4.5	6.5	0.125	0.042	3.8	0.59
$Ru(NH_3)_6^{3+}$	10.1	0.30	0.10	0.90	67	230
$Ru(NH_3)_6^{3+}$	10.6	0.68	0.10	0.40	135	200
$Ru(NH_3)_6^{3+}$	5.93	0.46	0.10	0.60	122	270
$Ru(en)_3^{3+}$	7.65	0.30	0.10	0.90	129	430
$Ru(en)_3^{3+}$	6.18	0.46	0.10	0.60	322	480

[a] $\mu = [OAc^-] + 0.01$.

From the results of Table IV, $Ru(NH_3)_6^{3+}$ and $Ru(en)_3^{3+}$ exchange deuterium for hydrogen more rapidly than do the corresponding Ru(II) complexes. If the rate of electron transfer between $Ru(NH_3)_6^{2+}$ and $Ru(ND_3)_6^{3+}$ is fast enough, the exchange of hydrogen in $Ru(NH_3)_6^{2+}$ for deuterium in D_2O will be catalyzed by $Ru(ND_3)_6^{3+}$ by

$$Ru(NH_3)_6^{2+} + Ru(ND_3)_6^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(ND_3)_6^{2+} + Ru(NH_3)_6^{3+} \qquad (11)$$

$$Ru(NH_3)_6^{3+} \xrightarrow{k_2[OD^-]} Ru(ND_3)_6^{3+} \qquad (12)$$

The catalyzed exchange will compete with the direct exchange of $Ru(NH_3)_6^{2+}$ with D_2O

$$Ru(NH_3)_6^{2+} \xrightarrow{k_3[OD^-]} Ru(ND_3)_6^{2+} \qquad (13)$$

If, for the catalyzed exchange, $[Ru(II)] \gg [Ru(III)]$, the net reaction observed is still isotopic exchange between Ru(II) and solvent, and, from eq 10, $R = k_{ex}H_a$.

In principle, then, the catalysis by $Ru(NH_3)_6^{3+}$ of the exchange of hydrogen between $Ru(NH_3)_6^{2+}$ and solvent provides a means of measuring the rate of electron exchange between $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$, and a large number of experiments were done directed to this end. These are not reported in detail here because the method proved to be less precise than the direct method which we have already described. Concentration conditions can be found under which electron transfer is rate determining or under which H exchange on $Ru(NH_3)_6^{3+}$ is rate determining. Only the former concentration region is interesting for the present purposes, and it was difficult to make precise measurements under the conditions required. A large body of data[24] is consistent with a value of $k_1 = 4 \times$

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[20] F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Phys. Chem.*, **64**, 778 (1960).

[21] J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem.*, **15**, 275 (1960).

[22] R. Gary, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, **69**, 2750 (1965).

[23] R. Kingerley and V. K. LaMer, *J. Am. Chem. Soc.*, **63**, 3260 (1941).

[24] T. E. Meyer, Ph.D. Thesis, Stanford University, 1966.

10^3 at $\mu = 0.16$ and 25°. This value is reasonable in comparison with that at lower ionic strength obtained by the direct method. The data (measured, it should be appreciated, as rate of exchange in $Ru(NH_3)_6^{2+}$ catalyzed by $Ru(NH_3)_6^{3+}$), moreover, lead to an independent determination of the rate of hydrogen exchange between $Ru(NH_3)_6^{3+}$ and solvent. The value of $k = 4 \pm 1 \times 10^9$ g-atoms l.$^{-1}$ sec^{-1} determined indirectly in this way is in reasonable agreement with $k = 2.3 \times 10^9$ l. g-atom^{-1} sec^{-1} as reported in Table IV.

In this series, as in the others which have been described, catalytic effects set in at a certain stage in the experiments. Catalysis was observed only in the concentration region in which the rate of electron transfer governs the net change observed and did not appear to affect the rate of hydrogen exchange between $Ru(NH_3)_6^{3+}$ and solvent.

The Rates of Oxidation of Hexaammineruthenium(II), Tris(ethylenediamine)ruthenium(II), and Aquopentaammineruthenium(II) by Fe(III).—The stoichiometries of the oxidations of hexaammineruthenium(II) and tris(ethylenediamine)ruthenium(II) by Fe(III) were shown to be 1:1, by oxidizing solutions of the reduced species with Fe(III) and determining the Fe(II) produced spectrophotometrically, as described in the Experimental Section. Measurements of the rates of the reactions were made using a stopped-flow apparatus. The reactions were followed at 240 mμ, which is an absorption maximum for $Fe(H_2O)_6^{3+}$.

