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Selenitometal Complexes. 2. Kinetics and Mechanism of the Reaction of Aquocobalt(III) Cations with Hydrogenselenite Anions

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The reaction of five aquocobalt(III) complexes with $HSeO_3^-$ to form selenito complexes occurs in aqueous solution at pH 1–3 in the millisecond time scale. These rates are at least 10^3 times faster than the rate of aquoligand exchange with solvent water. An I_a interchange mechanism is proposed involving rapid reversible formation (K_{os}) of an outer-sphere precursor $ROH_2^{3+}\cdot HSeO_3^-$ followed by rate-determining (k_{HSeO_3}) nucleophilic attack of O of the aquo ligand on the Se(IV) center with concerted Se–O bond rupture and H_2O as the leaving group. With *cis*-$Co(tn)_2(OH_2)_2^{3+}$ (where tn = $NH_2CH_2CH_2CH_2NH_2$), $K_{os} = 6.7 \pm 0.6$ M^{-1}, $k_{HSeO_3} = 63 \pm 4$ s^{-1} at 30 °C, $\Delta H^{\ddagger} = 53.8 \pm 1.3$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -41.5 \pm 3.5$ J K^{-1} mol^{-1}. For selenito formation at both pH 1 and pH 3, $\Delta H^{\ddagger}$ values all fall in the range 48–57 kJ mol^{-1} for the substrates $Co(NH_3)_5OH_2^{3+}$, *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$, and *cis*- and *trans*-$Co(tn)_2(OH_2)_2^{3+}$. The major reaction pathway involves outer-sphere association with $HSeO_3^-$ but at pH 1 there is a minor contribution from a H_2SeO_3 pathway. There is no significant effect on the selenito formation and aquation rates by the various ammine and amine ligands but there is a small trans effect attributable to the aquo ligand. Aquation of the five selenito complexes also involves $\Delta H^{\ddagger}$ values in the range 49–54 kJ mol^{-1} and a reverse I_a mechanism is proposed.

Introduction

Oxo anions of the group 6 elements differ widely in their lability, depending on the oxidation state of the group 6 element. The oxo anions SO_4^{2-} and SeO_4^{2-} are relatively inert to oxygen exchange with solvent water.[2] Their reactions with inert aquocobalt(III) substrates are also very slow, with reaction half-times somewhat greater than the half-times for exchange of aquo ligands and typically[3] of the order of 10^5 s at 25 °C.

In sharp contrast, the group 6 oxo anions SO_3^{2-} and SeO_3^{2-} are much more labile. The reactions of SO_3^{2-} with inert aquocobalt(III) cations exhibit half-times of seconds or milliseconds[4] to yield S-bonded complexes which exhibit marked trans activation due to $-SO_3$ ligands.[5-7] A short-lived O-bonded sulfito complex has recently been identified spectroscopically[8] and shown to be a precursor to the S-bonded sulfito complex. This high lability with respect to sulfito complex formation correlates with the high lability of SO_3^{2-} and especially its related protonated and dimeric forms, with respect to solvent water exchange.[9]

Our equilibrium and preparative studies[10] have shown that the protonated and dimeric forms of SeO_3^{2-} also coordinate rapidly with inert aquocobalt(III) cations to yield stable O-bonded selenito complexes. Likewise, the lability of Se(IV) species with respect to solvent water exchange has been recently demonstrated[11] at least over the range pH 8.7–12.5.

The purposes of work described in this paper were to identify the reactive form of Se(IV) responsible for selenito complex formation in acidic media, to investigate the influence of the stereochemistry and the nature of amine ligands on formation rates, and to seek evidence for the mechanism involved in these unusually rapid reactions. In order to simplify the interpretations, concentrations of Se(IV) were held reasonably low so that the predominant species were $HSeO_3^-$, H_2SeO_3, and $H_4(SeO_3)_2$ with minor amounts of $H_3(SeO_3)_2^{2-}$ and $H_2(SeO_3)_2^{2-}$.

Experimental Section

Materials. Crystalline samples of *trans*-$[Co(tn)_2OH(OH_2)](ClO_4)\cdot 2H_2O$,[12] *cis*- and *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$, and $[Co(NH_3)_5OH_2](ClO_4)_3$ were prepared as before.[10] Recrystallized sodium selenite was dried and analyzed as previously described.[10] Sodium perchlorate ($NaClO_4\cdot H_2O$, Fluka) was used without further purification for the adjustment of ionic strength.

Since the $Co(en)_2OH(OH_2)^{2+}$ complexes undergo rapid isomerization at room temperature, these salts were dissolved rapidly in dilute perchloric acid of appropriate pH to generate solutions of the diaquo complexes which could then be temperature equilibrated prior to kinetic runs.

Solutions of *cis*-$Co(tn)_2(OH_2)_2^{3+}$ were generated by dissolving crystalline *trans*-$Co(tn)_2OH(OH_2)^{2+}$ in perchloric acid and at least 6 half-times ($t_{1/2}$ = 70 s at 25 °C)[13] were allowed to elapse for isomerization of the *trans*-diaquo compound to form the pure *cis*-diaquo solution.

Isomerization of *trans*-$Co(tn)_2(OH_2)_2^{3+}$ is too rapid to allow solutions of this complex to be readily temperature equilibrated. Instead, crystalline *trans*-$Co(tn)_2OH(OH_2)^{2+}$ was dissolved in water at pH 9–10 to generate *trans*-$Co(tn)_2(OH)_2^+$, which isomerizes with a half-time of 2 h at 25 °C. The desired pH of the reaction solution was attained on mixing the temperature-equilibrated aquo and selenite solutions. This pH was checked after each set of kinetic runs.

