On the analogy of the dithiocarbamate complexes we assume that a cis configuration is favored in the $Fe(MNT)_2(solv)_2^-$ and $Fe(TDT)_2(solv)_2^-$ complexes. On heating in air, a $Fe(MNT)_2^-$ solution in acetone readily produces[21] $Fe(MNT)_3^{2-}$. When a solution of $Fe(MNT)_2^-$ or of $Fe(TDT)_2^-$ in DMF or in other solvents is evaporated on the vacuum line, the original Mössbauer spectrum is found again.

It is noteworthy that Stukan, *et al.*,[22] in studying the related bis(naphthadithiolato)iron(III) complex (Figure 1, IV), found four-line Mössbauer spectra. The authors discussed the possibility of the simultaneous occurrence of a cis- and trans-solvated complex. According to our view such complexes will not have strongly different Mössbauer spectra; therefore we propose an explanation similar to the one presented for $Fe(dtc)_2Cl$: the spectrum consists of one site with five-coordination [IS = 0.47, QS = 3.0 mm/sec; *cf.* $Fe(TDT)_2^-$ (solid state) IS = 0.59, QS = 3.09 mm/sec] and one site with six-coordinated iron [IS = 0.58, QS = 0.82 mm/sec; *cf.* $Fe(TDT)_2^-$ (in solution) IS = 0.68, QS = 0.85 mm/sec].

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[21] M. Gerloch, S. F. A. Kettle, J. Locke, and J. A. McCleverty, *Chem. Commun.*, **2**, 29 (1966).

[22] R. A. Stukan, V. I. Goldanskii, E. F. Makarov, and E. G. Ruchadse, *Zh. Strukt. Khim.*, **8**, 239 (1967).

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# Substitution Reactions of Ruthenium(III)–Ethylenediamine and Related Complexes. III. Halide Anation of *cis*-Diaquobis(ethylenediamine)-, *cis*-Halogenoaquobis(ethylenediamine)-, and Aquopentaammineruthenium(III) Complexes

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Chloride and bromide anation of *cis*-$Ru(H_2O)_2(en)_2^{3+}$, *cis*-$RuCl(H_2O)(en)_2^{2+}$, and *cis*-$RuBrH_2O(en)_2^{2+}$ and chloride, bromide, or iodide anation of $RuH_2O(NH_3)_5^{3+}$ have been studied spectrophotometrically. The kinetics fit a rate law $-d[\text{complex}]/dt = k_{AN}[\text{halide}][\text{complex}]$ with $k_{AN}$ typically $10^{-3}\ M^{-1}\ sec^{-1}$. The tripositively charged complexes show faster anation rates than the dipositively charged species. There is complete retention of configuration for these reactions.

## Introduction

Previous papers in this series have discussed the synthesis[1] and hydrolysis reactions[2,3] of ruthenium(III)–amine complexes. Further to these investigations we wish to add a report of kinetic studies on the halide anation of *cis*-$Ru(H_2O)_2(en)_2^{3+}$, *cis*-$RuH_2OX(en)_2^{2+}$, and $RuH_2O(NH_3)_5^{3+}$ (en = ethylenediamine; X = Cl, Br).

## Experimental Section

**Materials.**—*cis*-$[RuClH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2 \cdot H_2O$ and *cis*-$[RuBrH_2O(C_2H_8N_2)_2](C_7H_7SO_3)_2 \cdot H_2O$ were prepared as described previously.[1,2] *cis*-$Ru(H_2O)_2(C_2H_8N_2)_2^{3+}$ and $RuH_2O(NH_3)_5^{3+}$ were generated *in situ* by base hydrolysis of *cis*-$RuX_2(C_2H_8N_2)_2^+$ or $RuX(NH_3)_5^{2+}$ (X = Cl or Br), respectively, followed by acidification.

