are in the direction one would predict from both of these effects. However the magnitude of the variation is not large and indicates that changing the bridging carboxylate ion has little effect on the rate of water loss.

The variation of the rate constants for a particular carboxylate complex, tetrakis(μ-methoxyacetato)-dirhodium(II), for example, reacting with different ligands is from 4×10^5 to 6.2×10^6 M^{-1} s^{-1} for k_f and from 37 to 1300 s^{-1} for k_r. Though these figures indicate a greater variation in k_r than in k_f thus putting more weight in favor of a dissociative mechanism, the ligand dependency of the rates cannot be overlooked. Whether this results from variations in the extremely small values of K_o, the outer-sphere formation constant, or from participation of the entering ligand in the formation of an activated complex cannot be determined from the available data. It does mean though that the loss of an axial water molecule does not alone determine the rate of these reactions. Though all of the ligands act as monodentate ligands toward the tetra-μ-carboxylato-dirhodium(II) species, the presence of more than one donor atom, as in 5′-AMP or imidazole, increases the rate of formation by an order of magnitude to that with pyridine or histidine where only one binding site is available.

In conclusion, the thermodynamic data show that the order of stability of the adducts formed with nitrogen donor ligands does not always correlate with the biologic activity of these complexes. This does not rule out that simple adduct formation reactions are involved in the anticancer activity of these complexes, but it does show that if it is a factor, only certain types of ligands are involved. Certainly axial bonding with macromolecules such as proteins and polynucleic acids is a completely different situation. In these systems the magnitude and the order of stability of the rhodium(II) complexes will be determined by many factors not present with the monomer units.

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Registry No. $Rh_2(MeO_2Ac)_4 \cdot 2(5'\text{-AMP})$, 56437-38-8; $Rh_2(OAc)_4 \cdot 2(5'\text{-AMP})$, 56437-35-5; $Rh_2(prop)_4 \cdot 2(5'\text{-AMP})$, 56437-37-7; $Rh_2(MeO_2Ac)_4 \cdot 2(\text{imidazole})$, 59532-69-3; $Rh_2(OAc)_4 \cdot 2(\text{imidazole})$, 59532-70-6; $Rh_2(prop)_4 \cdot 2(\text{imidazole})$, 59532-71-7; $Rh_2(MeO_2Ac)_4 \cdot 2(\text{L-histidine})$, 62126-05-0; $Rh_2(OAc)_4 \cdot 2(\text{L-histidine})$, 62154-26-1; $Rh_2(prop)_4 \cdot 2(\text{L-histidine})$, 62154-27-2; $Rh_2(MeO_2Ac) \cdot 2(\text{pyridine})$, 62126-03-8.

References and Notes

(1) R. G. Hughes, J. L. Bear, and A. P. Kimball, *Proc. Am. Assoc. Cancer Res.*, **13**, 120 (1972).
(2) A. Erck, L. Rainen, J. Whileyman, I. Chang, A. P. Kimball, and J. L. Bear, *Proc. Soc. Exp. Biol. Med.*, **145**, 1278 (1974).
(3) J. L. Bear, H. B. Gray, Jr., L. Rainen, I. M. Chang, R. Howard, G. Serio, and A. P. Kimball, *Cancer Chemother. Rep., Part 1*, **59**, 611 (1975).
(4) L. Rainen, R. A. Howard, A. P. Kimball, and J. L. Bear, *Inorg. Chem.*, **14**, 2752 (1975).
(5) K. Das and J. L. Bear, *Inorg. Chem.*, **15**, 2093 (1976).
(6) C. T. Lin and J. L. Bear, *J. Phys. Chem.*, **75**, 3705 (1971).
(7) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).
(8) S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 264, 276 (1958).
(9) K. Kustin and R. F. Pasternack, *J. Phys. Chem.*, **73**, 1 (1969).

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Selenitometal Complexes. 1. Synthesis and Characterization of Selenito Complexes of Cobalt(III) and Their Equilibrium Properties in Solution

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We report the synthesis and characterization of the new selenito complexes $[Co(NH_3)_5OSeO_2](X,Y) \cdot H_2O$, *cis*- and *trans*-$[Co(en)_2(OH_2)OSeO_2H](X,Y)_2 \cdot H_2O$, *cis*-$[Co(en)_2(OH_2)OSeO_2]X \cdot H_2O$, and $[Co(NN)_2O_2SeO]Y \cdot H_2O$ where $X^- = Br^-$, $Y^- = ClO_4^-$, and NN = $NH_2CH_2CH_2NH_2$ (en) or $NH_2CH_2CH_2CH_2NH_2$ (tn). Infrared spectra of the crystalline selenito complexes show that in all complexes the selenito ligand is coordinated exclusively through oxygen, either in a monodentate or in a bidentate form. Acidity constants were determined at 25 °C and in 1.0 M ionic strength, adjusted with sodium perchlorate; for proton release from the aquo ligand in $Co(en)_2(OH_2)OSeO_2^+$, $pK_{aq} = 8.30 \pm 0.05$ for the cis isomer and $pK_{aq} = 7.70 \pm 0.05$ (trans) while for proton release from the hydrogenselenito ligand in $Co(en)_2(OH_2)OSeO_2H^{2+}$, $pK_{a2} = 4.35 \pm 0.05$ (cis) and $pK_{a2} = 4.55 \pm 0.05$ (trans). The overall formation quotient for selenito complexes, Q_s, was determined spectrophotometrically and Q_s varied greatly with pH and the nature of the selenium(IV) species. For four complexes at 25 °C and in 1 M ionic strength, $Q_s = 1.5$–5.4 at pH 1, 16–50 at pH 3, ≥ 100 at pH 7, and ~ 5 at pH 11.5. In the pH range 1–3, the biselenite species $HSeO_3^-$, $H_2(SeO_3)_2^{2-}$, and $H_3(SeO_3)_2^-$ all coordinate almost equally, with β values of about 55 for all diaquo complexes and 23 for the monoaquo complex. Below 40 °C, the equilibrium concentration of bidentate selenito complexes existing with monodentate selenito complexes and free selenite is undetectable under all pH conditions. There is no evidence for the existence of bis(selenito) complexes in aqueous media even in the presence of large concentrations of free selenite.

