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Selenitometal Complexes. 3. Kinetics and Mechanism of the Reaction of Hydroxocobalt(III) and Hydroxorhodium(III) Cations with Monomeric and Dimeric Selenite Anions

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The reactions of *cis*-$Co(en)_2(OH)OH_2^{2+}$ (pH 7), $Co(NH_3)_5OH^{2+}$ (pH 8), and $Rh(NH_3)_5OH^{2+}$ (pH 8) with excess selenite proceed with millisecond reaction times. A two-term rate law has been shown to apply at three or four temperatures, namely, $k_{an} = k_1[HSeO_3^-] + k_2$[Se(IV) dimer], where [Se(IV) dimer] is the combined concentration of $H(SeO_3)_2^{3-}$ and $H_2(SeO_3)_2^{2-}$. At 25 °C, for *cis*-$Co(en)_2(OH)OH_2^{2+}$, $k_1 = 4$ M^{-1} s^{-1} and $k_2 = 110$ M^{-1} s^{-1} with $\Delta H_2^{\ddagger} = 36.2 \pm 2.4$ kJ mol^{-1}; for $Co(NH_3)_5OH^{2+}$, $k_1 = 8$ M^{-1} s^{-1} and $k_2 = 20$ M^{-1} s^{-1} with $\Delta H_2^{\ddagger} = 48.1 \pm 2.5$ kJ mol^{-1}; and for $Rh(NH_3)_5OH^{2+}$, $k_1 = 20$ M^{-1} s^{-1} and $k_2 = 364$ M^{-1} s^{-1} with $\Delta H_2^{\ddagger} = 50.0 \pm 3.0$ kJ mol^{-1}. At pH 7, *cis*-$Co(tn)_2(OH)OH_2^{2+}$, *trans*-$Co(en)_2(OH)OH_2^{2+}$, and *trans*-$Co(tn)_2(OH)OH_2^{2+}$ exhibit very similar rates of reaction to those of *cis*-$Co(en)_2(OH)OH_2^{2+}$. An I_a mechanism with interchange between the hydroxo ligand and selenite in the outer sphere is proposed for all of these systems, the higher rate for the Se(IV) dimeric species compared to $HSeO_3^-$ arising almost entirely from a more favorable outer-sphere association constant for the former species. Reactions of all six complexes at pH 10 with SeO_3^{2-} are markedly slower (6–24 times) than those at pH 6–8. All six complexes exhibit $\Delta H^{\ddagger}$ values in the range 50–60 kJ mol^{-1} and $\Delta S^{\ddagger}$ values ranging from −57 to −104 J K^{-1} mol^{-1}. An I_a mechanism with hydroxo ligand attack at the Se(IV) center of SeO_3^{2-} with HO^- as a leaving group is proposed at this pH value. At both pH 6–8 and pH 10, rates of the interchange reactions are some 6 times faster than the rate of exchange of selenite with solvent water.

Introduction

In acidic aqueous media, protonated monodentate selenitocobalt(III) complexes are formed in millisecond reaction times[1,2] from aquocobalt(III) complexes and $HSeO_3^-$. At 25 °C, the formation constants are $\beta_{H-Se} = 23$ for a monoaquo complex and $\beta_{H-Se} \simeq 54$ for three diaquo complexes. In aqueous media from pH 5 to pH 8, the equilibrium for selenito complex formation is even more favorable with the overall formation quotient $Q_s \geq 150$. However, at pH 11.5, the equilibrium is less favorable with $Q_s \simeq 5$.

This paper describes a kinetic investigation of selenito complex formation for cobalt(III) and rhodium(III) at both pH 6–8 and at pH 10. The reactions of diaquo complexes were studied at pH 6–7 where the selenito formation reaction may be written in terms of the predominant reactants and products existing at this pH

$$M^{III}(NN)_2OH(OH_2)^{2+} + HSeO_3^- \rightarrow M^{III}(NN)_2OH_2(OSeO_2)^+ + H_2O \qquad (1)$$

The monoaquo complexes were studied at pH 8 where the formation reaction is predominantly

$$M^{III}(N)_5OH^{2+} + HSeO_3^- \rightarrow M^{III}(N)_5OSeO_2^+ + H_2O \qquad (2)$$

The mechanistic importance of the diaquo and dihydroxo complexes, together with SeO_3^{2-}, $H(SeO_3)_2^{3-}$, and $H_2(SeO_3)_2^{2-}$, requires assessment since significant concentrations of these species occur under some of the conditions of reactions 1 and 2. The effect of the nature and stereochemistry of the nitrogen ligands and the nature of the central metal upon the rates of (1) and (2) was also investigated.

At pH 10, the substrate complexes exist almost exclusively as hydroxo complexes while more than 99% of Se(IV) exists as SeO_3^{2-}. The selenito formation reactions may then be expressed in terms of the main reactants

$$M^{III}(NN)_2(OH)_2^+ + SeO_3^{2-} \rightarrow M^{III}(NN)_2(OH)OSeO_2^0 + HO^- \qquad (3)$$

and

$$M^{III}(N)_5OH^{2+} + SeO_3^{2-} \rightarrow M^{III}(N)_5OSeO_2^+ + HO^- \qquad (4)$$

Experimental Section

Materials. Anhydrous sodium selenite and the complexes $[Co(NH_3)_5OH_2](ClO_4)_3$, *cis*- and *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$, and *trans*-$[Co(tn)_2OH(OH_2)](ClO_4)_2 \cdot 2H_2O$ were prepared and analyzed as previously reported.[2] $[Rh(NH_3)_5OH_2](ClO_4)_3$ was prepared by the method of Swaddle and Stranks.[3]