In the kinetic studies chloride and bromide concentrations were adjusted with HCl or HBr. Ionic strength was maintained constant with sodium *p*-toluenesulfonate. Solutions of AR potassium iodide in *p*-toluenesulfonic acid were used in the iodide anation studies. Spectrophotometric analysis showed that less than a $10^{-4}$ *M* concentration of triiodide was generated during the reaction time for iodide anation and this did not interfere with the rate studies.

**Absorption Spectral Studies.**—The spectral curves obtained during chloride anation of *cis*-$RuClH_2O(en)_2^{2+}$ gave isosbestic points at 341 and 315 m$\mu$ which were essentially identical with those obtained during the aquation of *cis*-$RuCl_2(en)_2^+$. These isosbestic points remained throughout the approach to equilibrium. Regeneration experiments using optically active *cis*-$RuCl_2(en)_2^+$ have been described in part II and confirm the absence of any change in optical as well as geometrical configuration during chloride anation.[3] The other anation reactions have been studied at single wavelengths only. However the following experiments show that cis–trans rearrangements or dismutations of the complexes are absent. Treatment of *cis*-$Ru(H_2O)_2(en)_2^{3+}$ with excess HBr gave the spectrum of *cis*-$RuBr_2(en)_2^+$ quantitatively. The overnight reaction of $RuH_2O(NH_3)_5^{3+}$ with excess HBr likewise gave the spectrum of $RuBr(NH_3)_5^{2+}$ almost quantitatively. When a solution of *cis*-$RuBrH_2O(en)_2^{2+}$ in 6 *M* HCl was heated for 8 hr at 40°, a spectrum identical with that of *cis*-$RuCl_2(en)_2^+$ in 6 *M* HCl was obtained.

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[1] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 546 (1967).

[2] J. A. Broomhead and L. A. P. Kane-Maguire, *Inorg. Chem.*, **7**, 2519 (1968).

[3] J. A. Broomhead and L. A. P. Kane-Maguire, *ibid.*, **8**, 2124 (1969).

TABLE I

ABSORPTION SPECTRAL DATA FOR ANATION REACTIONS

| Initial complex | Anating species | Wavelength (λ) used, mμ | $\epsilon_\lambda$, $M^{-1}$ cm$^{-1}$<br>Initial complex | <br>Reaction product | Product |
|---|---|---|---|---|---|
| *cis*-$RuCl(H_2O)(en)_2^{2+}$ | $Cl^-$ (0.1–0.5 *M*) | 355 | 901 | 1750 | *cis*-$RuCl_2(en)_2^+$ |
| | $Br^-$ (1.0 *M*) | 425[a] | . . . | 1280 | *cis*-$RuClBr(en)_2^+$ |
| | $Br^-$ (3.6 *M*) | 427[a] | . . . | 1320 | *cis*-$RuClBr(en)_2^+$ |
| *cis*-$RuBr(H_2O)(en)_2^{2+}$ | $Br^-$ (0.1 *M*) | 445 | 610 | 1530 | *cis*-$RuBr_2(en)_2^+$ |
| | (0.5 *M*) | 445 | 625 | 1535 | *cis*-$RuBr_2(en)_2^+$ |
| *cis*-$Ru(H_2O)_2(en)_2^{3+}$ | $Cl^-$ | 329 | . . . | 1790 | *cis*-$RuCl(H_2O)(en)_2^{2+}$ |
| | $Br^-$ | 398 | . . . | 1646 | *cis*-$RuBr(H_2O)(en)_2^{2+}$ |
| | $I^-$ | 549 | | | *cis*-$RuI(H_2O)(en)_2^{2+}$ |
| $Ru(H_2O)(NH_3)_5^{3+}$ | $Cl^-$ | 327 | . . . | 1930 | $RuCl(NH_3)_5^{2+}$ |
| | $Br^-$ | 396 | . . . | 1860 | $RuBr(NH_3)_5^{2+}$ |
| | $I^-$ | 543 | . . . | 1870 | $RuI(NH_3)_5^{2+}$ |

[a] Isosbestic point for the reaction *cis*-$RuClBr(en)_2^+ + Br^- \rightarrow$ *cis*-$RuBr_2(en)_2^+ + Cl^-$.