If the only kinetically important species of Fe(III) in the reactions are Fe^{3+} and $Fe(OH)^{2+}$, which are related by the hydrolysis equilibrium

$$Fe^{3+} \overset{K_h}{\rightleftharpoons} FeOH^{2+} + H^+ \tag{14}$$

the rate equation in terms of the total concentration of Fe(III) is

$$-d[Fe_T(III)]/dt = k_a[Fe^{3+}][Ru(II)] + k_h[FeOH^{2+}][Ru(II)]$$

Relating $[Fe(OH)^{2+}]$ to the total Fe(III) concentration, $[Fe_T(III)]$, K_h, and $[H^+]$ gives

$$\frac{-d[Fe_T(III)]}{[Ru(II)][Fe_T(III)]} = \left[\left(k_a + k_h\frac{K_h}{[H^+]}\right)\Big/\left(1 + \frac{K_h}{[H^+]}\right)\right] dt$$

Integration of the differential equation for second-order reactions at unequal reactant concentrations leads to the expression

$$\log\left[\frac{((b/a) - 1)(A_0 - A_\infty)}{A_t - A_\infty} + 1\right] = \frac{(b - a)k_{obsd}}{2.3} + \log(b/a) \tag{15}$$

where

$$k_{obsd} = \left[k_a + k_h\frac{K_h}{[H^+]}\right]\Big/\left[1 + \frac{K_h}{[H^+]}\right] = \frac{k_a - k_h}{1 + (K_h/[H^+])} + k_h \tag{16}$$

and the reaction variables are related to the observed optical density changes.

From plots of k_{obsd} *vs.* $1 + (K_h/[H^+])$, $k_{obsd} = k_h$ at the intercept corresponding to $[H^+] = 0$, and $k_{obsd} = k_a$ at the intercept where $K_h/[H^+] = 0$. The value of K_h from eq 14 was calculated to be 1.3×10^{-3} at 10° and $\mu = 0.10$ from the data of Milburn and Vosburgh.[18] In Table V are values of k_{obsd} at various $[H^+]$ for the three reactions. Plots of k_{obsd} *vs.* $1/\{1 + (K_h/[H^+])\}$ are given in Figures 3 and 4, and the corresponding values for k_a and k_h, which represent the acid-independent and acid-dependent paths, respectively, for the three reactions are given in Table VI. The linearity of the plots indicates that, in the pH range studied, the only Fe(III) species participating to any extent in the reactions are Fe^{3+} and $FeOH^{2+}$, as assumed.

TABLE V

THE RATES OF THE IRON(III) OXIDATION OF HEXAAMMINERUTHENIUM(II), AQUOPENTAAMMINERUTHENIUM(II), AND TRIS(ETHYLENEDIAMINE)RUTHENIUM(II) AT 10.0 ± 0.10° AND $\mu = 0.10$[a]

Complex	$10^5[Fe_T(III)]$, M	$10^5[Ru(III)]$, M	$[H^+]$, M	$1 + (K_a/[H^+])$[b]	$10^{-4}k_{obsd}$, M^{-1} sec^{-1}
$Ru(NH_3)_6^{2+}$	22.2	11.0	0.102	0.127	30.8
$Ru(NH_3)_6^{2+}$	11.8	5.05	0.0105	1.124	25.9
$Ru(NH_3)_6^{2+}$	4.45	11.2	0.0022	1.592	19.1
$Ru(NH_3)_6^{2+}$	11.3	5.65	0.0044	1.295	27.4
$Ru(NH_3)_6^{2+}$	11.3	5.50	0.100	1.030	30.0
$Ru(NH_3)_6^{2+}$	11.8	5.30	0.0024	1.542	23.7
$Ru(NH_3)_6^{2+}$	4.45	11.8	0.0013	2.00	15.9
$Ru(en)_3^{2+}$	11.8	5.30	0.10	1.103	9.48
$Ru(en)_3^{2+}$	11.8	5.20	0.10	1.103	9.27
$Ru(en)_3^{2+}$	8.90	3.82	0.0014	1.930	5.98
$Ru(en)_3^{2+}$	8.90	3.59	0.0024	1.930	5.08
$Ru(en)_3^{2+}$	8.90	3.58	0.0024	1.542	6.65
$Ru(en)_3^{2+}$	8.90	3.59	0.0024	1.542	7.00
$Ru(NH_3)_5OH_2^{2+}$	8.90	4.16	0.100	1.013	8.70
$Ru(NH_3)_5OH_2^{2+}$	8.90	3.89	0.0103	1.126	12.0
$Ru(NH_3)_5OH_2^{2+}$	8.90	4.37	0.0023	1.565	22.0
$Ru(NH_3)_5OH_2^{2+}$	7.40	4.78	0.0014	1.930	26.5