Solutions of *cis*-$Co(tn)_2OH(OH_2)^{2+}$ were generated in situ by the rapid isomerization of *trans*-$[Co(tn)_2(OH_2)_2]^{3+}$ to *cis*-$[Co(tn)_2(OH_2)_2]^{3+}$ ($t_{1/2} = 25$ s at 25 °C) which then produced *cis*-$Co(tn)_2OH(OH_2)^{2+}$ on adjustment to pH 6 on mixing the complex and selenite solutions in the stopped-flow apparatus after thermal equilibration. This pH was checked on the completion of each set of kinetic runs to ensure that the anticipated pH had been achieved on mixing. Because of this high lability of the trans isomer, solutions of *trans*-$Co(tn)_2OH(OH_2)^{2+}$ were generated by dissolving the solid salt in solutions of high pH to form the less labile *trans*-$Co(tn)_2(OH)_2^+$ (for isomerization $t_{1/2} = 130$ min at 25 °C), and after thermal equilibration the solution was adjusted to pH 6 on mixing with the buffer in the stopped-flow apparatus.

Solutions of *cis*- and *trans*-$Co(en)_2OH(OH_2)^{2+}$ were stored as the diaquo cations at low pH, to avoid isomerization of the hydroxoaquo cations during the time necessary for thermal equilibration. The pH of the solutions was restored to pH 6–7 by mixing the diaquo solutions with the buffer in the stopped-flow apparatus. The buffer tris(hydroxymethyl)aminomethane ("Trizma Base", Sigma) was dried in vacuo over P_2O_5 and buffer solution was prepared directly from this material. This buffer solution gave adequate buffering capacity between pH 7.0 and pH 9.0 with maximum capacity at pH = pK_a = 8.20 at 25 °C.

Kinetic Procedures. Reactions were conducted in the stopped-flow apparatus according to procedures already described. Concentrations of the hydroxo complexes were usually maintained constant at 0.01 M (0.005 M for $Rh(NH_3)_5OH^{2+}$) and Se(IV) concentrations were used in 5–50-fold molar excess. The total buffer concentration used in all studies was 0.5 M. The final ionic strength of reaction mixtures was adjusted to 1.0 M with sodium perchlorate. The pH of all reacted solutions from the stopped-flow apparatus was checked in all cases (pH to an accuracy of ±0.002) to ensure that the desired pH had been sustained throughout the reaction.

Reactions were monitored for the hydroxocobalt(III) complexes at 530–550 nm (increase in absorbance) and at 460–480 nm (decrease in absorbance) and for $Rh(NH_3)_5OH^{2+}$ reactions were monitored at 350 nm (increase in absorbance).

Results

Reactions of Hydroxopentaammines with Se(IV) (pH 8). Reactions of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ with Se(IV) were conducted at pH 8 where 96.2% of the cobalt(III) exists as $Co(NH_3)_5OH^{2+}$ and 99% of the rhodium(III) exists as $Rh(NH_3)_5OH^{2+}$. The distribution of Se(IV) among the various monomeric and dimeric forms is complicated and this

Table I. Distribution of Various Selenium(IV) Species at pH 8.0, 298 K, and Ionic Strength 1.0 M $(NaClO_4)^a$

Total [Se(IV)], M	$10^2[HSeO_3^-]$, M	$10^2[H(SeO_3)_2^{3-}]$, M	$10^2[H_2(SeO_3)_2^{2-}]$, M	$10^2[SeO_3^{2-}]$, M
0.0375	1.351	0.051	0.027	2.242
0.0500	1.778	0.089	0.047	2.950
0.0750	2.602	0.191	0.100	4.317
0.100	3.389	0.324	0.170	5.623
0.150	4.873	0.669	0.351	8.087
0.200	6.256	1.103	0.579	10.381
0.250	7.556	1.608	0.844	12.539

[a] Calculated from ref 3.

Table II. Rate Data for Reaction of $Co(NH_3)_5OH^{2+}$ with Se(IV) at Ionic Strength 1.0 M $(NaClO_4)$, pH 8, and Initial $[Co(NH_3)_5OH^{2+}] = 0.0100$ M

10^2[Se(IV)], M	k_{an}, s^{-1} 25 °C	30 °C	35 °C	40 °C
5.0	0.40 ± 0.03	0.63 ± 0.04	1.18 ± 0.07	1.74 ± 0.06
7.5	0.78 ± 0.05	1.17 ± 0.05	1.92 ± 0.09	3.42 ± 0.19
10	1.25 ± 0.06	2.10 ± 0.10	3.19 ± 0.24	4.85 ± 0.30
15	2.37 ± 0.06	3.51 ± 0.39	5.57 ± 0.25	9.09 ± 0.41
25	4.35 ± 0.15	6.92 ± 0.16	11.8 ± 0.6	20.2 ± 1.3

Table III. Rate Data for Reaction of $Rh(NH_3)_5OH^{2+}$ with Se(IV) at Ionic Strength 1.0 M $(NaClO_4)$, pH 8, and Initial $[Rh(NH_3)_5OH^{2+}] = 0.0050$ M

10^2[Se(IV)], M	k_{an}, s^{-1} 25 °C	30 °C	40 °C
3.75	0.43 ± 0.02	0.79 ± 0.04	1.33 ± 0.11
5.0	0.82 ± 0.03	1.33 ± 0.05	2.07 ± 0.06
7.5	1.53 ± 0.05	2.80 ± 0.11	3.85 ± 0.11
10	2.55 ± 0.19	4.39 ± 0.37	7.32 ± 0.29
15	4.72 ± 0.22	7.16 ± 0.25	12.4 ± 0.4
25	10.3 ± 0.5	17.9 ± 0.8	27.5 ± 2.1

distribution at pH 8, calculated from the data of Barcza and Sillén,[5] is summarized in Table I. This distribution does not alter significantly with temperature as the relevant enthalpy changes for the interrelated equilibria[6] are close to zero. The increasing importance of dimeric species at higher Se(IV) concentrations is important in the subsequent kinetic analysis.