Kinetic Procedures. Selenito formation reactions were conducted under pseudo-first-order conditions with the concentrations of aquo complexes in the range (0.5–1.0) × 10^{-2} M and with Se(IV) concentrations 5–50 times the aquo concentrations after mixing. The reactions were detected in a stopped-flow apparatus based on the design of Tregloan and Laurence[14] but modified for spectrophotometric detection. Usually the reactions were followed in the region 480–560 nm, as appropriate for individual reaction systems. The stopped-flow apparatus had an optical path length of 2 mm and a dead time of about 5 ms. Thermal panels enclosed the entire storage, drive, and flow sections of the apparatus and thermostated water was rapidly circulated through these panels from an external thermostat tank to maintain temperature stability not worse than ±0.1 °C. The photomultiplier response of the stopped-flow apparatus was adjusted so that the intensity of the transmitted light (V, mV) was such that ($V_0 - V_t$) was proportional to the optical absorbance ($A_0 - A_t$) when ($V_0 - V_t/V_0$) < 0.1. First-order rate coefficients were evaluated from computer plots of log ($V_0 - V_t$) vs. time where values of V were read from Polaroid photographs of traces on a Tektronix Type 564 storage oscilloscope. Each quoted rate coefficient was the average of at least four separate determinations. Any individual rate coefficient which, on the basis of a least-squares analysis, had a linear correlation coefficient less than 0.995 for data taken up to at least 3 reaction half-lives was rejected.

In a given rate measurement, the two reactants were temperature equilibrated at a predetermined pH value as detailed above. For all reactions studied, the pH of all mixed solutions which had passed through the stopped-flow apparatus was rechecked to ensure that the anticipated pH on mixing had been attained.

Results

Concentration Dependence upon Se(IV) at pH 3.3. The dependence of selenito formation rate upon Se(IV) concentration was investigated in detail for the substrate *cis*-$Co(tn)_2(OH_2)_2^{3+}$. Under the concentration ratios employed, conversion of *cis*-$Co(tn)_2(OH_2)_2^{3+}$ to *cis*-$Co(tn)_2(OH_2)OSeO_2H^{2+}$ was almost complete (see Table III) and only a 2% correction to the observed rate coefficient for the reverse aquation process was necessary at pH 3.3.

At 22 °C and at an ionic strength of 1.0 M adjusted with sodium perchlorate, only an averaged pair of acidity constants, $pK_{a1}' = 4.75$ and $pK_{a2}' = 7.45$,[15] was obtained for $Co(tn)_2(OH_2)_2^{3+}$ due to the rapid (seconds) isomerization of this complex. Since these values are close to those for the *trans*-$Co(en)_2(OH_2)_2^{3+}$ complex ($pK_{a1} = 4.45$, $pK_{a2} = 7.94$ at 25 °C[16]), we estimate $pK_{a1} \simeq 6.0$ and $pK_{a2} \simeq 8.0$ for *cis*-$Co(tn)_2(OH_2)_2^{3+}$ by analogy with the measured values for *cis*-$Co(en)_2(OH_2)_2^{3+}$ ($pK_{a1} = 6.06$, $pK_{a2} = 8.19$ at 25 °C). Consequently at pH 3.3, less than 0.1% of the diaquo complex exists in the hydroxoaquo form. Likewise at pH 3.3 in the Se(IV) concentration range 0.025–0.25 M, the hydrogenselenite ion $HSeO_3^-$ constitutes 51–77% of the total Se(IV) and H_2SeO_3 from 10 to 14%. Only minor amounts of the dimeric species, $H_4(SeO_3)_2$, $H_3(SeO_3)_2^-$, and $H_2(SeO_3)_2^{2-}$ are present.[17]

The red *cis*-$Co(tn)_2(OH_2)_2^{3+}$ cation exhibits two visible absorption maxima at 510 nm (ϵ 62 M^{-1} cm^{-1}) and 360 nm (ϵ 78 M^{-1} cm^{-1}). The reaction at pH 3.3 with selenite yields exclusively red-purple *cis*-$Co(tn)_2(OH_2)OSeO_2H^{2+}$ with a single absorption maximum in the visible region at 540 nm (ϵ 78 M^{-1} cm^{-1}). The selenito formation reaction was therefore followed at two separate wavelengths, 560 and 480 nm, the former corresponding to an increase in optical absorbance on forming the selenito complex and the latter a decrease in optical absorbance. There was no statistically significant difference in the values of first-order rate coefficients measured at the two monitoring wavelengths (see Table I).

First-order rate coefficients for selenito formation, k_{an}, for reaction between *cis*-$Co(tn)_2(OH_2)_2^{3+}$ and Se(IV) at pH 3.3 are summarized in Table I. Values of k_{an} tend to a limiting value at high Se(IV) concentrations and Figure 1 illustrates the variation of k_{an} with the concentration of $HSeO_3^-$, the principal Se(IV) constituent. The $HSeO_3^-$ concentrations are calculated from the distribution data of Barcza and Sillén[17] for 1 M $NaClO_4$.