[a] μ was maintained with $LiClO_4$ and $HClO_4$. [b] K_h is the equilibrium constant for the hydrolysis of Fe^{3+} and is 1.3×10^{-3} at $\mu = 0.10$ and 10.0° as calculated from the data of ref 18.

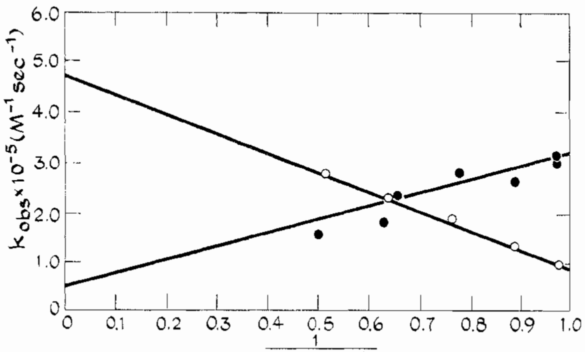

Figure 3.—The variation with $[H^+]$ of the rates of reaction between $Ru(NH_3)_6^{2+}$ and Fe(III) (filled circles) and between $Ru(NH_3)_5OH_2^{2+}$ and Fe(III) (open circles). The abscissas for the two filled circles at the extreme right should be 0.988 rather than 0.971. This change does not affect the calculated parameters within the limits of experimental error.

For the hexaammineruthenium(II) and tris(ethylenediamine)ruthenium(II) reactions in 0.1 M $HClO_4$ at 10°, more than 99% of the reaction occurs by the acid-independent path. The variation with temperature of k_a in 0.10 M $HClO_4$ was studied and the results are shown in Table VII. The values of $\Delta H^{\ddagger}$ are found to be 3.2 ± 0.5 and 4.3 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ values

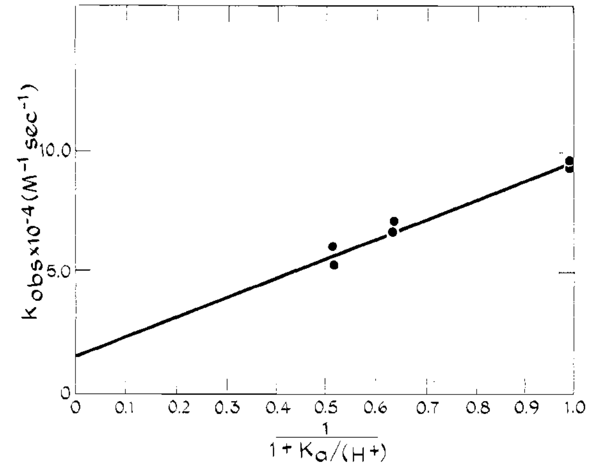

Figure 4.—The variation with [H$^+$] of the rate of the reaction between Ru(en)$_3^{2+}$ and Fe(III).

TABLE VI

RATE CONSTANTS[a] FOR THE ACID-INDEPENDENT AND ACID-DEPENDENT PATHS IN THE IRON(III) OXIDATIONS OF HEXAAMMINERUTHENIUM(II), TRIS(ETHYLENEDIAMINE)RUTHENIUM(II), AND AQUOPENTAAMMINERUTHENIUM(II) AT 10.0 ± 0.1° AND μ = 0.10

Reductant	$10^{-4}k_a$, M^{-1} sec^{-1}	$10^{-4}k_h$, M^{-1} sec^{-1}
Ru(NH$_3$)$_6^{2+}$	31.0 ± 2.0	5.0 ± 3.0
Ru(en)$_3^{2+}$	9.4 ± 0.5	1.5 ± 1.0
Ru(NH$_3$)$_5$OH$_2^{2+}$	8.0 ± 0.5	48.0 ± 05.