The variation of the first-order rate coefficient for selenito formation, k_{an}, with Se(IV) concentration and with temperature is summarized in Tables II and III for $Co(NH_3)_5OH^{2+}$ and $Rh(NH_3)_5OH^{2+}$, respectively. For both systems at all temperatures k_{an} exhibits a complicated dependence on Se(IV) concentration which is approximately proportional to the second power of Se(IV) concentration. Since $HSeO_3^-$ has been shown[4] to be the reactive form of Se(IV) at pH 3, a two-term rate expression

$$k_{an} = k_1[HSeO_3^-] + k_2'[HSeO_3^-]^2 \qquad (5)$$

was tested. Graphical tests of this rate expression are shown in Figures 1 and 2 where $k_{an}/[HSeO_3^-]$ is linear in $[HSeO_3^-]$. From these plots values of k_1 at different temperatures for the two hydroxo complexes were derived. Values of k_1 were assigned to a reaction pathway involving $HSeO_3^-$ and $M(NH_3)_5OH^{2+}$. For $Co(NH_3)_5OH^{2+}$, k_1 = 8 (25 °C), 14 (30 °C), 37 (35 °C), and 50 M^{-1} s^{-1} (40 °C). For $Rh(NH_3)_5OH^{2+}$, k_1 = 20 (25 °C), 30 (30 °C), and 40 M^{-1} s^{-1} (40 °C). The accuracy attainable with these k_1 values (±30%) does not justify the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for this pathway.

The term in k_2' may be identified with a second pathway involving the dimeric anions $H(SeO_3)_2^{3-}$ and $H_2(SeO_3)_2^{2-}$ since the combined concentration of these two anions is proportional to $[HSeO_3^-]^2$. At fixed pH, the ratio $[H(SeO_3)_2^{3-}]/[H_2(SeO_3)_2^{2-}] = 1.91$ at all concentrations of Se(IV). Rate expression 5 may therefore be written in the form

$$k_{cor} = k_{an} - k_1[HSeO_3^-] = k_2\{[H(SeO_3)_2^{3-}] + [H_2(SeO_3)_2^{2-}]\} \qquad (6)$$

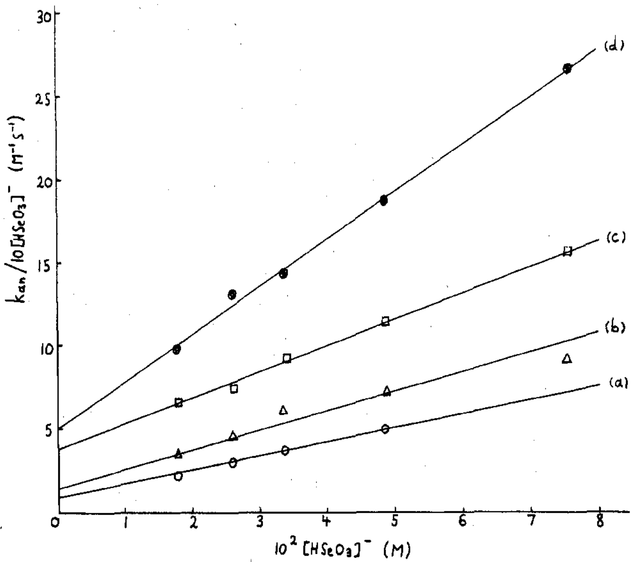


Figure 1. Plots of $k_{an}/[HSeO_3^-]$ vs. $[HSeO_3^-]$ for $Co(NH_3)_5OH^{2+}$ at pH 8.0 and μ = 1.0 M (adjusted with $NaClO_4$): (a) 25 °C, k_1 = 8 s^{-1}; (b) 30 °C, k_1 = 14 s^{-1}; (c) 35 °C, k_1 = 37 s^{-1}; (d) 40 °C, k_1 = 50 s^{-1}.

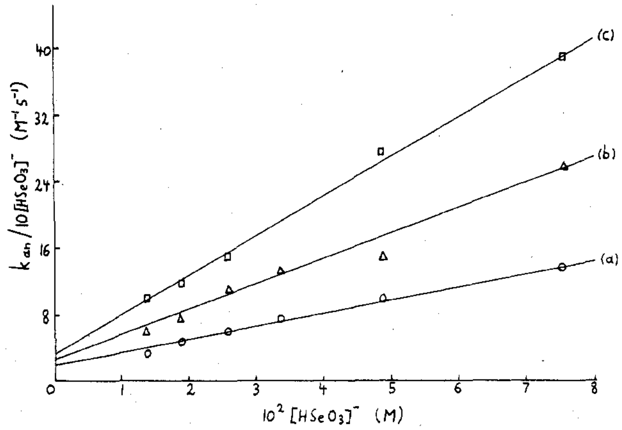


Figure 2. Plots of $k_{an}/[HSeO_3^-]$ vs. $[HSeO_3^-]$ for $Rh(NH_3)_5OH^{2+}$ at pH 8.0 and μ = 1.0 M (adjusted with $NaClO_4$): (a) 25 °C, k_1 = 20 s^{-1}; (b) 30 °C, k_1 = 30 s^{-1}; (c) 40 °C, k_1 = 40 s^{-1}.