The spectrum of the complex *cis*-$RuClBr(en)_2^+$ has been estimated in the following manner. Hydrobromic acid (3.6 *M*) was added to *cis*-$[RuClH_2O(en)_2](C_7H_7SO_3)_2 \cdot H_2O$ and the spectrum was recorded periodically. After an initial rapid change the spectrum remained fairly constant. This was interpreted as a rapid anation giving *cis*-$RuClBr(en)_2^+$ followed by a slow conversion to *cis*-$RuBr_2(en)_2^+$. The spectrum of *cis*-$RuClBr(en)_2^+$ was therefore obtained at the conclusion of the rapid initial reaction.

**Kinetic Studies.**—All rate measurements have been made spectrophotometrically at the wavelengths designated in Table I. Also given are the necessary extinction coefficients of the various species. In a typical experiment a solution of the appropriate hydrohalic acid was thermostated and then solid *cis*-$RuXH_2O(en)_2^{2+}$ (X = Cl, Br) was added to give a complex concentration of about $5 \times 10^{-4}$ *M*. The reaction vessel was shaken vigorously, the solution was transferred to a Beckman DK2A spectrophotometer thermostated cell compartment, and the rate of appearance of the appropriate halogeno complex spectrum was measured. Reaction solutions for the anations of *cis*-$Ru(H_2O)_2(en)_2^{3+}$ (and $RuH_2O(NH_3)_5^{3+}$) were prepared as follows. *cis*-$RuX_2(en)_2^+$ (X = Cl or Br) was added to sodium hydroxide solution (0.02 *M*) at the desired temperature and allowed to base hydrolyze for a period sufficient to give $Ru(OH)_2(en)_2^+$ on the basis of published data.[3] An equal volume of the appropriate hydrohalic acid (0.5 *M*) which had previously been thermostated was then added thus giving *cis*-$Ru(H_2O)_2(en)_2^{3+}$ and initiating the anation reaction.

For the conditions of excess halide ion employed the chloride and bromide anations of *cis*-$RuXH_2O(en)_2^{2+}$ (X = Cl, Br) were found to obey an opposed first-order–first-order rate law. Plots of $\log (x_e/(x_e - x))$ *vs.* time were linear with slopes equal to $(k_1 + k_{-1})/2.303$. Here $k_1$ and $k_{-1}$ refer to the (primary) aquation and anation reactions, respectively, while $x$ and $x_e$ refer to the concentrations of halogeno complex at times $t$ and equilibrium, respectively. Values of $x$ and $x_e$ were calculated from the data in Table I. Since the slopes of the above-mentioned plots are also equal to $k_{-1}a/2.303x_e$, where $a$ is the initial complex concentration, values of $k_{-1}$ could be calculated.

Anation rate constants ($k_{-2}$) for *cis*-$Ru(H_2O)_2(en)_2^{3+}$ and $RuH_2O(NH_3)_5^{3+}$ were obtained from the initial slopes of the plots of $\log (A_\infty - A_t)$ *vs.* time again making use of excess halide to obtain pseudo-first-order kinetics. Here $A_t$ and $A_\infty$ refer to the absorbance of the anation products at the wavelengths given (Table I) at times $t$ and infinity, respectively. $A_\infty$ was the calculated value for the anation product. With *cis*-$Ru(H_2O)_2(en)_2^{3+}$ linear plots were obtained for approximately 1 half-life before the consecutive anation of *cis*-$RuXH_2O(en)_2^{2+}$ interfered. Good linear plots of $k_{-2}$ *vs.* [halide] were obtained permitting evaluation of the second-order rate constants $k_{AN}$, since $k_{-1 \text{ or } -2} = k_{AN} \cdot$ [halide ion].