Introduction

Selenium is now recognized[2] as one of the essential trace elements in human and animal nutrition, yet at higher concentrations, selenium can cause acute and chronic poisoning. Much of this evidence has been derived from nutritional, toxicological, and microbiological studies in which sodium selenite has been fed to test animals. Representative examples include growth stimulation and the control of muscular dystrophies in poultry[3,4] and lambs,[5] the fertility of ewes,[6,7] the toxicity to bacteria,[8] the prolonged retention of trace cadmium in mice,[9] and the inhibitory effect upon carcinogenesis in mice.[10]

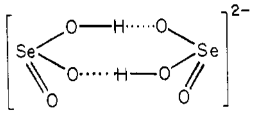
Despite the biological importance of sodium selenite, very little is known of the properties of sodium selenite as a nucleophile and as a potential ligand in metal complexes. The only selenito complexes previously reported[11] are several red hygroscopic compounds $[Co(en)_2SeO_3]X \cdot nH_2O$, where X^- is Cl^-, Br^-, NO_3^-, or SO_4^{2-}, which were prepared by oxidizing cobalt(II) selenite in the presence of ethylenediamine. The selenito group was considered to be only "weakly bound to the metal center" and "readily removed by hydrolysis".

In contrast, this paper shows that for a number of newly isolated selenito complexes of cobalt(III), the selenito ligand is relatively stable to aquation in acid media and that both monodentate and bidentate forms of the selenito ligand can be isolated. The characterization of these complexes is an essential prelude to work described in succeeding papers, in which selenite anions are shown to undergo remarkably rapid substitution of aquo ligands in inert metal complexes.

The properties of selenite anions in aqueous solution are also important in determining selenito complex formation. In dilute aqueous solution, the SeO_3^{2-} anion has a pyramidal structure[12] (C_{3v} symmetry) and is dibasic, forming $HSeO_3^-$ and selenious acid H_2SeO_3. The relevant pK_a values are reported in this paper. At higher selenite concentrations, extensive dimerization occurs with these species[13] to yield $H(SeO_3)_2^{3-}$, $H_2(SeO_3)_2^{2-}$, $H_3(SeO_3)_2^-$, and $H_4(SeO_3)_2$. Simon and Paetzold[14] adduced evidence for pyroselenites when they compared the Raman spectra of concentrated solutions of the species $MHSeO_3$ and $M_2Se_2O_5$. They concluded that the equilibrium

$$2HSeO_3^- \rightleftarrows Se_2O_5^{2-} + H_2O \qquad (1)$$

is established rapidly in solution. Evidence available from the crystal structure analyses of solid hydrogen selenites, however, has not indicated separate polynuclear groups but rather infinite chains or sheets of pyramidal SeO_3 units linked through hydrogen bonds.[15-17] It seems likely that extensive hydrogen bonding between selenites and water takes place in aqueous solution and that this may account for the high solubility of selenito complexes in water. Similarly the structure of dimeric species such as $H_2Se_2O_6^{2-}$ can be represented in terms of the hydrogen-bonded structure



The complications introduced by this characteristic dimerization of selenites necessitate use of the following terminology in this and in subsequent papers: "Se(IV)" will be taken to include all of the possible monomeric and dimeric forms of SeO_3^{2-}; "selenite" will be used to refer directly to the oxo anion SeO_3^{2-} itself; "biselenite" will be taken to include all of the charged species other than SeO_3^{2-}, i.e., $HSeO_3^-$, $H(SeO_3)_2^{3-}$, $H_2(SeO_3)_2^{2-}$, and $H_3(SeO_3)_2^-$; "selenious acid" will be taken to include the uncharged species H_2SeO_3 and $H_4(SeO_3)_2$. The percentage distribution of Se(IV) is quoted in mole percent of the particular Se(IV) species. Likewise, the generic term "aquo complex" will be used as a general reference to all of the protonated and isomeric forms of $Co(en)_2(OH_2)_2^{3+}$ and $Co(tn)_2(OH_2)_2^{3+}$, to the protonated forms of $Co(NH_3)_5OH_2^{2+}$, and, in later papers, to $Rh(NH_3)_5OH_2^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$.

Experimental Section

Materials. In all preparative work, selenious acid (BDH) and anhydrous sodium selenite (BDH) were used without further purification. For the measurement of equilibrium constants in aqueous solution, the anhydrous sodium selenite was recrystallized twice from concentrated aqueous solution by the addition of successive amounts of acetonitrile. The hydrated sodium selenite was then dried in vacuo over P_2O_5 at 60–80 °C. Analysis of the resultant anhydrous sodium selenite as selenium was conducted by the addition of excess iodide ion followed by back-titration of iodine with sodium thiosulfate. The selenium content was always greater than 99.5%.

Solutions of perchloric acid and sodium hydroxide were prepared by dilution of Analytical grade reagents and standardized titrimetrically. Sodium perchlorate ($NaClO_4 \cdot H_2O$, Fluka) was used without further purification. Doubly distilled water was used for all dilutions.

Preparation of Complexes. The complexes $[Co(NH_3)_5OH_2](ClO_4)_3$,[18] *cis*- and *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$,[19] and *trans*-$[Co(tn)_2OH(OH_2)](ClO_4)_2 \cdot 2H_2O$[20,21] were prepared according to published methods.