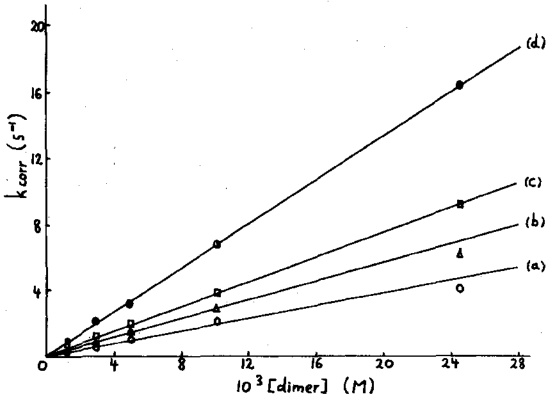


Figure 3. Plots of k_{cor} vs. [dimer] for $Co(NH_3)_5OH^{2+}$: (a) 25 °C, k_2 = 194 s^{-1}; (b) 30 °C, k_2 = 293 s^{-1}; (c) 35 °C, k_2 = 370 s^{-1}; (d) 40 °C, k_2 = 667 s^{-1}. Values of k_{cor} were determined according to eq 6 and [dimer] = $[H_2(SeO_3)_2^{2-}]$ + $[H(SeO_3)_2^{3-}]$.

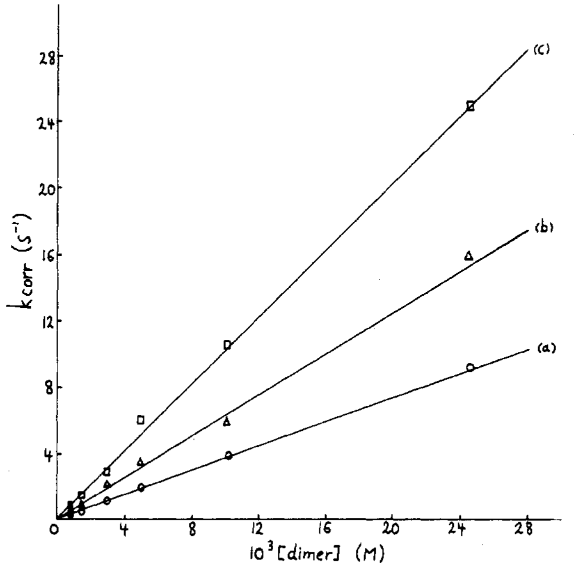


Figure 4. Plots of k_{cor} vs. [dimer] for $Rh(NH_3)_5OH^{2+}$: (a) 25 °C, k_2 = 364 s^{-1}; (b) 30 °C, k_2 = 625 s^{-1}; (c) 40 °C, k_2 = 1000 s^{-1}.

Table IV. Distribution of Various Selenium(IV) Species at pH 7.0, 298 K, and Ionic Strength 1.0 M ($NaClO_4$)[a]

Total [Se(IV)], M	$10^2[HSeO_3^-]$, M	$10^2[H(SeO_3)_2^{3-}]$, M	$10^2[H_2(SeO_3)_2^{2-}]$, M	$10^2[SeO_3^{2-}]$, M
0.050	3.837	0.042	0.220	0.638
0.075	5.514	0.086	0.451	0.915
0.100	7.066	0.141	0.741	1.173
0.150	9.902	0.276	1.450	1.644
0.200	12.459	0.438	2.299	2.068
0.250	14.811	0.618	3.244	2.459

[a] Calculated from ref 3.

and this rate expression is tested in Figures 3 and 4 from which values of k_2 for both hydroxo complexes were derived at various temperatures. For $Co(NH_3)_5OH^{2+}$, k_2 = 194 (25 °C), 293 (30 °C), 370 (35 °C), and 667 M^{-1} s^{-1} (40 °C) yielding an activation energy of 48.1 ± 2.5 kJ mol^{-1}. For $Rh(NH_3)_5OH^{2+}$, k_2 = 364 (25 °C), 625 (30 °C), and 1000 M^{-1} s^{-1} (40 °C) yielding an activation energy of 50.0 ± 3.0 kJ mol^{-1}.

Reactions of Hydroxoaquo Complexes with Se(IV) (pH 6–7). Reactions of *cis*-$Co(en)_2(OH_2)_2^{3+}$ with Se(IV) were conducted at pH 7 in order to maximize the concentration of the hydroxoaquo complex. At a total diaquo concentration of 0.0100 M, as employed in all kinetic runs, 80.5% exists as *cis*-$Co(en)_2OH(OH_2)^{2+}$, 12.5% as *cis*-$Co(en)_2(OH)_2^+$, and 7.0% as *cis*-$Co(en)_2(OH_2)_2^{3+}$. The calculated distribution of Se(IV) among the various monomeric and dimeric anions at pH 7 is listed in Table IV for a range of Se(IV) concentrations.

The measured variation of k_{an} for selenito formation with Se(IV) concentration at four different temperatures is summarized in Table V. As with the hydroxopentaammines at pH 8, the dependence of k_{an} upon [Se(IV)] is complicated for reaction of *cis*-$Co(en)_2OH(OH_2)^{2+}$ with Se(IV). A two term-rate expression (eq 5) holds and this is shown in Figure 5 from which values of k_1 may be deduced at the four temperatures: 4 (25 °C), 6 (30 °C), 8 (35 °C), and 10 M^{-1} s^{-1} (40 °C). This k_1 term is again identified with a reaction pathway involving $HSeO_3^-$. The poor accuracy attainable with k_1 values does not justify the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.