[a] k_a and k_h were evaluated from the intercepts of Figures 3 and 4.

TABLE VII

THE VARIATION WITH TEMPERATURE[a] OF ACID-INDEPENDENT RATE CONSTANTS FOR THE IRON(III) OXIDATION OF HEXAAMMINERUTHENIUM(II) AND TRIS(ETHYLENEDIAMINE)RUTHENIUM(II) AT μ = 0.10[b]

10^5[Fe(III)], M	10^5[Ru(III)], M	$10^{-4}k_a$,[c] M^{-1} sec^{-1}	Temp,[d] °C
	Ru(NH$_3$)$_6^{2+}$		
11.8	4.90	24.6	2.0
11.8	4.90	35.3	17.0
11.8	5.20	35.8	17.0
	Ru(en)$_3^{2+}$		
11.8	5.20	11.3	18.0
11.8	5.20	11.2	18.0
11.8	5.40	14.1	25.0
3.87	7.40	14.0	25.0

[a] See Table V for data at 10.0°. [b] Ionic strength was maintained with 0.10 M HClO$_4$. [c] Under these conditions $k_{obsd} \approx k_a$. [d] The given temperatures were known to ±0.1°.

were -22 ± 2 and -22 ± 2 eu for Ru(NH$_3$)$_6^{2+}$ and Ru(en)$_3^{2+}$, respectively.

Because the reactions between Fe^{3+} and the Ru(II) complexes are so rapid, the rates of electron transfer are faster than the rate of formation of FeX^{2+} from Fe^{3+} and X$^-$ for the reaction conditions used.[25] If the Fe(III) solution contains X$^-$ before the oxidation–reduction reaction is initiated, Fe^{3+} and the various Fe(III)–X$^-$ complexes will react with Ru(II) as independent species. The effect on the rate of electron transfer of X$^-$ in the inner coordination of Fe(III) can be studied by observing the rate of disappearance of the FeX^{2+} species. If X$^-$ is in the Ru(II) solution before mixing, but not in the Fe(III) solution, the observed effect on the rate constants will be an ion-atmosphere or outer-sphere effect, because now the redox reaction is completed before the substitution of X$^-$ into Fe(III) becomes important.

The relative inner and outer coordination sphere effects for X$^-$ = Cl$^-$ were studied for the hexaammine- and tris(ethylenediamine)ruthenium(II) reactions. For the reactions with FeCl^{2+} the value of K for the equilibrium Fe^{3+} + Cl$^-$ $\rightleftarrows$ FeCl^{2+} at μ = 0.20 and 10° was calculated to be 4.0 M^{-1} from the data of ref 26, assuming that ΔH for the equilibrium was approximately independent of μ for μ = 0.50–0.20. The calculations of K were based on μ = 0.20, since, for the inner coordination sphere reaction with Cl$^-$, the Fe(III) solution contained 0.10 M HClO$_4$ and 0.10 M HCl before mixing.

The inner and outer coordination sphere effects of Cl$^-$ for the two reactions are given in Table VIII. The reactions with Fe^{3+} as oxidant were followed spectrophotometrically at 240 mμ and with FeCl^{2+} at the absorption maximum for FeCl^{2+} at 336 mμ, where neither Fe^{3+} nor FeOH^{2+} absorbs appreciably. For comparison, the values of k_a for the reactions in 0.10 M HClO$_4$ are also given in Table VIII.

TABLE VIII

THE INNER AND OUTER SPHERE COORDINATION EFFECTS OF CHLORIDE ION ON THE RATES OF OXIDATION OF HEXAAMMINERUTHENIUM(II) AND TRIS(ETHYLENEDIAMINE)RUTHENIUM(II) BY FE(III) AT 10.0 ± 0.1° AND μ = 0.10[a]

Reductant	10^5-[Fe-(III)], M	10^5-[Ru-(II)], M	10^5-[Fe-Cl^{2+}], M	10^5-k, M^{-1} sec^{-1}	Position[b] of Cl$^-$	10^5k,[c] M^{-1} sec^{-1}
Ru(NH$_3$)$_6^{2+}$	4.45	11.4	. . .	3.97	OS	3.04
Ru(NH$_3$)$_6^{2+}$	14.8	6.60	10.0	>200	IS	. . .
Ru(en)$_3^{2+}$	2.96	7.35	. . .	1.72	OS	0.94
Ru(en)$_3^{2+}$	14.8	5.60	9.87	>200	IS	. . .