Table I. Kinetic Data for the Reaction of *cis*-$Co(tn)_2(OH_2)_2^{3+}$ with Se(IV) at 30.3 °C, pH 3.3, Ionic Strength 1.0 M ($NaClO_4$), and [*cis*-$Co(tn)_2(OH_2)_2^{3+}$] = 0.005 M

10^2[Se(IV)], M	k_{obsd},[a,c] s^{-1}	k_{obsd},[b,c] s^{-1}	k_{an},[d] s^{-1}
2.5	6.86 ± 0.23	6.10 ± 0.35	6.35
3.75	10.6 ± 0.4	10.1 ± 0.3	10.1
5.0	12.3 ± 0.6	12.1 ± 0.5	12.0
7.5	15.2 ± 0.3	15.8 ± 0.6	15.2
10	18.5 ± 0.3	18.1 ± 0.4	17.9
15	21.1 ± 0.6	23.1 ± 1.0	21.7
25		28.7 ± 1.2	28.1

[a] Measured at 480 nm. [b] Measured at 560 nm. [c] Errors shown are one standard deviation. [d] Mean value corrected for reverse aquation.

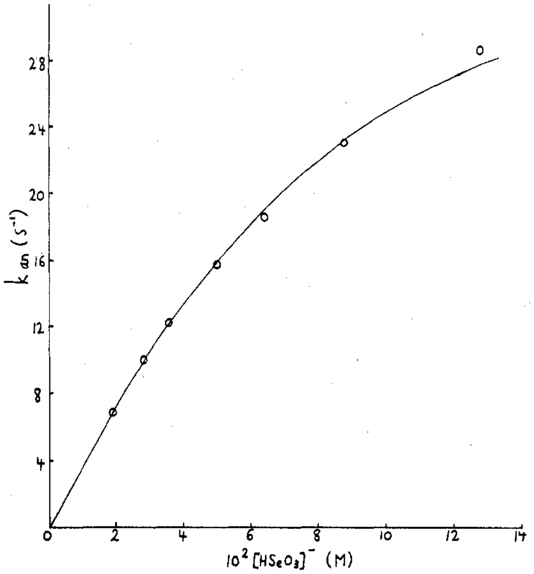


Figure 1. Plot of k_{an} vs. [$HSeO_3^-$] for *cis*-$Co(tn)_2(OH_2)_2^{3+}$ at pH 3.3, T = 30.3 °C, and μ = 1.0 M (adjusted with $NaClO_4$). Values of [$HSeO_3^-$] were calculated from the Se(IV) distribution data of Barcza and Sillén[17] for a 1 M $NaClO_4$ medium.

The data are consistent with an interchange mechanism (I) involving the rapid formation of a precursor outer-sphere species in a preequilibrium, followed by rate-determining interchange (or substitution) between outer and inner spheres of the complex

$$cis\text{-}Co(tn)_2(OH_2)_2^{3+} + HSeO_3^- \xrightleftharpoons{K_{os}} cis\text{-}Co(tn)_2(OH_2)_2^{3+}\cdot HSeO_3^- \quad (1)$$

$$cis\text{-}Co(tn)_2(OH_2)_2^{3+}\cdot HSeO_3^- \xrightarrow{k_{HSeO_3}} cis\text{-}Co(tn)_2(OH_2)OSeO_2H^{2+} + H_2O \quad (2)$$

for which it follows that

$$k_{an} = k_{HSeO_3}K_{os}[HSeO_3^-]/(1 + K_{os}[HSeO_3^-]) \quad (3)$$

Values of k_{HSeO_3} and K_{os} may be deduced (eq 3) from a graphical plot of $1/k_{an}$ vs. $1/[HSeO_3^-]$ yielding an intercept $1/k_{HSeO_3}$ and a gradient $1/K_{os}k_{HSeO_3}$. This plot is shown in Figure 2 and yields the values $K_{os} = 6.7 \pm 0.6$ M^{-1} and $k_{HSeO_3} = 63 \pm 4$ s^{-1} at 30.3 °C, pH 3.3, and ionic strength 1.0 M ($NaClO_4$). Possible contributions from other reaction pathways involving H_2SeO_3 and the hydroxoaquo complex are considered in detail below.

Table II. Activation Parameters for the Reaction of Aquocobalt(III) Complexes with Se(IV) Determined at pH 3.3 and Ionic Strength 1.0 M ($NaClO_4$), with [Aquo Complex] = 0.01 M and [Se(IV)] = 0.1 M

Aquo complex	$\Delta H^{\ddagger}$,[a] kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$,[a] J K^{-1} mol^{-1}
cis-$Co(en)_2(OH_2)_2^{3+}$	54.3 ± 1.9	−40.0 ± 4.0
trans-$Co(en)_2(OH_2)_2^{3+}$	48.0 ± 2.5	−52.8 ± 5.4
cis-$Co(tn)_2(OH_2)_2^{3+}$	53.8 ± 1.3	−41.5 ± 3.5
trans-$Co(tn)_2(OH_2)_2^{3+}$	50.5 ± 3.1	−42.1 ± 4.5
$Co(NH_3)_5OH_2^{3+}$	56.6 ± 2.0	−37.8 ± 4.1

[a] Errors shown are one standard deviation determined by a weighted least-squares program.