The second pathway described by k_2 (eq 5) may be expressed in terms of the rate expression involving the two dimeric anions (eq 6). At pH 7, the $H_2(SeO_3)_2^{2-}$ anion is the dominant dimeric anion with the ratio $[H_2(SeO_3)_2^{2-}]/[H(SeO_3)_2^{3-}]$ = 5.25 at all Se(IV) concentrations. The rate expression of the form of eq 6 is tested in Figure 6 for the reaction of *cis*-$Co(en)_2OH(OH_2)^{2+}$ with both $H_2(SeO_3)_2^{2-}$ and $H(SeO_3)_2^{3-}$. The plots are linear at low concentrations of the dimeric anions but deviations occur at higher concentrations. These deviations may be attributed to a significant degree of association (or ion pairing) of the cationic reactant with the multiply charged anions. Approximate estimates may be made

Table V. Temperature and Concentration Dependence of Rate of Reaction of *cis*-$Co(en)_2OH(OH_2)^{2+}$ [a] with Se(IV) at pH 7 and Ionic Strength 1.0 M ($NaClO_4$)

10^2[Se(IV)], M	k_{an}, s^{-1} 25 °C	30 °C	35 °C	40 °C
5.0	0.74 ± 0.04	0.93 ± 0.03		
7.5	1.43 ± 0.04	1.88 ± 0.06	2.38 ± 0.11	2.83 ± 0.10
10		2.68 ± 0.11	3.50 ± 0.14	4.27 ± 0.21
15	4.90 ± 0.18	6.24 ± 0.17	7.66 ± 0.37	9.06 ± 0.32
20	7.11 ± 0.19	8.70 ± 0.25	10.9 ± 0.4	13.0 ± 0.4
25	7.90 ± 0.45	10.2 ± 0.6	12.4 ± 0.5	15.0 ± 1.0

[a] Total concentration of diaquo complex is 0.01 M. At pH 7, $[Co(en)_2OH(OH_2)^{2+}]$ = 0.008 04 M, $[Co(en)_2(OH_2)_2^{3+}]$ = 0.000 70 M, and $[Co(en)_2(OH)_2^+]$ = 0.001 25 M.

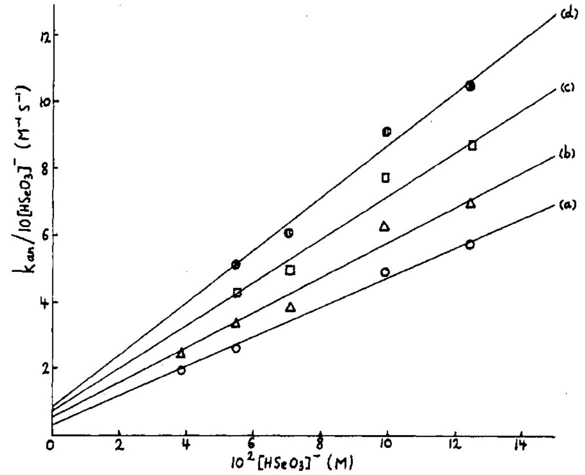


Figure 5. Plots of $k_{an}/[HSeO_3^-]$ vs. $[HSeO_3^-]$ for *cis*-$Co(en)_2OH(OH_2)^{2+}$ at pH 7.0 and μ = 1.0 M (adjusted with $NaClO_4$: (a) 25 °C, k_1 = 4 s^{-1}; (b) 30 °C, k_1 = 6 s^{-1}; (c) 35 °C, k_1 = 8 s^{-1}; (d) 40 °C, k_1 = 10 s^{-1}.

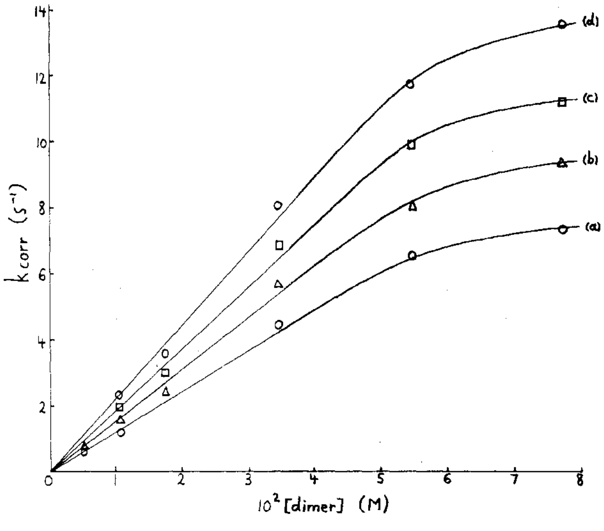


Figure 6. Plots of k_{cor} vs. [dimer] for *cis*-$Co(en)_2OH(OH_2)^{2+}$: (a) 25 °C, k_2 = 110 s^{-1}; (b) 30 °C, k_2 = 140 s^{-1}; (c) 35 °C, k_2 = 170 s^{-1}; (d) 40 °C, k_2 = 210 s^{-1}.

Table VI. Temperature Variation of Rate of Reaction of Hydroxo(aquo)cobalt(III) Complexes with Se(IV) at pH 6, Ionic Strength 1.0 M ($NaClO_4$), [Se(IV)] = 0.10 M, and [Initial Aquo] = 0.01 M

	k_{an}, s^{-1}		
Temp, °C	*cis*-$Co(tn)_2$-$OH(OH_2)^{2+}$	*trans*-$Co(tn)_2$-$OH(OH_2)^{2+}$	*trans*-$Co(en)_2$-$OH(OH_2)^{2+}$
10		1.00 ± 0.05	1.18 ± 0.04
15		1.38 ± 0.04	1.55 ± 0.05
20		1.90 ± 0.10	2.01 ± 0.07
25	2.65 ± 0.15		
30	3.56 ± 0.29		
40	5.70 ± 0.30		

for an outer-sphere association constant, K_{os}. At all temperatures, $K_{os} \simeq 15 \pm 5$. Values of k_2 (eq 2) were evaluated from the initial slopes of the plots of Figure 6; k_2 = 110 (25 °C), 140 (30 °C), 170 (35 °C), 210 M^{-1} s^{-1} (40 °C) corresponding to $\Delta H^{\ddagger} = 36.2 \pm 2.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -109 \pm 7$ J K^{-1} mol^{-1}.