[a] μ = 0.05 M HCl + 0.05 M HClO$_4$. [b] OS refers to outer coordination sphere Cl$^-$ ion; IS refers to Cl$^-$ ion in the inner coordination sphere of Fe^{3+}. [c] k in 0.1 M HClO$_4$ from Table V.

In contrast to the self-exchange reactions, the rates of the Fe(III) reactions were reproducible and independent of the source of the Ru(II) complexes.

Discussion

Standard Oxidation Potentials and the Characterization of the Ethylenediamine Complexes.—The results described in the Experimental Section demonstrate that acidic solutions of tris(ethylenediamine)ruthenium(II) under nitrogen retain constant total reducing power and unchanged spectra for at least 1 hr. The similar stability of acidic tris(ethylenediamine)ruthenium(III) solutions and the interchangeability of the two oxidation states by redox reactions ensure that the electron-transfer reactions studied are of the outer-sphere type, as they are for reactions of the hexaammineruthenium(II) and -(III) complexes in acidic solution.[1,2]

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The standard oxidation potentials obtained for the three ruthenium–ammine couples are given in Table IX[27-29] along with oxidation potentials for other ruthenium(II,III) couples. The discrepancy between the $Ru(NH_3)_5H_2O^{2+,3+}$ values reported here and observed by Endicott and Taube may arise from the assumptions used in estimating the latter value. The cause for the discrepancy in the hexaammine case is less clear; however, we feel that the present values, obtained with the advantage of the experience gained in the earlier work, are reliable as reported.

TABLE IX

THE STANDARD OXIDATION POTENTIALS FOR VARIOUS RUTHENIUM(II,III) COUPLES

Couple	$E°$, V	Ref
$RuCl_4^{2-} \rightarrow RuCl_4^- + e^-$	$>0.1^a$	27
$Cl^- + RuCl^+ \rightarrow RuCl_2^+ + e^-$	-0.08^b	28
$Ru(NH_3)_6^{2+} \rightarrow Ru(NH_3)_6^{3+} + e^-$	-0.10 ± 0.01	*c*
$Ru(NH_3)_5OH_2^{2+} \rightarrow$	-0.214	2
$Ru(NH_3)_5OH_2^{3-} + e^-$	-0.16 ± 0.01	*c*
	-0.20	2
$Ru(en)_3^{2+} \rightarrow Ru(en)_3^{3+} + e^-$	-0.21 ± 0.005	*c*
$Ru(H_2O)_6^{2+} \rightarrow Ru(H_2O)_6^{3+} + e^-$	-0.22 ± 0.03	29

[a] Estimated since $RuCl_4^{2-}$ reduces water at pH ~1.5. [b] Potential observed in 1.53 *M* HCl. The small effect on the measured *E* values of ionic strength implies that $RuCl_2^0$ is the electrode-active species. [c] Present work.

As expected, the value for the aquopentaammine couple lies between the hexaammine and hexaaquo values. The comparison between the ruthenium and cobalt hexaaquo and hexaammine couples is worth noting. The standard oxidation potential of the hexaaquocobalt(II,III) couple has been estimated as less than −1.9 V, while for the hexaammine couple Latimer calculates $E°$ as about −0.1 V.[30]

Comments on the Measurements of the Rates of Self-Exchange.—The self-exchange reactions were studied in D_2O with the +3 complex deuterated. Comparisons with other systems must take into account the effects of substituting deuterium for hydrogen in the inner and outer coordination spheres of the reactants. The solvent isotope effect is probably small since k_{H_2O}/k_{D_2O} is about 1 for the outer-sphere reaction between $Co(NH_3)_6^{3+}$ and $Cr(bipy)_3^{2+}$.[31] Inner-sphere substitution of deuterium for hydrogen in the reaction between $Co(NH_3)_6^{3+}$ and $Cr(bipy)_3^{2+}$ gave k_{H_2O}/k_{D_2O} as 1.36.[31] Ratios in the same range might be expected for the two ruthenium self-exchange reactions.