Activation parameters for the rate-determining interchange process (k_{HSeO_3}) were evaluated from the measured temperature variation of k_{an} at a fixed Se(IV) concentration of 0.1 M. At this concentration, the fraction of outer-sphere association at 30 °C is $f = K_{os}[HSeO_3^-]/(1 + K_{os}[HSeO_3^-]) = 0.40$ and $k_{an} = fk_{HSeO_3}$. A temperature variation of k_{an} therefore will include a possible contribution from the temperature variation of f. However, ΔH° for outer-sphere association of selenites with cobalt(III) amines is very small[20] ranging from 0.8 to 4.2 kJ mol^{-1}. For a maximum value of 4 kJ mol^{-1}, f varies only by 4% in the typical 25–40 °C temperature range, with a contribution of $\Delta H = 2.2$ kJ mol^{-1}. Since there are grounds for believing that this is an overestimate (see below), we have assumed that the temperature variation of k_{an} arises solely from the temperature variation of k_{HSeO_3}. While higher concentrations of Se(IV) would have ensured almost complete association ($f = 1$) and thereby reduced the systematic uncertainty in the activation parameters, these higher Se(IV) concentrations would have introduced additional complications from other pathways involving dimeric biselenite species.

Similar considerations apply to the other aquo complexes for which variations of k_{an} with temperature were measured at [Se(IV)] = 0.1 M. Values of K_{os} were not evaluated for each of these aquo complexes, but limited concentration dependences of selenito formation rates indicated very similar behavior for *cis*-$Co(tn)_2(OH_2)_2^{3+}$. The activation parameters determined under these conditions are summarized in Table II and rate coefficients at various temperatures are listed in Table III.

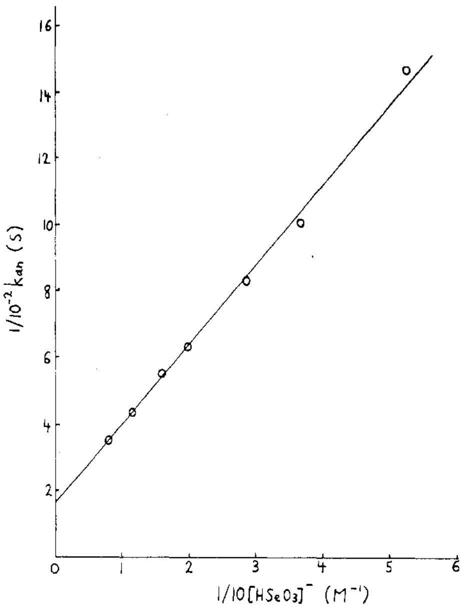


Figure 2. Plot of $1/k_{an}$ vs. $1/[HSeO_3^-]$ for *cis*-$Co(tn)_2(OH_2)_2^{3+}$; $k_{an} = 63 \pm 4$ s^{-1}, $K_{os} = 6.7 \pm 0.6$ M^{-1}.

pH Dependence of Selenito Formation Rates. Rate coefficients for the reaction of Se(IV) with a range of aquo complexes were measured in perchlorate media at both pH 1 and pH 3.3. In no system was there more than 2.2% of the aquo complex present in the hydroxoaquo (or hydroxo) form at pH 3.3 while at pH 1 the proportion of hydroxo complexes present was insignificant. The relevant acidity constants at 25 °C and 1 M ionic strength are as follows: $Co(NH_3)_5OH_2^{3+}$, pK_a = 6.60; *cis*-$Co(en)_2(OH_2)_2^{3+}$, pK_{a1} = 6.06; *trans*-$Co(en)_2(OH_2)_2^{3+}$, pK_{a1} = 4.45; *trans*-$Co(tn)_2(OH_2)_2^{3+}$, p$K_{a1} \simeq$ 4.75. At a fixed Se(IV) concentration, the effect of reducing the pH of the medium from pH 3.3 to pH 1 is to cause a drastic reduction in the proportion of Se(IV) existing as $HSeO_3^-$.[17] At [Se(IV)] = 0.1 M, $HSeO_3^-$ constitutes only 3.2% of Se(IV) while H_2SeO_3 constitutes 59.1% at pH 1; at pH 3.3, the proportion of Se(IV) present as $HSeO_3^-$ is 71.0% and only 6.6% exists as H_2SeO_3.

At pH 1, the rates of selenito complex formation (k_{an}) and the rates of aquation (k_{aq}) of the selenito complexes are comparable in magnitude. It is therefore possible to split observed rate coefficients into k_{an} and k_{aq} using the equilibrium quotients determined in our previous study.[10] Values of k_{an} at pH 1 and at pH 3.3 are collected in Table III for a fixed Se(IV) concentration of 0.1 M. The values of k_{an} fall by a

Table III. Temperature and pH Dependence Studies of the Reaction of Aquocobalt(III) Complexes with Se(IV) at Ionic Strength 1.0 M ($NaClO_4$), with [Aquo Complex] = 0.01 M and [Se(IV)] = 0.1 M

Aquo complex	Temp, °C	k_{an}(pH 3.3),[a] s^{-1}	k_{an}(pH 1.0),[a] s^{-1}	k_{an}^{calcd}(pH 1.0), s^{-1}
cis-$Co(tn)_2(OH_2)_2^{3+}$	25	17.4 ± 0.6	0.56 ± 0.03	0.5
	30	25.9 ± 0.8	0.78 ± 0.02	0.8
	35	37.2 ± 1.1	1.11 ± 0.01	1.0
	40	50.5 ± 2.8	1.61 ± 0.02	3.0
trans-$Co(tn)_2(OH_2)_2^{3+}$	10	20.2 ± 0.7	1.90 ± 0.04	0.6
	15	29.9 ± 1.1	2.79 ± 0.10	0.9
	20	44.1 ± 1.4	4.33 ± 0.26	1.1
cis-$Co(en)_2(OH_2)_2^{3+}$	25	16.8 ± 0.5	0.40 ± 0.01	0.4
	30	25.1 ± 0.7	0.58 ± 0.02	0.7
	35	35.2 ± 0.3	0.67 ± 0.02	1.0
	40	50.0 ± 0.8	1.17 ± 0.06	1.5
trans-$Co(en)_2(OH_2)_2^{3+}$	15	22.9 ± 0.6	2.93 ± 0.10	0.7
	20	30.6 ± 0.6	4.06 ± 0.28	0.9
	25	47.0 ± 1.0	6.08 ± 0.17	1.3
$Co(NH_3)_5OH_2^{3+}$	25	8.8 ± 0.2	0.43 ± 0.02	0.3
	30	13.6 ± 0.4	0.60 ± 0.03	0.4
	35	18.8 ± 0.5	0.83 ± 0.03	0.5
	40	27.1 ± 0.5	1.16 ± 0.04	0.8

[a] Errors are one standard deviation.