The reactions of *trans*-$Co(en)_2OH(OH_2)^{2+}$ and *cis*- and *trans*-$Co(tn)_2OH(OH_2)^{2+}$ with Se(IV) were studied at pH 6 to maximize the concentrations of the hydroxoaquo complexes. At pH 6, the concentration ratios of $HSeO_3^-$, $H_2(SeO_3)_2^{2-}$, and $H(SeO_3)_2^{3-}$ are very similar to those at pH 7 (Table V) but the concentration of SeO_3^{2-} is much reduced. Temperature dependence studies were conducted at a single Se(IV) concentration only (0.10 M) for these three hydroxoaquo complexes. The rate data are summarized in Table VI.

Discussion

This investigation has established two reaction pathways for selenito complex formation in the pH 6–8 range: one (k_1) involves the monomeric $HSeO_3^-$ anion, and the other (k_2) involves the dimeric anions $H_2(SeO_3)_2^{2-}$ and $H(SeO_3)_2^{3-}$. Although the concentration of these dimeric anions is relatively low in the Se(IV) concentrations employed (Tables I and IV), their reactivity is sufficiently high that the k_2 pathway is the major contributor to the overall rate of selenito formation at pH 6–8. Nevertheless the rate of selenito formation at pH 3 is about 10 times greater for most cobalt(III)–aquo complexes[2] than the rate at pH 6–8 under comparable conditions. Although the equilibrium for selenito formation is more favorable at pH 6–8, than at pH 3, this situation arises from the absence of acid- or base-catalyzed aquation at pH 6–8 and not from a faster rate of selenito formation.

Reaction of Hydroxo Complexes with $HSeO_3^-$ (pH 6–8). The rate term $k_1[HSeO_3^-]$ in the two-term rate expression (eq 5) has been observed for the reactions of *cis*-$Co(en)_2OH(OH_2)^{2+}$ at pH 7 and of $Co(NH_3)_5OH^{2+}$ and $Rh(NH_3)_5OH^{2+}$ at pH 8. The values of k_1 are comparable for all three complexes and since the hydroxo ligand must react with $HSeO_3^-$ in the pentaammine complexes, a similar route is implied with *cis*-$Co(en)_2OH(OH_2)^{2+}$ although reaction with an aquo ligand cannot be excluded.

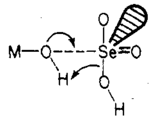
At pH 3, our previous studies[4] showed that an interchange mechanism operated for reaction of an aquo complex with $HSeO_3^-$. An analogous mechanism may be proposed for the hydroxo complexes, especially as there is evidence, discussed below, that the hydroxo complexes react with the dimeric anions through an interchange mechanism. For the reaction described by the rate term k_1 the mechanism of eq 7 and 8

$$M(L)_5OH^{2+} + HSeO_3^- \underset{}{\overset{K_{os}}{\rightleftharpoons}} M(L)_5OH^{2+}\cdot HSeO_3^- \qquad (7)$$

$$M(L)_5OH^{2+}\cdot HSeO_3^- \xrightarrow{k_{Se}'} M(L)_5OSeO_2^+ + H_2O \qquad (8)$$

may proposed. Here $k_1 = K_{os}\, k_{Se}'[HSeO_3^-]/(1 + K_{os}\cdot[HSeO_3^-])$. Within the limitations of the uncertainties imposed by a two-term rate law, the rate term $k_1[HSeO_3^-]$ holds for [Se(IV)] = 0.05–0.25 M so that $K_{os}[HSeO_3^-] << 1$ and $k_1 \simeq K_{os}k_{Se}$. For association of $Co(tn)_2(OH_2)_2^{3+}$ with $HSeO_3^-$, $K_{os} = 6$, and in view of the 2+ charge of the hydroxo substrate, a value $K_{os} \simeq 1$ may be assumed. This suggests that k_1 values approximate to the actual k_{Se} values. For *cis*-$Co(tn)_2(OH_2)_2^{3+}$, the interchange rate coefficient is $k_{HSe} = 63$ s^{-1} at 30 °C while for *cis*-$Co(tn)_2OH(OH_2)^{2+}$, k_{Se}' (reaction 8) can be estimated (if $K_{os} = 1$) to have a value of 50 s^{-1}. This suggests that the higher reactivity of the 3+ aquo complexes for $HSeO_3^-$ is largely attributable to a more favorable outer-sphere constant K_{os} and that the interchange reaction (8) proceeds at a comparable rate to that at pH 3.

The activated complex for the interchange step may be formulated as



in which the O atom of the hydroxo ligand substitutes at the Se(IV) center, which assumes a formal trigonal-bipyramidal arrangement, and the leaving group is H_2O. While rates of this interchange process are comparable for the various stereochemistries and ligands used in the cobalt(III) complexes, the rate for the rhodium(III) complex is twice that for cobalt(III). In the case of the hydroxo(aquo)cobalt(III) complexes, there is a minor contribution to the measured k_1 values which arises from the small percentage of the complexes existing as diaquo complexes at pH 6–7. However, the foregoing conclusions are not invalidated from this minor contribution. The rate contribution from dihydroxo complexes present at pH 7 is insignificant.