From the indirect infrared technique, k_1 for the hexaammine self-exchange reaction is found to be $(4 \pm 3) \times 10^3\ M^{-1}\ sec^{-1}$ at 25° and $\mu = 0.16$ in NaOAc, which is in fair agreement with $k_1 = 8.2 \times 10^2$ at 25° and $\mu = 0.013$ in DTFA from the direct infrared experiments. Navon has found that $k_1 > 10^2$ at 25° from nmr N^{15} line-broadening experiments.[32]

Rate Effects of Added Electrolytes.—In addition to the expected Debye–Hückel effects of ionic strength on the rates of outer-sphere reactions, specific counterion effects have been observed. Specific counterion effects can be expected because of the large concentration of charge in the activated complexes. In the $Fe(H_2O)_6^{3+}$ oxidations of $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$, the rates observed in 0.05 *M* $HClO_4^-$ and 0.05 *M* HCl are 1.3 and 1.8 times faster, respectively, than the rates in 0.1 *M* $HClO_4$, indicating a specific effect of Cl^- on both reactions. The sulfate ion, even at low concentration, seemed to enhance the rate of the hexaammine self-exchange reaction. On the other hand, the rates of both the hexaammine and ethylenediamine self-exchange reactions are, within experimental error, unaffected by the change from 0.01 *M* DTFA to 0.01 *M* $DClO_4$. Endicott and Taube have found the expected Debye–Hückel behavior in solutions of low ionic strength for the reductions of a series of pentaammine- and tetraamminecobalt(III) complexes by $Ru(NH_3)_6^{2+}$.[2] Unfortunately, the detailed effects of ionic strength and specific anions in the ammineruthenium self-exchange reactions could not be studied because of experimental difficulties.

Comparisons with Other Systems.—The reactions between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_n(H_2O)_{6-n}^{2+}$ have also been studied, and for $n = 3–6$, $k < 3 \times 10^{-12}\ M^{-1}\ sec^{-1}$ at 25°.[33] The slowness of the cobalt reaction has been attributed to the large difference in cobalt–nitrogen bond distances between the two oxidation states (0.6 Å). However, the bond distances have been redetermined recently, and the difference in Co–N bond distances between $Co(NH_3)_6Cl_2$ and $Co(NH_3)_6I_3$ is only 0.15 Å, which is in line with the usual decrease of ionic radius of the metal ion with increasing charge.[34] The anomalous slowness of the cobalt reaction apparently arises mainly from the difference in spin multiplicity of the two exchanging oxidation states. (Direct electron transfer without prior electron rearrangement leaves both products in excited states; electron arrangement prior to electron transfer requires at least one partner to be in an excited state; electron rearrangement concomitant with electron transfer would seem to reduce the probability of the event enormously.)

In contrast to the behavior of the corresponding cobalt complexes, self-exchange for $Ru(NH_3)_6^{2+,3+}$ is more rapid than for $Ru(en)_3^{2+,3+}$. The Ru systems are the simpler in that the complication of drastic electronic reorganization at each center is absent, and it is tempting to ascribe the lower rate of the $Ru(en)_3^{2+,3+}$ complex to the greater bulk of the ligands which prevents the close approach of the reaction partners. This result could, however, not have been predicted with confidence, because, taking into account only the interaction of the ions with the solvent, the opposite order

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TABLE X

THE COMPARISON OF OBSERVED k_{12} VALUES AT 25° TO VALUES CALCULATED FROM EQ 17

Reaction	k_{11},[a] M^{-1} sec^{-1}	k_{22},[b] M^{-1} sec^{-1}	K_{12}[c]		k_{12}, M^{-1} sec^{-1}	
					Calcd	Obsd
$Fe^{3+} + Ru(NH_3)_6^{2+} \rightarrow$	4.2[d]	4.0×10^3 [e,f]	2.1×10^{11}	0.016	7.5×10^6	3.4×10^5 [e]
$Fe^{3+} + Ru(en)_3^{2+} \rightarrow$	4.2	2.0×10^2 [e]	3.3×10^9	0.065	4.2×10^5	8.4×10^4 [e]
$V^{2+} + Ru(NH_3)_6^{3+} \rightarrow$	4×10^3 [e]	1.2×10^{-2} [g]	1.07×10^6	0.35	4.2×10^3	82[h]

[a] Rate of self-exchange for the oxidant. [b] Rate of self-exchange for the reductant. [c] Except where otherwise noted $E°$ values are taken from ref 30 at infinite dilution and 25°. [d] Taken from J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [e] Ph.D Thesis, Stanford University, Stanford, Calif., 1966. [f] 0.17 M NaOAc. [g] Taken from K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). [h] Taken from ref 3.

would have been predicted. In any case, detailed discussion of the implications of the comparison are unwarranted until good data for both couples on rates and activation parameters are in hand. At this stage, the results are mainly useful in suggesting the potential interest in generating comparisons with complexes containing saturated ligands even bulkier than en.