## Results and Discussion

Good agreement with the second-order rate law is shown by the results in Tables II and III. The bis(ethylenediamine)ruthenium(III) complexes also display significant ionic strength retardations (Tables IV, V) which may be accounted for since the reactions involve oppositely charged ions. In general the rate constants have a reproducibility of 5%. Activation energies obtained from the usual Arrhenius plots and analyzed by the method of least squares are given in Table VI.

Combination of the anation results with the pre-

TABLE II

DEPENDENCE OF PSEUDO-FIRST-ORDER ANATION RATE CONSTANTS ON HALIDE ION CONCENTRATIONS FOR VARIOUS RUTHENIUM(III) COMPLEXES

| $[Cl^-]$, *M* | $10^3k_{-1}$, sec$^{-1}$ | $[Br^-]$, *M* | $10^3k_{-1}$, sec$^{-1}$ |
|---|---|---|---|
| *cis*-$RuClH_2O(en)_2^{2+}$ | | *cis*-$RuClH_2O(en)_2^{2+}$ | |
| 0.10[a] | 0.296[d] | 1.0 | 2.14[d] |
| 0.20[a] | 0.646[d] | 3.6 | 8.67[d] |
| 0.40[a] | 1.29[d] | | |
| 0.50[a] | 1.52[d] | *cis*-$RuBrH_2O(en)_2^{2+}$ | |
| | | 0.10[a] | 0.122[d] |
| *cis*-$Ru(H_2O)_2(en)_2^{3+}$ | | 0.20[a] | 0.329[d] |
| 0.052[b] | 0.133[f] | 0.40[b] | 0.734[d] |
| 0.202[b] | 0.539[f] | 0.50[a] | 0.936[d] |
| 0.252[b] | 0.649[f,i] | | |
| 0.254[b] | 0.671[f,j] | *cis*-$Ru(H_2O)_2(en)_2^{3+}$ | |
| | | 0.052[b] | 0.286[e] |
| | | 0.102[b] | 0.547[e] |
| | | 0.199[b] | 1.24[e] |
| | | 0.251[b] | 1.38[e] |
| | | 0.250[b] | 1.41[g,e] |
| | | 0.250[b] | 1.48[h,e] |
| | | 0.052[c] | 0.59[e] |

[a] Ionic strength $\mu = 0.5$. [b] $\mu = 0.26$. [c] $\mu = 0.06$. [d] Temperature 45°. [e] Temperature 35°. [f] Temperature 25°. [g] [Complex] = $3.85 \times 10^{-4}$ *M*. [h] [Complex] = $17.7 \times 10^{-4}$ *M*. [i] [Complex] = $5.58 \times 10^{-4}$ *M*. [j] [Complex] = $14.3 \times 10^{-4}$ *M*.

TABLE III

DEPENDENCE OF PSEUDO-FIRST-ORDER ANATION RATE CONSTANTS FOR $RuH_2O(NH_3)_5^{3+}$ ON HALIDE ION CONCENTRATIONS AT 54.7°[a]

| [Cl], *M* | $10^4k_{-1}$, sec$^{-1}$ | [Br], *M* | $10^4k_{-1}$, sec$^{-1}$ | [I], *M* | $10^4k_{-1}$, sec$^{-1}$ |
|---|---|---|---|---|---|
| 0.100[b] | 2.11 | 0.051[e] | 0.639 | 0.099[f] | 0.696 |
| 0.199[d] | 3.84 | 0.100[b] | 1.32 | 0.148[b] | 1.09 |
| 0.248[c] | 4.51 | 0.248[c] | 3.06 | 0.198[e] | 1.55 |

[a] Ionic strength 0.26; [complex] = $5 \times 10^{-4}$ *M*. [b] $[H^+]$ = 0.096 *M*. [c] $[H^+]$ = 0.244 *M*. [d] $[H^+]$ = 0.195 *M*. [e] $[H^+]$ = 0.046 *M*. [f] $[H^+]$ = 0.145 *M*.