Selenito(pentaammine)cobalt(III) Perchlorate. $[Co(NH_3)_5OH_2](ClO_4)_3$ (10 g) and Na_2SeO_3 (4 g) were dissolved together in the minimum volume of warm water and the resultant red-purple solution was heated to 70 °C for several minutes. The red-purple crystals which formed on cooling the solution were collected and washed with ethanol. The crude product was recrystallized from the minimum volume of hot water to yield red crystals which were washed with ethanol and then with ether and air-dried. The yield was 5.1 g (60%). Anal. Calcd for $[Co(NH_3)_5OSeO_2](ClO_4) \cdot H_2O$: Co, 15.2; NH_3, 22.0; Se, 20.4. Found: Co, 14.8; NH_3, 21.9; Se, 20.0.

Selenito(pentaammine)cobalt(III) Bromide. $[Co(NH_3)_5OH_2](ClO_4)_3$ (6 g) was dissolved in a water–acetone mixture (sufficient water being added to the acetone to just dissolve the complex) and excess LiBr was added to form the bromide salt of the aquo complex as a red precipitate which was then collected and washed with acetone. The yield was 5.0 g (95%). The red $[Co(NH_3)_5OH_2]Br_3$ complex (5 g) was then reacted with Na_2SeO_3 (2.1 g) using the same procedure as for the perchlorate salt. The bromide salt was obtained as a bright pink crystalline solid. The yield was 3.3 g (60%). Anal. Calcd for $[Co(NH_3)_5OSeO_2]Br \cdot H_2O$: Co, 16.0; NH_3, 23.1; Se, 21.4. Found: Co, 15.6; NH_3, 22.9; Se, 22.9.

***cis*-Hydrogenselenitoaquobis(ethylenediamine)cobalt(III) Perchlorate, $[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$.** *cis*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ (5 g) was added to selenious acid (2 g) and dissolved in the minimum volume of warm water to give a deep red-purple solution which formed a red-purple oil on cooling. Successive additions of ethanol to the oil yielded a pink-purple hygroscopic solid. Recrystallization of this crude product from the minimum volume of hot water produced mauve crystals on the addition of ethanol. The purified product was washed with ethanol followed by ether and air-dried. The yield was 2.6 g (40%). Anal. Calcd for *cis*-$[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$: C, 9.2; N, 10.7; H, 3.6; Cl, 13.6; Se, 15.1. Found: C, 9.5; N, 10.7; H, 3.5; Cl, 14.4; Se, 15.4.

***cis*-Selenitoaquobis(ethylenediamine)cobalt(III) Bromide, $[Co(en)_2(OH_2)OSeO_2]Br \cdot H_2O$.** *cis*-$[Co(en)_2OH(OH_2)]Br_2$ (4 g) was dissolved with sodium selenite (1.9 g) in a minimum volume of cold water at room temperature. Addition of excess LiBr followed by acetone formed a dark red oil, which was allowed to stand overnight under acetone. The resultant wine red crystalline solid was washed with acetone and air-dried. The yield was 1.7 g (40%). Anal. Calcd for *cis*-$[Co(en)_2(OH_2)OSeO_2]Br \cdot H_2O$: C, 12.0; N, 13.9; H, 4.5; Br, 19.9; Se, 19.6. Found: C, 12.0; N, 13.5; H, 4.1; Br, 20.1; Se, 18.8.

Selenitobis(ethylenediamine)cobalt(III) Perchlorate, $[Co(en)_2O_2SeO]ClO_4 \cdot H_2O$. *cis*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ (6 g) was added to sodium selenite (2.5 g) dissolved in a minimum volume of warm water and the resultant deep red-purple solution was heated to 60 °C for 10 min. A deep red-purple oil formed on cooling the solution and this was precipitated as a mauve solid by successive additions of ethanol. The crude hygroscopic product was washed with ethanol followed by ether and air-dried briefly. The purple ethanolic filtrate was concentrated to yield further solid product which was then combined with the first batch for recrystallization from a minimum volume of hot water. The solution was allowed to cool slowly to yield crimson crystalline plates which were washed and dried as above. The yield was 1.5 g (25%). Anal. Calcd for $[Co(en)_2O_2SeO]ClO_4 \cdot H_2O$: C, 11.9; N, 13.9; H, 4.0; Cl, 8.9; Se, 19.6. Found: C, 11.3; N, 13.6; H, 3.9; Cl, 8.8; Se, 18.9.

***trans*-Hydrogenselenitoaquobis(ethylenediamine)cobalt(III) Perchlorate, $[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$.** *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ (5 g) was added to selenious acid (2 g) dissolved in the minimum volume of water whose temperature was maintained below 10 °C. The red *trans*-hydroxoaquo complex dissolved to form a dark gray-green solution from which a gray precipitate rapidly formed. The crude product was collected, washed with ethanol, and air-dried. The yield at this stage of the synthesis was 2.7 g (40%). Recrystallization of the crude trans selenito complex was conducted in dilute acidic solution to prevent the rapid isomerization to the more stable cis isomer which occurs under neutral pH conditions. The purified trans product was collected as blue-green needles which were washed with ethanol and then ether and air-dried. The yield was 1.3 g (20%). Anal. Calcd for *trans*-$[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$: C, 9.2; N, 10.7; H, 3.6; Cl, 13.5; Se, 15.1. Found: C, 8.8; N, 10.2; H, 3.6; Cl, 13.4; Se, 15.3.