Table IV. Activation Parameters for the Reaction (k_{an}) of Aquocobalt(III) Complexes with Se(IV) Determined at pH 1 and Ionic Strength 1.0 M ($NaClO_4$), with [Aquo Complex] = 0.01 M and [Se(IV)] = 0.1 M

Aquo complex	$\Delta H^{\ddagger}$,[a] kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$,[a] J K^{-1} mol^{-1}
cis-$Co(tn)_2(OH_2)_2^{3+}$	52.7 ± 2.4	−73.7 ± 10.0
trans-$Co(tn)_2(OH_2)_2^{3+}$	54.0 ± 2.6	−49.4 ± 7.4
cis-$Co(en)_2(OH_2)_2^{3+}$	52.2 ± 2.5	−78.2 ± 10.2
trans-$Co(en)_2(OH_2)_2^{3+}$	48.8 ± 2.4	−67.0 ± 8.6
$Co(NH_3)_5OH_2^{3+}$	49.5 ± 2.0	−86.7 ± 10.5

[a] Errors quoted are standard deviations determined by a weighted least-squares program.

factor of about 10 for the two trans complexes when the pH is reduced from 3.3 to 1. For the cis complexes and for $Co(NH_3)_5OH_2^{3+}$, the fall in k_{an} values is by a factor of 20–40 times. The marked fall in k_{an} with pH can be correlated with a similar reduction in the concentration of the species active at pH 3.3, namely, $HSeO_3^-$.

At pH 1, the simplest reaction pathway to be considered is that in which reaction proceeds entirely through the I mechanism, involving only $HSeO_3^-$, as proposed in eq 1 and 2. The values of k_{an} measured at high concentrations of $HSeO_3^-$ at pH 3.3 may be used to calculate values k_{an}^{calcd} at pH 1 assuming that at the low (0.005 M) concentration of $HSeO_3^-$, $k_{an} \propto [HSeO_3^-]$ (see Figure 1). The calculation of k_{an}^{calcd} is subject to some uncertainties, especially in the estimated pH variations in $[HSeO_3^-]$ in different electrolyte media, and values of k_{an}^{calcd} are quoted only to a limited accuracy. Nevertheless, the values in Table III show that for cis complexes, $k_{an} \simeq k_{an}^{calcd}$ which implies that for the cis complexes selenito complex formation proceeds almost exclusively through an outer-sphere complex involving $HSeO_3^-$ as the only effective Se(IV) species. For the trans aquo complexes, and to a lesser extent with $Co(NH_3)_5OH_2^{3+}$, $k_{an} > k_{an}^{calcd}$. This implies that there is another reaction pathway probably involving H_2SeO_3. At 20 °C, this pathway would contribute $k_{H_2SeO_3} \simeq 3.3$ s^{-1} for *trans*-$Co(tn)_2(OH_2)_2^{3+}$ whereas at pH 3.3 $k_{an} = 44$ s^{-1} for the $HSeO_3^-$ pathway; for *trans*-$Co(en)_2(OH_2)_2^{3+}$, $k_{H_2SeO_3} \simeq 3.0$ s^{-1} whereas $k_{an} = 30.6$ s^{-1}; and for $Co(NH_3)_5OH_2^{3+}$ at 35 °C, $k_{H_2SeO_3} \simeq 0.33$ s^{-1} whereas $k_{an} = 18.8$ s^{-1}. The pathway involving H_2SeO_3 contributes significantly to the overall rate of trans selenito formation at pH 1 but the intrinsic value of the rate coefficient is only $^1/_{10}$th the value for reaction due to $HSeO_3^-$.

At pH 3.3, another possible reaction pathway could involve the more labile hydroxoaquo complexes, present only as 2% of the aquo complexes, through an outer-sphere species such as $ROH^{2+}\cdot HSeO_3^-$. If this pathway had contributed significantly to the overall rate of selenito formation at pH 3, then it would be expected that $k_{an}^{calcd} > k_{an}$. Table III shows no cases where $k_{an}^{calcd} > k_{an}$ and this pathway is unlikely to be important. Our direct measurements[19] of selenito formation at pH 7–8, where the hydroxoaquo complexes predominate, confirm that this pathway is insignificant at pH 3.3.

Activation parameters for selenito formation at pH 1 from various aquo complexes are listed in Table IV. For all systems, the $\Delta H^{\ddagger}$ values are within the unusually low range 49–54 kJ mol^{-1}. Furthermore, values of $\Delta H^{\ddagger}$, determined at pH 1, are equal within experimental error to the corresponding values determined at pH 3.3 (compare Table II). At pH 1, $k_{an} = k_{HSeO_3}K_{os}[HSeO_3^-]$ (since $K_{os}[HSeO_3^-] \simeq 0.02$) (eq 3) for the $HSeO_3^-$ pathway, and the temperature variation of k_{an} should contain a full $\Delta H°$ contribution from K_{os}. The observation that $\Delta H^{\ddagger}$ values are virtually equal at pH 1 and at pH 3.3 supports our earlier assumption that $\Delta H_{os}°$ for these complexes is close to zero. Activation enthalpies should therefore refer directly to the interchange reaction.