TABLE IV

RATE DATA FOR CHLORIDE ANATION OF RUTHENIUM(III) COMPLEXES

| *cis*-$RuClH_2O(en)_2^{2+}$ | | *cis*-$Ru(H_2O)_2(en)_2^{3+}$ | |
|---|---|---|---|
| Temp, °C | $10^3k_{AN}$, $M^{-1}$ sec$^{-1}$ | Temp, °C | $10^3k_{AN}$, $M^{-1}$ sec$^{-1}$ |
| 25.0 | 0.274[a] | 25.0 | 2.58[c] |
| 35.5 | 1.04,[a] 1.64[b] | 30.1 | 4.38[c] |
| 45.0 | 3.06,[a] 5.38[b] | 35.0 | 7.50[c] |
| 54.8 | 16.2[b] | 25.0 | 5.27[d] |
| | | 25.0 | 1.98[e] |

[a] Ionic strength ($\mu$) 0.5. [b] $\mu = 0.1$. [c] $\mu = 0.26$. [d] $\mu = 0.06$. [e] $\mu = 1.98$.

TABLE V

RATE DATA FOR BROMIDE ANATION OF RUTHENIUM(III) COMPLEXES

| *cis*-$RuBrH_2O(en)_2^{2+}$ | | *cis*-$Ru(H_2O)_2(en)_2^{3+}$ | |
|---|---|---|---|
| Temp, °C | $10^3k_{AN}$, $M^{-1}$ sec$^{-1}$ | Temp, °C | $10^3k_{AN}$, $M^{-1}$ sec$^{-1}$ |
| 35.5 | 0.647[a] | 25.1 | 1.84[c] |
| 45.0 | 1.89[a] | 30.0 | 3.16[c] |
| 50.0 | 3.20[a] | 35.0 | 5.53[c,e] |
| 54.5 | 5.14[a] | 35.0 | 11.4[d] |
| 45.0 | 2.79[b] | | |
| 54.5 | 7.58[b] | | |

[a] Ionic strength ($\mu$) 0.5. [b] $\mu = 0.1$. [c] $\mu = 0.25$. [d] $\mu = 0.06$. [e] Complex concentration varied over the range (3.85–17.7) × $10^{-4}$ *M*.

TABLE VI

RATE CONSTANTS AND ARRHENIUS PARAMETERS FOR ANATION OF $RuXH_2O(en)_2^{2+}$, $Ru(H_2O)_2(en)_2^{3+}$, AND $RuH_2O(NH_3)_5^{3+}$ COMPLEXES

| Complex | Anating ion (*M*) | $10^3k_{AN}$, $M^{-1}$ sec$^{-1}$ | $E_a$, kcal mol$^{-1}$ |
|---|---|---|---|
| $RuClH_2O(en)_2^{2+}$ | $Cl^-$ (0.10)[f] | 1.64[a,c] | 24.0 ± 0.1 |
| $RuClH_2O(en)_2^{2+}$ | $Cl^-$ (0.50)[g] | 1.04[a,d] | 22.8 ± 0.4 |
| $RuBrH_2O(en)_2^{2+}$ | $Br^-$ (0.50)[g] | 0.65[a,d] | 22.0 ± 0.1 |
| $Ru(H_2O)_2(en)_2^{3+}$ | $Cl^-$ (0.25)[h] | 7.50[a,e] | 19.4 ± 0.4 |
| $Ru(H_2O)_2(en)_2^{3+}$ | $Br^-$ (0.25)[h] | 5.53[a,e] | 20.2 ± 0.6 |
| $RuH_2O(NH_3)_5^{3+}$ | $Cl^-$ (0.10)[f] | 2.10[b,e] | ... |
| $RuH_2O(NH_3)_5^{3+}$ | $Br^-$ (0.10)[f] | 1.32[b,e] | ... |
| $RuH_2O(NH_3)_5^{3+}$ | $I^-$ (0.15)[f] | 0.74[b,e] | ... |