***trans*-Hydrogenselenitoaquobis(ethylenediamine)cobalt(III) Bromide, $[Co(en)_2(OH_2)OSeO_2H]Br_2 \cdot 2H_2O$.** A solution of *trans*-$[Co(en)_2OH(OH_2)]Br_2$ (5 g) in water was treated with an equimolar amount of selenious acid (2 g) and gave a blue solution which was reduced in volume at low temperature on a rotary evaporator. Addition

Table I. Selenito IR Absorption Frequencies in the Region 250–900 cm^{-1} [a]

	Absorption freq, cm^{-1}					
Selenito complex	$\nu_1'(A')$	$\nu_2'(A')$	$\nu_3'(A')$	$\nu_4'(A')$	$\nu_5'(A'')$	$\nu_6'(A'')$
$[Co(NH_3)_5OSeO_2]Br \cdot H_2O$	805 m, b	755 s, b	520 m, b	390 m, b	695 s, b	360 m, b
cis-$[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$	830 m, b	770 s, b	530 m, b	400 w, b	580 m, b	350 w, b
trans-$[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2 \cdot H_2O$	830 m, b	760 s, b	520 m, b	380 w, b	600 m, b	360 w, b
cis-$[Co(en)_2(OH_2)OSeO_2]Br \cdot H_2O$	835 s, sp	760 s, b	510 m, b	385 w, b	678 w, b	365 w, b
$[Co(en)_2O_2SeO]ClO_4 \cdot H_2O$	830 s, sp	762 s, sp	515 m, sp	405 s, sp	678 m, sp	360 s, sp
$[Co(tn)_2O_2SeO]ClO_4 \cdot H_2O$	832 s, sp	762 s, sp	520 s, sp	390 m, sp	673 m, sp	362 m, sp

	Absorption freq, cm^{-1}			
Uncoordinated selenite	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(E)$	$\nu_4(E)$
$[Co(NH_3)_6]_2(SeO_3)_3$	788 s, b	450 m, b	740 s, b	395 w, b
Na_2SeO_3	790 s, b	460 s, b	742 s, b	400 s, b

[a] Key: w, weak; m, medium; s, strong; sp, sharp; b, broad.

of acetone to the concentrated deep blue solution yielded a purple-blue precipitate which was washed with acetone and air-dried. The yield was 2.0 g (30%). Anal. Calcd for *trans*-$[Co(en)_2(OH_2)OSeO_2H]Br_2 \cdot 2H_2O$: C, 9.6; N, 11.2; H, 3.8; Br, 31.9; Se, 15.8. Found: C, 9.5; N, 11.3; H, 3.8; Br, 31.8; Se, 15.5.

Selenitobis(1,3-propanediamine)cobalt(III) Perchlorate, $[Co(tn)_2O_2SeO]ClO_4 \cdot H_2O$. *trans*-$[Co(tn)_2OH(OH_2)](ClO_4)_2 \cdot 2H_2O$ (3 g) and sodium selenite (1.4 g) were dissolved in a minimum volume of warm water and the resultant deep red-purple solution was heated to 60 °C for 15 min. Slow cooling of the solution yielded pink needle crystals which were washed with ethanol and then ether and finally air-dried. (If the reactant solution was cooled rapidly, a thick red oil formed which could be crystallized as a pink solid by successive additions of ethanol.) The pink crystals were recrystallized from water, washed, and dried as before. The yield was 0.9 g (30%). Anal. Calcd for $[Co(tn)_2O_2SeO]ClO_4 \cdot H_2O$: C, 16.6; N, 12.9; H, 4.7; Cl, 8.2; Se, 18.2. Found: C, 17.3; N, 12.4; H, 4.7; Cl, 7.9; Se, 17.7.

Spectral Measurements. Infrared spectra of the selenito complexes were measured on a Perkin-Elmer Model IR-457 grating infrared spectrophotometer using KBr disks of the complexes with either bromide or perchlorate as the supporting anion of the selenito complexes. UV–visible solution spectra were recorded on a Unicam Model SP800 spectrophotometer equipped with thermostated cell holders. Optical absorbance values required for molar absorptivities in equilibrium studies were measured at constant temperature on a manual Shimadzu Model QR50 spectrophotometer to an accuracy of ±0.001 absorbance unit.

Titrimetric Measurements. The pK_a values for the free selenite oxo anion were determined by dissolving pure, anhydrous sodium selenite (0.1 M) in perchloric acid and potentiometrically titrating against 0.1 M sodium hydroxide. The initial ionic strength was adjusted to 1 M with sodium perchlorate. Similar pK_a determinations were made for the *cis*- and *trans*-$[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2$ complexes in water. All pH measurements were made using a Radiometer pH meter, Type 25, with an expanding-scale accessory reading to an accuracy of ±0.002.

Results and Discussion

IR Spectra and Mode of Selenito Bonding. The free selenite anion SeO_3^{2-} has C_{3v} symmetry and absorbs in the region 900–250 cm^{-1}. There are six fundamental modes of vibration, two pairs of which are degenerate, giving rise to four fundamental frequencies $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(E)$, and $\nu_4(E)$ which are infrared active. Table I shows that the fundamental frequencies of SeO_3^{2-} differ slightly when the supporting cation is either Na^+ or $Co(NH_3)_6^{3+}$. Comparable variations have been noted with other group 1 alkali metal cations[22] and the frequencies in Table I agree well with Raman frequencies determined in solution.[12]

If the selenito ligand were to coordinate to a metal center through the selenium atom, then the C_{3v} symmetry of the selenite would be retained and only four fundamental frequencies should be observed. On the other hand, if the selenito ligand were to coordinate through either one or two of its oxygen atoms, then the C_{3v} symmetry would be lowered to C_s and six fundamental frequencies should be observed.

All six selenito complexes listed in Table I exhibit six absorption bands which can be assigned to the selenito ligand and this confirms that the selenito ligands are coordinated through oxygen atoms. Positive identification of the selenito absorptions was achieved by deuteration of the ammine and amine hydrogen atoms in the metal complexes thereby shifting interfering N–H bending mode frequencies to lower frequencies away from the region of interest. Furthermore, interference from the perchlorate anion, which has a strong absorption between 630 and 640 cm^{-1}, was found to be not serious when the infrared spectra of both bromide and perchlorate salts of some of these selenito complexes were compared.