Aquation of Selenito Complexes. Rate coefficients observed for selenito formation at pH 1 (k_{obsd}) are collected in Table V together with the values of rate coefficients for the aquation of the selenito complexes (k_{aq}) as derived using our earlier[10] equilibrium quotients for selenito formation. Values of k_{aq} may also be calculated from k_{obsd} for selenito formation at pH 3.3 and these are also listed in Table V. Values of k_{aq} derived at pH 3.3 are equal to or greater than values of k_{aq} at pH 1 showing that there is no evidence for acid-catalyzed aquation due to a second stage of protonation of the monodentate selenito ligands. The aquation process can therefore be written generally, at both pH 1 and pH 3, in the form

$$R\text{-}OSeO_2H^{2+} + H_2O \xrightarrow{k_{aq}} R\text{-}OH_2^{3+} + HSeO_3^- \quad (4)$$

In general, values of k_{aq} derived at pH 1 are considered to be of a greater reliability than those values at pH 3.

Our equilibrium studies[10] have shown that values of the equilibrium quotient Q_s for selenito formation are essentially temperature invariant. Consequently activation enthalpies for aquation equal those for selenito formation. Values of the activation parameters for aquation of five selenito complexes are listed in Table VI.

Table V. Temperature Dependence of Rates of Aquation of Selenitocobalt(III) Complexes at Ionic Strength 1.0 M ($NaClO_4$)

Selenito complex[a]	Temp, °C	k_{obsd}[b,c](pH 1), s^{-1}	k_{aq}(pH 1), s^{-1}	k_{aq}(pH 3.3), s^{-1}
cis-$Co(tn)_2(OH_2)OSeO_2H^{2+}$	25	0.76 ± 0.03	0.20	0.40
	30	1.05 ± 0.02	0.27	0.60
	35	1.50 ± 0.01	0.39	0.89
	40	2.17 ± 0.02	0.56	1.20
trans-$Co(tn)_2(OH_2)OSeO_2H^{2+}$	10	2.27 ± 0.04	0.32	(0.46)[d]
	15	3.26 ± 0.10	0.47	(0.60)
	20	5.05 ± 0.26	0.72	(1.0)
cis-$Co(en)_2(OH_2)OSeO_2H^{2+}$	25	0.58 ± 0.01	0.18	0.34
	30	0.83 ± 0.02	0.25	0.50
	35	1.10 ± 0.02	0.33	0.70
	40	1.68 ± 0.06	0.51	1.0
trans-$Co(en)_2(OH_2)OSeO_2H^{2+}$	15	3.47 ± 0.10	0.54	0.52
	20	4.81 ± 0.28	0.75	0.70
	25	7.21 ± 0.17	1.1	1.1
$Co(NH_3)_5OSeO_2H^{2+}$	25	0.71 ± 0.02	0.28	0.55
	30	1.00 ± 0.03	0.40	0.85
	35	1.39 ± 0.03	0.56	1.2
	40	1.93 ± 0.04	0.77	1.7

[a] The selenito complexes were generated in situ by the reaction of the aquo complex (0.01 M) with Se(IV) (0.1 M); the selenito complex concentrations were in the range 0.0015–0.003 M. [b] $k_{obsd} = k_{aq} + k_{an}$. [c] Errors quoted are one standard deviation. [d] This trans isomer is too labile for direct equilibrium measurements; values quoted assume $Q_s = 44$ as for the corresponding trans $(en)_2$ complex.

Table VI. Activation Parameters for Aquation of Selenitocobalt(III) Complexes at pH 1 and Ionic Strength 1.0 M ($NaClO_4$)

Selenito complex[a]	$\Delta H^{\ddagger}$,[b] kJ mol^{-1}	$\Delta S^{\ddagger}_{298}$,[b] J K^{-1} mol^{-1}
cis-$Co(tn)_2(OH_2)OSeO_2H^{2+}$	52.9 ± 2.6	−81.7 ± 10.6
trans-$Co(tn)_2(OH_2)OSeO_2H^{2+}$	54.0 ± 2.6	−64.0 ± 8.0
cis-$Co(en)_2(OH_2)OSeO_2H^{2+}$	52.0 ± 2.9	−85.6 ± 11.0
trans-$Co(en)_2(OH_2)OSeO_2H^{2+}$	48.8 ± 2.4	−81.3 ± 10.8
$Co(NH_3)_5OSeO_2H^{2+}$	51.3 ± 3.0	−78.7 ± 10.2

[a] The selenito complexes were generated in situ by the reaction of the aquo complex (0.01 M) with Se(IV) (0.1 M); the selenito complex concentrations were in the range 0.0015–0.003 M.

[b] Errors quoted are standard deviations determined by a weighted least-squares program.