[a] Temperature 35.5°. [b] Temperature 54.7°. [c] Ionic strength $\mu = 0.10$. [d] $\mu = 0.50$. [e] $\mu = 0.26$. [f] $[H^+] = 0.1$ *M*. [g] $[H^+] = 0.5$ *M*. [h] $[H^+] = 0.25$ *M*.

viously reported aquation rate constants enables a calculation of equilibrium constants for the reaction

$$RuH_2O(NH_3)_5^{3+} + X^- \underset{k_{H_2O}}{\overset{k_{AN}}{\rightleftharpoons}} RuX(NH_3)_5^{2+} + H_2O$$

At 54.7° and ionic strength 0.25 the equilibrium constants are 88, 43, and 63 for $X^- = Cl^-$, $Br^-$, and $I^-$, respectively. This order agrees well with previously published work[2,4] despite the larger errors associated with the use of rate constants. An analogous calculation for the reaction

$$cis\text{-}RuXH_2O(en)_2^{2+} + X^- \underset{k_{H_2O}}{\overset{k_{AN}}{\rightleftharpoons}} cis\text{-}RuX_2(en)_2^{+} + H_2O$$

gives good agreement between the equilibrium quotients obtained from the rate data and those calculated by spectrophotometric analyses of the equilibrium solutions. The results are given in Table VII.

TABLE VII

COMPARISON OF EQUILIBRIUM QUOTIENTS FOR THE REACTION *cis*-$RuXH_2O(en)_2^{2+} + X^- = $ *cis*-$RuX_2(en)_2^{+} + H_2O$ AT VARIOUS TEMPERATURES AND IONIC STRENGTH 0.1

| Halide ion | Temp, °C | $K_{AN}$[a] | $K_{AN}$[b] |
|---|---|---|---|
| $Cl^-$ | 35.5 | 12.4 | 13.5 |
| $Cl^-$ | 45.0 | 14.5 | 15.9 |
| $Br^-$ | 45.0 | 8.1 | 8.4 |
| $Br^-$ | 54.5 | 9.4 | 8.8 |

[a] $K_{AN} = k_{AN}/k_{H_2O}$. [b] $K_{AN}$ by analysis.

The second-order rate law does not permit a distinction to be made between a direct bimolecular attack and a mechanism involving the preequilibrium formation of an outer-sphere complex. Comparisons of the halide anation rates for *cis*-$RuXH_2O(en)_2^{2+}$ and *cis*-$Ru(H_2O)_2(en)_2^{3+}$ can be made using the data in Tables II and IV–VI. After allowing for the statistical factor of 2 favoring the diaquo complex and for ionic strength variations the anations of $Ru(H_2O)_2(en)_2^{3+}$ are about 3 times faster than those of $RuXH_2O(en)_2^{2+}$ and the faster rates are accompanied by lower activation energies (Table VI). There is also a correlation between the relative rates of entry of halide into any of the aquo complexes and the hardness of the entering anion. Thus the relative rate order is $Cl^- > Br^- > I^-$. On the assumption of an $S_N2$ mechanism this order agrees with the predictions made by Pearson and Songstad[5] and with previous observations.[2] However the corresponding activation energy differences for the entry of the various halide ions do not offer further support for these predictions. A similar order ($Cl^- > Br^- > I^-$) is also found on inspection of the equilibrium constants for the outer-sphere association of halide ions with complex cations[6] leading to a similar expectation for the relative rates. However, microscopic reversibility and the observation of retention of geometrical and optical configuration during the chloride anations of *cis*-$Ru(H_2O)_2(en)_2^{3+}$ and *cis*-$RuClH_2O(en)_2^{2+}$ requires a similar transition state to that proposed earlier[2] for the reverse aquation reactions. An octahedral wedge-type geometry is appropriate but from the present data it is not possible to separate a direct $S_N2$ process from an outer-sphere to inner-sphere interchange process of the kind discussed by Basolo and Pearson.[7]

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

(5) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

(6) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 197.