O-Bonded monodentate and bidentate selenito complexes cannot be distinguished on the basis of the number of fundamental frequencies of the selenito ligand. The complexes $[Co(en)_2O_2SeO]ClO_4 \cdot H_2O$ and $[Co(tn)_2O_2SeO]ClO_4 \cdot H_2O$ may be presumed to involve bidentate selenito ligands on the basis of their chemical analysis taken with the evidence of the absence of basic oxygen atoms which can be pH titrated. The infrared spectra of these presumed bidentate complexes include selenito absorptions which are characteristically sharper than those of the monodentate complexes. Moreover, the degenerate $\nu_3(E)$ vibration of free selenite, which is split on coordination into a doublet for the monodentate selenito complexes, is split into two distinct bands for the bidentate complexes. These qualitative distinctions enable the monodentate and bidentate selenito complexes to be readily identified.

The observation that the selenito ligand is O bonded provides an explanation for the facile synthesis of the selenito complexes. The monodentate selenito complexes were all formed immediately on mixing free selenite with the relevant aquo complexes even though the lifetime of the aquo ligand in substrate complexes like $Co(NH_3)_5OH_2^{3+}$ and $Co(en)_2(OH_2)_2^{3+}$ was several hours at the reaction temperature. This suggests that selenite substitution occurs at the intact oxygen of the aquo ligand rather than by Co–OH_2 bond rupture. The detailed mechanism for these reactions is examined in the two subsequent papers.

Acidity Constants of Selenito Complexes. The determination of pK_a values for the selenite anion is complicated by the occurrence of selenite dimerization even in moderately concentrated solutions greater than 0.1 M. In dilute solutions, the values reported for pK_{a1} and pK_{a2}[23-27] vary according to the ionic strength, type of supporting electrolyte, temperature, and the method of measurement but most values cluster around $pK_{a1} \approx 2.5$ and $pK_{a2} \approx 8.0$ at 20–25 °C. Our own measurements employed direct pH titrimetry of 0.1 M selenite. At 20 °C and in an ionic strength of 1 M adjusted with sodium perchlorate, the following values were found: $pK_{a1} = 2.36 \pm 0.05$ and $pK_{a2} = 8.06 \pm 0.05$.

The complexes $Co(en)_2O_2SeO^+$ and $Co(tn)_2O_2SeO^+$, which are presumed to involve bidentate selenito ligands on the basis of their chemical analysis, are much less soluble in water than their monodentate counterparts. When acidic solutions of $Co(en)_2O_2SeO^+$ and $Co(tn)_2O_2SeO^+$ are back-titrated with alkali, there is no detectable end point attributable to the selenito group, suggesting that the pK_a value for the single exposed oxygen atom of the bidentate selenito group is less than 2. This is analogous to the behavior of phosphato ligands[28] for which the corresponding value is $pK_a = -0.3$.

The cis and trans isomers of $Co(en)_2(OH_2)OSeO_2H^{2+}$ dissolve readily in water to yield aqueous solutions of pH ~3.3 and ~3.5 respectively. Our equilibrium measurements (below) reveal that above pH 3, the extent of dissociation for each complex is less than 2%. It is therefore possible to determine pK_a values without serious complications arising from release of free selenite from the complexes. Both complexes exhibit two sharp pH end points; for the cis isomer $pK' = 4.35 \pm 0.05$ and $pK'' = 8.30 \pm 0.05$ while for the trans isomer $pK' = 4.55 \pm 0.05$ and $pK'' = 7.70 \pm 0.05$.

The assignment of the two pK values to specific hydrolytic equilibria is best done on the basis of the accompanying shifts in the visible spectra of the complexes. The end point characterizing the pK'' value is accompanied with a marked change in λ_{max} and ϵ consistent with conversion of the aquo ligand to hydroxo ligand for both isomers of $Co(en)_2(OH_2)OSeO_2H^{2+}$. For the cis isomer, λ_{max} 520 nm (ϵ 91) shifts on neutralization to λ_{max} 532 nm (ϵ 100) while for the trans isomer λ_{max} 590 nm (ϵ 38) is shifted to λ_{max} 595 nm (ϵ 50). Similar shifts occur for the $Co(en)_2(OH_2)_2^{3+}$ ion. The alternative conversion of $-OSeO_2H$ to $-OSeO_2$ would not be expected to cause large shifts in the visible spectrum. Accordingly, the pK'' values may be attributed to the reaction

$$Co(en)_2(OH_2)OSeO_2^+ + H_2O \rightleftarrows Co(en)_2(OH)OSeO_2^0 + H_3O^+ \quad pK_{aq} \tag{2}$$

where $pK_{aq}(cis) = 8.30$ and $pK_{aq}(trans) = 7.70$ at 20 °C and at 1 M ionic strength.

It is significant that the selenito ligand enhances the basicity of the aquo ligand more than do most other common ligands. This is shown in the series *cis*-$Co(en)_2(OH_2)X$ for which values of pK_{aq} are 5.9 ($X = SO_4^{2-}$), 6.1 (NH_3 and OH_2), 6.35 (NO_2^-), 6.70 (PO_4H^{2-}), 6.8 (NCS^-), and 7.1 (Cl^-). The relatively high basicity of the aquo ligand in *cis*-$Co(en)_2(OH_2)OSeO_2^+$ correlates with the relatively slow formation (minutes at 60 °C) of the bidentate selenito complexes. If formation of the bidentate complexes depends on intramolecular attack by a $-OSeO_2$ ligand upon a vicinal $-OH_2$ ligand ($pK_a = 8.3$), then the rate will be reduced by the relative difficulty of removal of protons from the more basic oxygen center. In contrast the more acidic aquo ligand in *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ ($pK_a = 6.1$) yields the monodentate selenito complex much more rapidly (seconds around room temperature).