Reaction of Hydroxo Complexes with Dimeric Anions (pH 6–8). The rate term $k_2'\{[H(SeO_3)_2^{3-}] + [H_2(SeO_3)_2^{2-}]\}$ in a two-term rate expression (eq 6) was established at pH 7 for *cis*-$Co(en)_2OH(OH_2)^{2+}$ and at pH 8 for both $Co(NH_3)_5OH^{2+}$ and $Rh(NH_3)_5OH^{2+}$. At pH 7 the total combined concentration of the dimeric anions is greater than that concentration at pH 8, for the same Se(IV) concentration (Tables I and IV). As a consequence, the reaction of *cis*-$Co(en)_2OH(OH_2)^{2+}$ with the dimeric anions exhibits a deviation from a first-order dependence on their concentration (Figure 6). This has been interpreted as arising from outer-sphere association between the 2+ substrate cation and the highly charged dimeric anions.

An interchange mechanism may therefore be proposed for the reaction of the hydroxo complexes with the dimeric anions, as shown by

$$M(L)_5OH^{2+} + \left\{\begin{matrix} H(SeO_3)_2^{\ 3-} \\ \\ H_2(SeO_3)_2^{\ 2-} \end{matrix}\right. \overset{K_{os}''}{\rightleftharpoons} M(L)_5OH^{2+}\cdot\left\{\begin{matrix} H(SeO_3)_2^{\ 3-} \\ \\ H_2(SeO_3)_2^{\ 2-} \end{matrix}\right. \qquad (9)$$

$$M(L)_5OH^{2+}\cdot\left\{\begin{matrix} H(SeO_3)_2^{\ 3-} \\ \\ H_2(SeO_3)_2^{\ 2-} \end{matrix}\right. \xrightarrow{k_{Se}''} ML_5OSeO_2^{\ 2+} + \left\{\begin{matrix} H_2O + SeO_3^{\ 2-} \\ \\ H_2O + HSeO_3^{\ -} \end{matrix}\right. \qquad (10)$$

for which $k_{obsd} = K_{os}''k_{Se}''[\text{dimer}]/(1 + K_{os}''[\text{dimer}])$. At low [dimer], where $k_{obsd} = k_2'[\text{dimer}]$, $k_2' \equiv K_{os}''k_{Se}''$. Curvature of these rate plots at higher dimer concentrations (Figure 6) is consistent with a value $K_{os}'' \simeq 15$, this value being a composite constant for association of the 3– and 2– dimeric anions but a more detailed analysis of the data is not justified by the small concentration range available. A value of K_{os} = 6.7 was derived[2] from the association of a 3+ cation with $HSeO_3^-$ which seems compatible with a value K_{os}'' = 15 for association of a 2+ cation with 3– and 2– anions. Nevertheless, these relatively large K_{os} values suggest that specific binding forces are involved in the association rather than purely electrostatic forces. We have reviewed these considerations in our previous paper.[2]

The values of k_2' for the hydroxopentaammine complexes at pH 8 (at 25 °C, k_2' = 194 M^{-1} s^{-1} for $Co(NH_3)_5OH^{2+}$ and

Table VII. Temperature Dependence of Rates of Reaction of Se(IV) with Hydroxocobalt(III) Complexes at Ionic Strength 1.0 M ($NaClO_4$), pH 10, [Hydroxo Complex] = 0.01 M, and [Se(IV)] = 0.10 M

	k_{an}, s^{-1}					
Temp, °C	*cis*-$Co(tn)_2(OH)_2^+$	*trans*-$Co(tn)_2(OH)_2^+$	*cis*-$Co(en)_2(OH)_2^+$	*trans*-$Co(en)_2(OH)_2^+$	$Co(NH_3)_5OH^{2+}$	*a*
10		0.021 ± 0.001				
15		0.055 ± 0.001		0.050 ± 0.001		
20		0.132 ± 0.007		0.110 ± 0.006		
25	0.110 ± 0.001		0.130 ± 0.004	0.194 ± 0.004	0.210 ± 0.005	0.025
30	0.178 ± 0.004		0.191 ± 0.004		0.31 ± 0.02	0.042
35	0.260 ± 0.003		0.245 ± 0.003			
40	0.375 ± 0.005		0.347 ± 0.005		0.599 ± 0.009	0.097

[a] Maximum rate contribution calculated for reaction of $HSeO_3^-$, $H_2(SeO_3)_2^{2-}$, and $H(SeO_3)_2^{3-}$ from their reaction rates measured at pH 8.

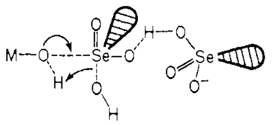
$k_2' = 364\ M^{-1}\ s^{-1}$ for $Rh(NH_3)_5OH^{2+}$) are distinctly higher than the value $k_2' = 110\ M^{-1}\ s^{-1}$ for *cis*-$Co(en)_2OH(OH_2)^{2+}$ at pH 7. This arises from the form of the assumed rate term in which the concentrations of $H(SeO_3)_2^{3-}$ and $H_2(SeO_3)_2^{2-}$ are combined. At pH 8, the concentration of $H(SeO_3)_2^{3-}$ is higher at a given Se(IV) concentration than at pH 7 and a higher reactivity for the 3− anion might be expected in contributing to K_{os}'' and hence k_2'.

If $K_{os}'' = 15$ for all hydroxo complexes and K_{os}' is assigned a value of unity, then values of the interchange rate coefficients at 25 °C are as follows.

	k_{Se}', s^{-1}	k_{Se}'', s^{-1}
cis-$Co(en)_2(OH)(OH_2)^{2+}$	4	7
$Co(NH_3)_5OH^{2+}$	8	13
$Rh(NH_3)_5OH^{2+}$	20	24

These estimates suggest that the difference in reactivities between $HSeO_3^-$ (k_{Se}') and the dimeric anions (k_{Se}'') is almost wholly attributable to the differences in the outer-sphere association constants, K_{os}' and K_{os}''. Again, the rhodium(III) complex is more reactive than the cobalt(III) complexes whose reactivities are little influenced by the nature of the amine and ammine ligands, and their stereochemistry. Within the accuracy attainable K_{os}'' is temperature independent, and thus the $\Delta H^{\ddagger}$ values for the interchange reaction (10) are in the range 45–55 kJ mol^{-1} which now seems characteristic of O substitution at a Se(IV) center.