The decrease in the rate of self-exchange in replacing *o*-phen on Ru by en, which is strongly indicated by the comparisons made below,[35] is striking and worthy of comment. The ions are likely of about the same size, and thus the effect of interaction with the solvent is about the same. Since only t_{2g} electrons are present in either oxidation state, the change in dimensions on change in oxidation state is probably less for either couple than it is for $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ and is probably not an important factor affecting the rate difference. The major factor would appear to be electron delocalization which is expected to be much greater when *o*-phen rather than en is the ligand.

The Oxidation of $Ru(NH_3)_6^{2+}$, $Ru(en)_3^{2+}$, and $Ru(NH_3)_5H_2O^{2+}$ by Fe(III).—The Fe(III) reactions with $Ru(NH_3)_6^{2+}$ and with $Ru(en)_3^{2+}$ were free of the problems with catalysis encountered in the Ru(II)–Ru(III) self-exchange reactions. The observed rate constants were satisfactorily reproducible regardless of the source of the Ru(II) complex.

The outer-sphere enhancement of the two rates in the presence of added Cl^- relative to a purely ClO_4^- medium has already been mentioned. The rates of reaction with $FeCl^{2+}$ are faster than with Fe^{3+} by factors of >50 for $Ru(NH_3)_6^{2+}$ and >120 for $Ru(en)_3^{2+}$. Since the reactions with $FeCl^{2+}$ were too rapid to be studied with the techniques used, reactions with other anions were not investigated. Chloride as compared to H_2O in the inner coordination sphere of $Co(NH_3)_5{}^{3+}$ also enhances the rate of outer-sphere reduction.[36]

In contrast to $FeCl^{2+}$ $FeOH^{2+}$ reacts with $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$ a factor of 6 slower than does Fe^{3+}. Similarly, $Co(NH_3)_5OH^{2+}$ reacts more slowly with $Cr(bipy)_3^{2+}$ [31] and $Ru(NH_3)_6^{2+}$ than does $Co(NH_3)_5H_2O^{3+}$ by factors of 1.7 and 100, respectively, even though the inner-sphere reduction of $Co(NH_3)_5OH^{2+}$ by Cr^{2+} is 10^6 times faster than for $Co(NH_3)_5H_2O^{3+}$. The rate decreases emphasize the importance of factors other than electrostatic effects in determining the rates of outer-sphere reactions.

However, the reaction between $FeOH^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ is *faster* by a factor of 6 than the reaction with Fe^{3+}. The second-order rate constant for the reaction at 10° (4.8×10^5 M^{-1} sec^{-1}) is in the same range as the rate of SO_4^{2-} and N_3^- entry into $Fe(H_2O)_5OH^{2+}$ at 25° and faster by >10 than the corresponding rates of halide substitution.[25] The rate is, moreover, considerably faster than the expected rate of substitution into $Ru(NH_3)_5H_2O^{2+}$,[15] and it is likely, therefore, that the reaction is of the outer-sphere type. The increase of 36 in the ratios of k_{OH^-}/k_{H_2O} for the $Fe(III)$–$Ru(NH_3)_6^{2+}$ or –$Ru(en)_3^{2+}$ and $Fe(III)$–$Ru(NH_3)_5H_2O^{2+}$ reactions, although not large, reflects the effect of replacing a coordinated ammonia in Ru(II) by a water molecule, and raises the possibility that proton transfer from Ru^{II}-OH_2 to $Fe^{III}OH$ accompanies electron transfer.

Comparisons between Calculated and Observed Rate Constants.—Marcus has derived an equation for the correlation of rate data for outer-sphere reactions[37]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{17}$$

in which k_{12} is the rate constant of reaction for reactants 1 and 2, k_{11} and k_{22} are the self-exchange rate constants for the two oxidation states of systems 1 and 2, K_{12} is the equilibrium constant for the reaction, and f is a correction term (usually small), calculated from $\ln f = (\ln K_{12})^2/4 \ln (k_{11}k_{22}/Z^2)$, where Z is the collision frequency between uncharged molecules in solution (10^{11} M^{-1} sec^{-1}). The equation applies only to systems of the same charge type with similar ligands and assumes adiabatic mechanisms of electron transfer.