The pK' values for aquoselenito complexes may be assigned to protonation of the selenito ligand, for which there is little observable spectral effect, i.e.

$$Co(en)_2(OH_2)OSeO_2H^{2+} + H_2O \rightleftarrows Co(en)_2(OH_2)OSeO_2^+ + H_3O^+ \quad pK_{a2} \tag{3}$$

where $pK_{a2}(cis) = 4.35$ and $pK_{a2}(trans) = 4.55$. Thus the coordination of hydrogen selenite to the positive cobalt center causes an enhancement in its acidity of 3.5–3.7 pK units as compared to $HSeO_3^-$ ($pK_{a2} = 8.06$). On the other hand, H_2SeO_3 ($pK_{a1} = 2.36$) is more acidic than the formally equivalent species $Co-OSeO_2H$ ($pK_{a1} = 4.35$ and 4.55 for cis and trans). Similar acidity enhancements for coordinated ligands have been noted with phosphato complexes.[28]

Table II. Molar Absorptivity Values of Visible Absorption Maxima for Selenito Complexes at Neutral pH

Selenito complex	λ_1, nm	ϵ_1, M^{-1} cm^{-1}	λ_2, nm	ϵ_2, M^{-1} cm^{-1}
$Co(NH_3)_5OSeO_2^+$	519	62		
cis-$Co(en)_2(OH_2)OSeO_2^+$	532	100	360[a]	
trans-$Co(en)_2(OH_2)OSeO_2^+$	590	50	450	31
cis-$Co(tn)_2(OH_2)OSeO_2^+$	540	78		
$Co(en)_2O_2SeO^+$	510	155	360	142

[a] Shoulder on charge-transfer band.

Likewise, the value of pK_{a1} for the equilibrium

$$Co(en)_2(OH_2)OSeO_2H_2^{3+} + H_2O \rightleftarrows Co(en)_2(OH_2)OSeO_2H^{2+} + H_3O^+ \tag{4}$$

would be expected to be much lower than the pK_{a1} value for H_2SeO_3 (2.36). A direct determination of pK_{a1} for coordinated selenite is not possible in acidic media since the labile selenito complexes are quite extensively aquated below pH 1.

The pK_{a2} value for the complex $Co(NH_3)_5OSeO_2^+$ also cannot be determined since this complex undergoes significant dissociation below pH 4. Acid–base titrations in the region of pH 3 are masked by the rapid release of approximately 10% of selenite from the complex.

Selenito Complex Formation. The *cis*- and *trans*-aquoselenito complexes dissolve readily in water to form red-purple and blue solutions, respectively, while the slowly soluble bidentate selenito complexes yield deep red solutions. Their visible spectra, as detailed in Table II, are distinct from those of the corresponding aquo complexes and these spectral differences may be used to evaluate the degree of coordination of selenite under various pH conditions. The bidentate selenito complexes, which exhibit two visible bands of unusually high molar absorptivity, were found not to exist in any significant concentration after true equilibrium had been established between free selenite and the aquo complexes. Furthermore, there was neither preparative nor spectrophotometric evidence for the formation of bis(selenito) complexes even when a 50-fold excess of free selenite was used with respect to diaquo complexes. Consequently, selenito complex formation in aqueous solution may be treated as a single-stage equilibrium between aquo complexes (ROH_2) and Se(IV) (in the various protolytic forms) and monodentate selenito complexes ($R-OSeO_2$) as is represented in the generalized equilibrium (5),

$$ROH_2 + Se(IV) \rightleftarrows R-OSeO_2 + H_2O \quad Q_s \tag{5}$$

in which degrees of protonation and charges have been omitted. The overall degree of coordination of selenite is represented by Q_s, the selenito complex formation quotient, where

$$Q_s = [R-OSeO_2]/[ROH_2][Se(IV)] \tag{6}$$

$$[Se(IV)] = [Se(IV)]_{initial} - [R-OSeO_2] \tag{7}$$

In principle, Q_s can be evaluated spectrophotometrically from the change in optical absorbance as the Se(IV) concentration is varied at a fixed ROH_2 concentration.

Between pH 5 and pH 8, formation of the selenito complexes is virtually complete at all accessible Se(IV) concentrations and only an estimate of $Q_s \geq 100$ can be set for equilibrium 5. In the region of pH 7, there is no effective competition from acid- and base-catalyzed hydrolysis of the selenito complexes which exist predominantly in the nonprotonated forms $Co(NH_3)_5OSeO_2^+$ and $Co(N)_4(OH_2)OSeO_2^+$. At pH 5-6, Se(IV) exists almost exclusively[13] as the biselenite species $HSeO_3^-$ and $H_2(SeO_3)_2^{2-}$, the proportions varying with the total Se(IV) concentration. At pH 7 and [Se(IV)] = 0.10 M in 1 M $NaClO_4$, 78.1% of Se(IV) exists as $HSeO_3^-$ and $H_2(SeO_3)_2^{2-}$ and only 11.7% as SeO_3^{2-}. We conclude that both

Table III. Selenito Complex Formation Data (25 °C; $[\mathrm{R{-}OH_2}] = 0.01$ M)[a]

	pH 1.1-1.3		pH 2.9-3.5	
Aquo species, R-OH$_2$	Q_s[b]	$\beta_{\mathrm{H-Se}}$	Q_s	$\beta_{\mathrm{H-Se}}$
$\mathrm{Co(NH_3)_5OH_2}^{3+}$	1.5 ± 0.2	27 ± 2	16 ± 2	19 ± 2
cis-$\mathrm{Co(en)_2(OH_2)_2}^{3+}$	2.0 ± 0.3	54 ± 4	50 ± 6	58 ± 5
trans-$\mathrm{Co(en)_2(OH_2)_2}^{3+}$	5.4 ± 0.4	90 ± 15	44 ± 4	50 ± 4
cis-$\mathrm{Co(tn)_2(OH_2)_2}^{3+}$	2.9 ± 0.3	59 ± 4	42 ± 5	50 ± 4