Discussion

A major finding of this study is that for the formation of selenito complexes and for their reverse aquation in acidic media, the activation enthalpies for all of the cobalt(III) complexes cluster in the relatively low range 48–57 kJ mol^{-1} (Tables II, IV, and VI). These low values contrast with activation enthalpies of the order of 100–130 kJ mol^{-1} usually observed for reactions based on Co–O bond fission. For example, solvent water exchange with *cis*-$Co(en)_2(OH_2)_2^{3+}$ exhibits[20] $\Delta H^{\ddagger}_{ex} = 126$ kJ mol^{-1} with similar values for interchange substitution by nucleophiles such as $H_2C_2O_4$ and $HC_2O_4^-$ ($\Delta H^{\ddagger} = 104$ kJ mol^{-1})[21] and $H_2PO_4^-$ ($\Delta H^{\ddagger} = 126$ kJ mol^{-1})[22] whereas substitution by $HSeO_3^-$ exhibits $\Delta H^{\ddagger}_{an} = 54.3$ kJ mol^{-1}. Moreover the value of k_{an} for *cis*-$Co(en)_2(OH_2)_2^{3+}$ is 2.2×10^6 times greater than the value of k_{ex} for the aquo-exchange process involving Co–O bond fission.[18] Even for the most labile of the aquo complexes studied, namely, the *trans*-$Co(tn)_2(OH_2)_2^{3+}$ complex which isomerizes 1450 times faster than its en analogue,[13] the value of k_{an} for this complex is 1650 times greater than the estimated water-exchange rate, $k_{ex} = 3.6 \times 10^{-2}$ s^{-1}. These observations are strong evidence for a selenito formation mechanism in which the Co–O bond remains intact.

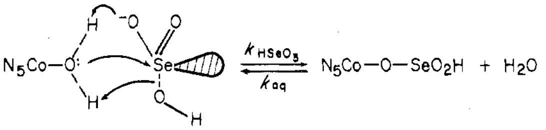
Okumura and Okazaki[11] have shown that at 0 °C solvent $H_2{}^{18}O$ exchange with selenite is relatively rapid and that the rate increases sharply as the pH of the medium is reduced from pH 12 to pH 8.7. The exchange rate, R_{ex}, is described by a multiple rate law

$$R_{ex} = k_1[SeO_3{}^{2-}] + k_2[HSeO_3{}^-] + k_3[HSeO_3{}^-]^2 + k_4[HSeO_3{}^-][SeO_3{}^{2-}] \qquad (5)$$

in which the influence of Se(IV) dimers is represented by the terms in k_3 and k_4 and where $k_2 >> k_1$.

The activation enthalpy for exchange at pH 8.7 is $\Delta H^{\ddagger}_{ex} = 58.6 \pm 3.8$ kJ mol^{-1}. These exchange processes probably proceed by associative mechanisms involving nucleophilic attack by the oxygen of water at a Se(IV) center accompanying rupture of Se–O bonds. The close similarity of $\Delta H^{\ddagger}_{ex}$ and the activation enthalpies for selenito formation and aquation suggests a similarity in associative mechanism with O–Se bond formation and Se–O bond fission as concurrent processes. This conclusion is further reinforced by our experiments[23] on the base hydrolysis of $Co(NH_3)_5OSeO_2^+$ in which $\Delta H^{\ddagger} = 48.1 \pm 1.4$ kJ mol^{-1} and for which ^{18}O-tracer experiments provide clear evidence for attack of HO^- at a selenium center with Se–O bond fission.

In the proposed mechanism for selenito formation, the rate-determining interchange step (eq 2) may be visualized in terms of a hydrogen-bonded activated complex in which the selenium(IV) center assumes a pseudo-trigonal-bipyramidal symmetry (see eq 6). In this activated complex water will function as a leaving group with Se–O bond fission and substitution proceeds by nucleophilic attack of the oxygen atom of the aquo ligand at the Se(IV) center. The reverse process of aquation should pass through the same state again with Se–O bond fission and attack of oxygen from bulk water at the Se(IV) center. Both processes are thus classified mechanistically as associative interchange (I_a) and should exhibit comparable $\Delta H^{\ddagger}$ values, as is observed.



(6)

Values of $\Delta S^{\ddagger}_{an}$ for the I_a process represented by eq 4 are all negative, in the region of −38 to −53 J K^{-1} mol^{-1}. This would be consistent with an associative activated complex sterically hindered by hydrogen bonding. The values of $\Delta S^{\ddagger}_{aq}$ for the reverse aquation process are more negative by 35 ± 10 J K^{-1} as compared to $\Delta S^{\ddagger}_{an}$. This is to be expected for the aquation process which should include a cratic entropy[24] contribution of $R \ln 10^3/M$ (where M is the molecular weight of the solvent) = −33 J K^{-1} mol^{-1} as bulk water is brought in to form the activated complex envisaged in eq 6.

The measured value of $K_{os} = 6.7$ at 30 °C and 1.0 M ionic strength for formation of *cis*-$Co(tn)_2(OH_2)_2^{3+}{\cdot}HSeO_3^-$ might appear rather large in comparison with that of other systems. For similarly charged systems, values assumed at high ionic strengths include $K_{os} = 5$[25] for $Cr(NH_3)_5OH_2^{3+}{\cdot}IO_3^-$, $K_{os} = 1$[25] for *cis*-$Co(en)_2(OH_2)_2^{3+}{\cdot}IO_3^-$, and $K_{os} = 1$ for $Ti^{3+}(aq){\cdot}SCN^-$.[26] However, there is good evidence that quite specific bonding effects occur when SeO_3^{2-} is coordinated in the outer-sphere of cobalt(III) amines. The CD spectrum[27] of $Co(en)_3^{3+}$ shows large shifts in the presence of SeO_3^{2-} and $K_{os} = 130$ was assigned to $Co(en)_3^{3+}{\cdot}SeO_3^{2-}$ at 2 M ionic strength but at an unspecified pH. A much lower value, $K_{os} = 1.2$, was derived[28] from the UV spectrum of SeO_3^{2-}. Extensive potentiometric, solubility, and CD measurements yield $K_{os} = 3.6$ for $Co(en)_3^{3+}{\cdot}SeO_3^{2-}$ at 3 M ionic strength. However, none of these studies appear to have allowed for the extensive protolysis of SeO_3^{2-} to form $HSeO_3^-$ and the outer-sphere complexes will include a contribution from $HSeO_3^-$ association. Our value for $HSeO_3^-$ association, $K_{os} = 6.7$, is therefore probably compatible with this last value taking into consideration the lower ionic strength used here.