Including the results of the present investigation, all of the parameters of eq 17 are available for the V^{2+} reduction of $Ru(NH_3)_6^{2+}$ and for the Fe^{3+} oxidations of $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$. Values for k_{12} calculated from eq 17 are compared with observed values in Table X.

The calculations are made with several reservations. For the aquo ions, the mechanism of self-exchange is not certain and may not be outer sphere. The reactions were not all studied in the same ionic medium, and the

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[35] Taking account of the lower limit on k for self-exchange in $Fe(o\text{-}phen)_3^{2+,3+}$ as $>3 \times 10^7$ M^{-1} sec^{-1} at 25° (D. W. Larsen and A. C. Wahl, *J. Chem. Phys.*, **43**, 3765 (1965)) and the similarity in terms of electron structure and of reactivity of this couple to $Ru(o\text{-}phen)_3^{2+,3+}$, a similar rate of self-exchange for the latter can be expected.

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deuterium isotope effect for the Ru(II)–Ru(III) self-exchange reactions is not known.

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The Exciton Circular Dichroism and the Absolute Configurations of Molecules Containing Nonidentical Chromophores. The Cases of the Bis(*o*-phenanthroline)-2,2'-bipyridylruthenium(II) and Bis(2,2'-bipyridyl)-*o*-phenanthrolineruthenium(II) Ions

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The exciton theory of optical activity has been applied to dissymmetric systems containing coupled nonidentical chromophores. Calculations have been carried out in order to determine the expected absorption and circular dichroism spectra resulting from the coupling of the long-axis-polarized transitions of the *o*-phenanthroline (phen) and the 2,2'-bipyridyl (bipy) ligands in the two systems $Ru(phen)_2bipy^{2+}$ and $Ru(bipy)_2phen^{2+}$. For the purpose of testing the theory and its assumptions, the two ions $Ru(phen)_2bipy^{2+}$ and $Ru(bipy)_2phen^{2+}$ have been prepared and resolved, and their absorption and circular dichroism spectra have been recorded. It has been found that the correlation between theory and experiment is satisfactory and allows for the determination of the absolute configurations of these molecules.

The purely spectroscopic methods of determining the absolute configurations of dissymmetric molecules rely only on a knowledge of the polarization directions of particular electronic transitions of the molecule. This so-called coupled-oscillator method has been developed for and applied to a variety of systems since it was first set out classically by Kuhn[1] and modified within the formalism of the exciton theory by Moffitt.[2] That the method offers reliable means of arriving at the absolute configurations of inorganic complexes[3-6] of simple organic molecules[7,8] and of regular oligomers and polymers[9,10] has been amply verified by experiment. In all of these systems, however, the exciton exchange is assumed to occur between a set of essentially identical chromophores and formally no account has been taken of the possibility of mixing between nondegenerate transitions, although it has been generally recognized as a possible complication if the system is not judiciously chosen.[11]

It is the purpose of this article to outline briefly the methods for dealing with the nondegenerate problem, to apply it in detail to a number of representative examples, and to show that the treatment is necessary for the determination of the absolute configurations of the ions $Ru(phen)_2bipy^{2+}$ and $Ru(bipy)_2phen^{2+}$.

I. The General Formulation

The formalism of the nondegenerate problem follows closely that used for degenerate systems. Let the system contain n residues, whose ground-state wave functions are represented by χ_i; then the ground-state wave function, Ψ_0, for the total system is given by the product

$$\Psi_0 = \chi_1\chi_2\chi_3\ldots\chi_i\ldots\chi_n \qquad (1)$$

in which any number of the functions, χ, may or may not be the same. We shall suppose for the present purposes that we need consider only one excited state of the individual chromophores of the assembly. This allows us to write the (singly) excited state wave functions, Φ_i, of the system in the following way

$$\Phi_1 = \chi_1'\chi_2\chi_3\ldots\chi_n,\ \Phi_2 = \chi_1\chi_2'\chi_3\ldots\chi_n,\ \text{etc.}$$

or more generally

$$\Phi_i = \chi_1\chi_2\chi_3\ldots\chi_i'\ldots\chi_n \qquad (2)$$

where the primes represent excited-state functions. The total wave function, Ψ_j, corresponding to the jth excited state of the assembly, may therefore be expressed as a linear combination of the unperturbed singly excited-state wave functions, Φ_i, with apposite

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