[a] Errors quoted are mean deviations. [b] Each Q_s value is the mean of at least five separate determinations in the [Se(IV)] range 0.01-1.0 M.

biselenite species are powerful nucleophiles toward the aquo- and hydroxocobalt(III) complexes in the neutral pH region. Equilibrium 5 is established with half-times not exceeding 1 s at 25 °C and the kinetics of these reactions are discussed in a succeeding paper.[29]

Between pH 8 and pH 12, the value of Q_s falls sharply as the principal Se(IV) species is $\mathrm{SeO_3}^{2-}$. Equilibrium 5 is only slowly established with the base hydrolysis of the selenito complexes, with half-times of hours, competing with the slow formation reaction. Further complications occur from concomitant basic decomposition of the hydroxocobalt(III) substrates. Direct spectrophotometric evaluation of Q_s is therefore unreliable and estimates can only be given from rates of forward and back reactions. At pH 11.5, the rate of base hydrolysis of $\mathrm{Co(NH_3)_5OSeO_2}^+$ is competitive with its rate of formation, yielding a value of $Q_s \simeq 5$ at 25 °C and at an ionic strength of 0.5 M. Similar values probably apply to the other selenito complexes which are, however, more susceptible to basic decomposition. These observations demonstrate that $\mathrm{SeO_3}^{2-}$ is a relatively poor nucleophile for the hydroxocobalt(III) substrates.

Below pH 4, equilibrium 5 is established rapidly with half-times[30] less than 1 s at 25 °C. Both *cis*- and *trans*-aquoselenito complexes also undergo slow isomerization to yield an equilibrium mixture containing more than 90% of the cis isomer. The half-times for this isomerization, in the region of 25 min at 25 °C, are conveniently slow and do not cause serious interference with measurements of the main equilibrium (5). Details of the isomerization processes are discussed in a subsequent paper.[31]

Values of Q_s were determined at both pH 3.0 and pH 1.0 for four aquo complexes of fixed concentration (0.01 M) using the Se(IV) concentration range 0.01-1.0 M. Values of Q_s, which are listed in Table III, are mean values for at least five separate Se(IV) concentrations. The major observation is that for a given selenito complex, Q_s decreases 10-30 times when the pH of the reaction medium is reduced from 3.0 to 1.0. Within this pH range, all of the selenito complexes exist exclusively in the protonated form and the aquo complexes exclusively in the aquo form. Consequently, the major variations in Q_s must arise from variations in the relative concentrations of various Se(IV) species.

The Se(IV) distribution studies of Barcza and Sillên,[13] supported by the earlier studies of Sabbah and Carpêni,[32] reveal that at pH 3, 61.2-75.2% of all Se(IV) exists as biselenites within the Se(IV) concentration range 0.10-1.0 M. However, at pH 1, only 4-5% of Se(IV) exists as biselenite. This tenfold fall in the proportion of biselenites as the pH is reduced from 3 to 1 corresponds to a comparable fall in Q_s over the same pH range. To a first approximation, equilibrium 5 may then be rewritten as

$$\mathrm{R{-}OH_2 + H{-}Se^{IV} \rightleftarrows R{-}OSeO_2H + H_2O} \qquad (8)$$

where $\mathrm{H{-}Se^{IV}}$ includes the species $\mathrm{HSeO_3}^-$, $\mathrm{H_2(SeO_3)_2}^{2-}$, and $\mathrm{H_3(SeO_3)_2}^-$. A formation constant $\beta_{\mathrm{H-Se}}$ may therefore be defined as

$$\beta_{\mathrm{H-Se}} = [\mathrm{R{-}OSeO_2H}]/[\mathrm{ROH_2}][\mathrm{H{-}Se^{IV}}] \qquad (9)$$

and calculated values of this quantity are listed in Table III. Considering the errors introduced by slight pH variations in the media and in the uncertainties arising from the Se(IV) distribution studies,[13,32] values of $\beta_{\mathrm{H-Se}}$ are reasonably constant. This implies that the biselenites are the predominant form of Se(IV) which coordinates in the range pH 1-3. Coordination by selenious acid ($\mathrm{H_2SeO_3}$ and $\mathrm{H_4(SeO_3)_2}$), which represents 60-76% of all Se(IV) at pH 1, evidently makes only a minor contribution.

At constant pH, slight variations in Q_s were observed for individual complexes as the total Se(IV) concentration was varied. Thus the mean values of Q_s listed in Table III appear to be associated with relatively large uncertainties which are much greater than the errors in individual determinations of Q_s. Nevertheless, the variations in Q_s were too slight to justify a reliable assignment of individual β values for the three biselenite species. For the range of Se(IV) concentrations which were employed, there are wide variations in the relative importance of the three biselenite species. Thus at pH 3 and with [Se(IV)] = 0.1 M, 63.6% of all of the Se(IV) exists as $\mathrm{HSeO_3}^-$, 6.0% as $\mathrm{H_2(SeO_3)_2}^{2-}$, and 5.6% as $\mathrm{H_3(SeO_3)_2}^-$. However, at [Se(IV)] = 1.0 M, there is a 15.1% contribution from $\mathrm{H_3(SeO_3)_2}^-$, 14.1% from $\mathrm{H_2(SeO_3)_2}^{2-}$, and 32.0% from $\mathrm{HSeO_3}^-$ making up 61.2% of all of the Se(IV). The observation that Q_s values are virtually constant over this widely different range of contributions from $\mathrm{HSeO_3}^-$, $\mathrm{H_2(SeO_3)_2}^{2-}$, and $\mathrm{H_3(SeO_3)_2}^-$ indicates that these three biselenite species have very similar β values for formation of selenito complexes.