The lower reactivity of H_2SeO_3 toward aquo complexes, as compared to $HSeO_3^-$, is explicable in terms of the outer-sphere I_a mechanism. The outer-sphere association constant K_{os} for the uncharged H_2SeO_3 should be less than that for the $HSeO_3^-$ anion. In analogous cases, values of K_{os} which are reduced by a factor of 10 have been assumed.[25] An additional factor contributing to the lower reactivity of H_2SeO_3 is the hydrogen-bonding requirements in the proposed activated complex (eq 6). When $HSeO_3^-$ is a reactant, a hydrogen bond is established with $^-$O–Se whereas this bond must be established with HO–Se when H_2SeO_3 is a reactant. A much reduced rate would be expected in the latter case.

The effect of introducing the six-membered tn chelate, instead of the five-membered en chelate, is often to cause substantial labilization of reactions involving Co–O bond rupture.[13] For example, the isomerization *trans*- → *cis*-$Co(NN)_2(OH_2)_2^{3+}$ is 1450 times faster for the tn complex. The rate data in Table III show that the effect on the selenito formation rate is negligible. For example, at 25 °C $k_{an} = 17.4$ s^{-1} for *cis*-$Co(tn)_2(OH_2)_2^{3+}$ and $k_{an} = 16.8$ s^{-1} for *cis*-$Co(en)_2(OH_2)_2^{3+}$ with similar comparisons for the trans complexes. Likewise, $Co(NH_3)_5OH_2^{3+}$ exhibits k_{an} values almost exactly half those values for *cis*-diaquo complexes and this difference is attributable to a statistical factor of 2 for the number of aquo reaction sites.

The various amine ligands used in this investigation confer different acidities upon the aquo ligand, the pK_a values varying from 4.45 to 6.60 (see above). This is not reflected in corresponding differences in the selenito formation rates. However, the interchange mechanism evisages two distinct functions for the aquo ligand: nucleophilic attack by O at the Se(IV) center and hydrogen transfer to the O atoms of the oxo anion. A large value of pK_a for an aquo ligand should favor the nucleophilic function but reduce the hydrogen-bonding function. Since there is no significant difference in rates, these two effects evidently counterbalance. The importance of the hydrogen-bonding function is shown by comparison of selenito formation and aquation rates at pH 1. Solvent water has a much greater nucleophilicity than an aquo ligand; the rate of aquation is somewhat less than that of selenito formation presumably because of the readier transfer of hydrogen from the more acidic aquo ligand.

There is a small, but significant, trans effect attributable to the aquo ligand in both the selenito formation and selenito aquation rates (Tables III and V). Differences in rate of 3–7 times arise for trans and cis isomers but a clear assignment to differences in $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ values cannot be drawn (Tables II, IV, VI). The effect might be due to hindrance from intermolecular hydrogen bonding between the $HSeO_3^-$ and the vicinal aquo ligand in cis complexes rather than to a specific bond activation by the trans aquo ligand.

Comparable interchange mechanisms involving hydrogen-bonded activated complexes have recently been proposed for the rapid formation of arsenato[29] and iodato[25] complexes from inert aquometal cations. In these cases also, the metal–oxygen bond remains intact, the stoichiometry of the activated complex allows for H_2O as a leaving group, and the O atom of the aquo ligand attacks at the central atom of the oxo anion. A further common feature of these mechanisms is the increase in the coordination number of the central element of the oxo anion. When the oxo anion reacts through associative mechanisms, this property will be related both to the high rate of complex formation and to the high rate of exchange with solvent $H_2{}^{18}O$. This might also be involved in the rapid reactions of WO_4^{2-} and MoO_4^{2-} with $Co(NH_3)_5OH_2^{3+}$,[30] of SO_3^{2-} with $Cr(OH_2)_6^{3+}$,[31] and possibly of CrO_4^{2-} with $Co(NH_3)_5OH_2^{3+}$.[32]

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Registry No. *cis*-$Co(en)_2(OH_2)_2^{3+}$, 21247-59-6; *trans*-$Co(en)_2(OH_2)_2^{3+}$, 19314-32-0; *cis*-$Co(tn)_2(OH_2)_2^{3+}$, 51286-38-5; *trans*-$Co(tn)_2(OH_2)_2^{3+}$, 61687-67-0; $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; *cis*-$Co(tn)_2(OH_2)OSeO_2H^{2+}$, 61687-68-1; *trans*-$Co(tn)_2(OH_2)OSeO_2H^{2+}$, 61634-14-8; *cis*-$Co(en)_2(OH_2)OSeO_2H^{2+}$, 61634-15-9; *trans*-$Co(en)_2(OH_2)OSeO_2H^{2+}$, 61687-69-2; $Co(NH_3)_5OSeO_2H^{2+}$, 61634-16-0; $HSeO_3^-$, 20638-10-2.

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