The activated complex for the interchange reaction may then be visualized as



in which the two leaving groups are H_2O and $HSeO_3^-$. A hydrogen-bonded structure for $H_2(SeO_3)_2^{2-}$ and $H(SeO_3)_2^{3-}$ accounts for the ease with which these dimeric anions can reversibly dissociate with negligible enthalpy changes[6] with little effect on $\Delta H^{\ddagger}$ for selenito formation.

The rate of O substitution at the Se(IV) center may be compared for the hydroxo ligand and for $H_2{}^{18}O$ exchange.[7] The exchange process at pH 8 also has a complex rate law with a predominant contribution from the dimeric anions, especially $H(SeO_3)_2^{3-}$. At 25 °C, the extrapolated data of Okumura and Okazaki yield $k_{ex} = 0.062\ s^{-1}$ at [Se(IV)] = 0.05 M while for $Co(NH_3)_5OH^{2+}$, $k_{an} = 0.40\ s^{-1}$. This sixfold greater rate for the interchange process is comparable to the sevenfold greater rate observed[8] for IO_3^- complexing with $Cr(NH_3)_5OH_2^{3+}$.

Enthalpies of activation for the reactions of *cis*- and *trans*-$Co(tn)_2OH(OH_2)^{2+}$ and *trans*-$Co(en)_2OH(OH_2)^{2+}$ cannot be reliably estimated since the two rate terms have not been evaluated at the various temperatures. Nevertheless the apparent activation energies are all very close to the value deduced for *cis*-$Co(en)_2OH(OH_2)^{2+}$ suggesting that the same interchange mechanism is applicable in these complexes.

Table VIII. Activation Parameters for Reaction of Se(IV) with Hydroxocobalt(III) Complexes at pH 10 and Ionic Strength 1.0 M ($NaClO_4$)

Hydroxo complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$, J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298}$, kJ mol^{-1}
cis-$Co(en)_2(OH)_2^+$	48.1 ± 1.0	−101 ± 6	78.2 ± 2.8
trans-$Co(en)_2(OH)_2^+$	59.2 ± 3.0	−60.8 ± 8.1	77.3 ± 5.4
cis-$Co(tn)_2(OH)_2^+$	61.8 ± 1.0	−56.8 ± 3.3	78.7 ± 2.0
trans-$Co(tn)_2(OH)_2^+$	45.1 ± 1.3	−104 ± 9	76.1 ± 4.0
$Co(NH_3)_5OH^{2+}$	52.3 ± 1.2	−91 ± 4.9	79.5 ± 2.7

Reactions of Hydroxo Complexes with SeO_3^{2-}. Reactions of the dihydroxo complexes with SeO_3^{2-} (Table VII) are 15–24 times slower than rates at pH 6–7 (Tables V and VI). For the cis and trans isomers of $Co(en)_2(OH)_2^+$ and $Co(tn)_2(OH)_2^+$, which exist predominantly as the divalent hydroxoaquo species at pH 6–7, the increased rate at this lower pH must be partly due to higher degrees of association with the dimeric anions.

In the case of $Co(NH_3)_5OH^{2+}$, where the same charged substrate exists at both pH 10 and pH 8, the increase in rate at the lower pH—at 25 °C and 0.10 M Se(IV), k_{an} = 1.25 and 0.185 s^{-1} at pH 8 and 10, respectively—can be directly attributed to the different reacting forms of Se(IV).

A similar interchange mechanism to that at pH 3.3 is proposed for reaction at pH 10 with HO^- as the leaving group. For the various complexes at pH 10, the average value of the entropy of activation (−83 J K^{-1} mol^{-1}) is much more negative than the average value ($\Delta S^{\ddagger}$ = −43 J K^{-1} mol^{-1}) at pH 3.3 where water is the leaving group. This is consistent with the high degree of electrostriction associated with the HO^- ion in solvent water.[9]

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Registry No. *cis*-$Co(tn)_2(OH)_2^+$, 61634-29-5; *trans*-$Co(tn)_2(OH)_2^+$, 61687-73-8; *cis*-$Co(en)_2(OH)_2^+$, 21247-61-0; *trans*-$Co(en)_2(OH)_2^+$, 21772-94-1; $Co(NH_3)_5OH^{2+}$, 16632-75-0; $Rh(NH_3)_5OH^{2+}$, 26214-91-5; *cis*-$Co(en)_2OH(OH_2)^{2+}$, 16787-15-8; *cis*-$Co(tn)_2OH(OH_2)^{2+}$, 61687-74-9; *trans*-$Co(tn)_2OH(OH_2)^{2+}$, 61634-19-3; *trans*-$Co(en)_2OH(OH_2)^{2+}$, 24458-51-3; $HSeO_3^-$, 20638-10-2; SeO_3^{2-}, 14124-67-5.

References and Notes

(1) To whom correspondence should be addressed at The University of Melbourne.
(2) A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, **16**, 1271 (1977).
(3) T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc.*, **94**, 8357 (1972).
(4) A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, preceding paper in this issue.
(5) L. Barcza and L. G. Sillén, *Acta Chem. Scand.*, **25**, 1250 (1971).
(6) R. Arnek and L. Barcza, *Acta Chem. Scand.*, **26**, 213 (1972).
(7) A. Okumura and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 1084 (1973).
(8) R. K. Wharton, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **14**, 33 (1975).
(9) R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 971 (1964).