Table III also shows that the three diaquo complexes exhibit similar values of $\beta_{\mathrm{H-Se}}$ of about 55 and this suggests that neither the stereochemical configuration nor the nature of the amine ligands has a significant influence on the selenito formation reaction. The monoaquo complex exhibits a value of $\beta_{\mathrm{H-Se}} \approx 23$ which is about half that for the diaquo complexes; a statistical factor of 2 is to be expected for the diaquo complexes. The values of β contradict the earlier report[11] that selenito complexes are susceptible to hydrolysis. The selenito complexes in acidic media would be better described as stable, yet labile, complexes.

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Registry No. $\mathrm{[Co(NH_3)_5OSeO_2](ClO_4)}$, 61634-22-8; $\mathrm{[Co(NH_3)_5OSeO_2]Br}$, 61634-23-9; *cis*-$\mathrm{[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2}$, 61634-25-1; *trans*-$\mathrm{[Co(en)_2(OH_2)OSeO_2H](ClO_4)_2}$, 61687-71-6; *cis*-$\mathrm{[Co(en)_2(OH_2)OSeO_2]Br}$, 61634-26-2; $\mathrm{[Co(en)_2O_2SeO]ClO_4}$, 61634-28-4; *trans*-$\mathrm{[Co(en)_2(OH_2)OSeO_2H]Br_2}$, 61687-72-7; $\mathrm{[Co(tn)_2O_2SeO]ClO_4}$, 61665-37-0; $\mathrm{[Co(NH_3)_5OH_2](ClO_4)_3}$, 13820-81-0; *cis*-$\mathrm{[Co(en)_2OH(OH_2)](ClO_4)_2}$, 14099-49-1; *cis*-$\mathrm{[Co(en))_2OH(OH_2)]Br_2}$, 61634-17-1; *trans*-$\mathrm{[Co(en)_2OH(OH_2)](ClO_4)_2}$, 14099-22-0; *trans*-$\mathrm{[Co(en)_2OH(OH_2)]Br_2}$, 61634-18-2; *trans*-$\mathrm{[Co(tn)_2OH(OH_2)](ClO_4)_2}$, 61634-20-6; *cis*-$\mathrm{Co(en)_2(OH_2)_2}^{3+}$, 21247-59-6; *trans*-$\mathrm{Co(en)_2(OH_2)_2}^{3+}$, 19314-32-0; *cis*-$\mathrm{Co(tn)_2(OH_2)_2}^{3+}$, 51286-38-5; *cis*-$\mathrm{Co(tn)_2(OH_2)OSeO_2}^+$, 61687-75-0.

References and Notes

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(2) *W. H. O., Tech. Rep. Ser.*, **No. 532** (1973).
(3) M. L. Scott, G. Olson, L. Krook, and W. R. Brown, *J. Nutr.*, **91**, 573 (1967).
(4) K. J. Jenkins, R. C. Dickson, and M. Hidiroglou, *Can. J. Physiol. Pharmacol.*, **48**, 192 (1970).
(5) M. Hidiroglou, I. Hoffman, K. J. Jenkins, and R. R. Mackay, *Anim. Prod.*, **13**, 315 (1971).
(6) J. G. Buchanan-Smith, E. C. Nelson, B. I. Osburn, M. E. Wells, and A. D. Tillman, *J. Anim. Sci.*, **29**, 808 (1969).
(7) K. O. Goodwin, R. E. Kachel, and R. A. Buckley, *Aust. J. Exp. Agric. Anim. Husb.*, **10**, 672 (1970).
(8) L. E. den Dooren De Jong and W. R. Roman, *J. Microbiol. Serol.*, **37**, 119 (1971).
(9) V. Eybe, J. Sykora, and F. Mertl, *Arch. Toxikol.*, **26**, 169 (1970).
(10) R. J. Shamberger, *J. Natl. Cancer Inst.*, **44**, 931 (1970).

(11) P. Ray and A. N. Gosh, *J. Indian Chem. Soc.*, **13**, 494 (1936).
(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970.
(13) L. Barcza and L. G. Sillên, *Acta Chem. Scand.*, **25**, 1250 (1971).
(14) A. Simon and R. Paetzold, *Z. Anorg. Allg. Chem.*, **303**, 46 (1960).
(15) A. F. Wells and M. J. Bailey, *J. Chem. Soc.*, 1282 (1949).
(16) K. D. Chou and Y. C. Tang, *Chem. Abstr.*, **53**, 8761 (1959).
(17) M. S. Lehmann and F. K. Larsen, *Acta Chem. Scand.*, **25**, 3859 (1971).
(18) F. Basolo and R. K. Murmann, *Inorg. Synth.*, **4**, 171 (1953).
(19) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).
(20) I. R. Jonasson, S. F. Lincoln, and D. R. Stranks, *Aust. J. Chem.*, **23**, 2267 (1970).
(21) tn = 1,3-propanediamine or trimethylenediamine.
(22) O. N. Erstaf'eva and T. V. Kleishina, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **18**, 771 (1973).
(23) L. G. Sillên and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 7** (1958).
(24) A. Treinin and J. Wilf, *J. Phys. Chem.*, **74**, 4131 (1970).
(25) C. Th. Kawassiades, G. E. Manoussakis, and J. A. Tossidis, *J. Inorg. Nucl. Chem.*, **29**, 401 (1967).
(26) J. Sekine, H. Iwaki, M. Sakairi, F. Shimada, and M. Inarida, *Bull. Chem. Soc. Jpn.*, **41**, 1 (1968).
(27) V. A. Nazarenko, G. G. Shitareva, and E. N. Polulktova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **18**, 609 (1973).
(28) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 37 (1968).
(29) A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, **16**, 1282 (1977).
(30) A. D. Fowless and D. R. Stranks, *Inorg. Chem.*, following paper in this issue.
(31) A. D. Fowless and D. R. Stranks, to be submitted for publication.
(32) R. Sabbah and G. J. Carpêni, *J. Chim. Phys. Phys.-Chim. Biol.*, **63**, 1549 (1966).

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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