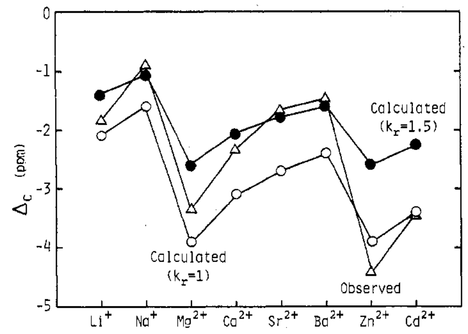

Figure 3. Graphic display of the observed and calculated Δ_C depending on the cations.

changes due to cations by using the result in Figure 1. The theoretical and experimental shifts are shown in Figure 3. The used cation–oxygen distances are the values of the X-ray diffraction studies by Lawrence and Kruh.[10] Figure 3 shows that the theoretical shifts are larger than the experimental ones, except those of the zinc and cadmium ions. In a study of this type, we should be gratified with a qualitative agreement with the available experimental data. There are at least three probable sources of error. First, a point-charge model is too crude an approximation to cation–water association. We should include atomic orbitals of the ion. Second, there are errors due to use of the 4-31G basis set (without gauge factors) in the magnetic calculations. Although the 4-31G magnetic shielding values are considerably more accurate than those calculated by using a minimal set,[13] it does not allow an estimate of the value of σ_H which would correspond to the Hartree–Fock limit.[14] However, gauge dependences of σ_H will be canceled in the calculation of the shielding change, Δ_C. Finally, there are errors due to the counterion effect and the dielectric constant of the solvent. Our calculation neglected the fields originating from counterions and dipolar solvent molecules. We have assumed the dielectric constant of the vacuum (ϵ_0) for the space intervening between the point charge and the water molecule. This is not necessarily so, but the vacuum value is reasonably considered to be much better than the bulk value of acetone, $20.7\epsilon_0$, in this case by reason of the dielectric saturation effect.[15] The shielding effect of the anions and the polarization of the acetone solvent would attenuate the electrostatic field of the cations and make the calculated Δ_C smaller.

Among the above three sources of error, we suspect the dielectric effect is the most important. The effect of a dielectric constant should be discussed briefly. Buckingham[16] showed that the σ^d effect depends on the relative dielectric constant, k_r, inversely, but the σ^p term is proportional to k_r^{-2}. The σ^d term is much larger than the σ^p term on cation hydration. Therefore, we can simply suppose that the total σ change by ion, namely, Δ_C, depends on k_r inversely. We calculated the appropriate k_r value from the observed Δ_c's of alkali and alkaline earth metal ions and obtained 1.5 as the effective value for k_r in acetone solvent. This value is close to $n^2 = 1.85$ in which n is the index of refraction of acetone. The dielectric saturation theory[17] predicts that k_r in infinite strength of the electric field will decrease to n^2 asymptotically, that is the square of the optical refractive index. The calculated Δ_C values for $k_r = 1.5$ are also shown in Figure 3.

Acknowledgment. The calculations were performed on a FACOM 230-75 instrument at the Hokkaido University Computing Center. It is a pleasure to express our appreciation to Dr. F. Sasaki for providing us with several useful computer programs. This research was supported in part by the Scientific Research Fund of the Japanese Ministry of Education (Grant No. 364143).

Registry No. H_2O, 7732-18-5; Mg^{2+}, 22537-22-0; Ca^{2+}, 14127-61-8; Sr^{2+}, 22537-39-9; Ba^{2+}, 22541-12-4; Li^+, 17341-24-1; Na^+, 17341-25-2; Zn^{2+}, 23713-49-7; Cd^{2+}, 22537-48-0.

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(13) R. Ditchfield, *J. Chem. Phys.*, **65**, 3123 (1976).
(14) P. Lazzeretti and R. Zanasi, *J. Chem. Phys.*, **68**, 1523 (1978).
(15) W. A. Millen and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 6051 (1967).
(16) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
(17) F. Booth, *J. Chem. Phys.*, **19**, 391, 1327, 1615 (1951).

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Kinetic Study of the Rapid Complexation of *cis*-Diaquobis(ethylenediamine)cobalt(III) with Tungstate(VI). Substitution at Tungstate(VI)

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Received May 18, 1979

The complexing of *cis*-$Co(en)_2(H_2O)_2^{3+}$ with WO_4^{2-} has been studied at 25 °C, pH 8.0–9.0 (Tris), and $I = 1.0$ M ($NaClO_4$). A 1:1 reaction is observed: $Co(en)_2(OH)(H_2O)^{2+} + WO_4^{2-} \rightleftarrows Co(en)_2(OH)(WO_4) + H_2O$, with $K_C = 1160$ M^{-1}. The kinetics was studied by the stopped-flow method, the rapid complexation corresponding to substitution at W(VI). With [W(VI)] = 0.010–0.100 M, the reaction proceeds to completion, and the [H^+] dependence is consistent with two paths: $Co(en)_2(OH)_2^+ + HWO_4^- \rightarrow Co(en)_2(OH)(WO_4) + H_2O$ ($k_1 = 3.22 \times 10^7$ M^{-1} s^{-1}); $Co(en)_2(OH)(H_2O)^{2+} + HWO_4^- \rightarrow Co(en)_2(OH)(WO_4) + H_2O + H^+$ ($k_2 = 1.03 \times 10^7$ M^{-1} s^{-1}). The results obtained complement previous data on the exchange of H_2O ($k_a = 0.44$ s^{-1}) and OH^- ($k_b = 273$ M^{-1} s^{-1}) with WO_4^{2-} and give a rate constant of ca. 10^7 M^{-1} s^{-1} for substitution at HWO_4^-.

The oxygen-18 exchange of molybdate and tungstate oxyanions (XO_4^{2-}) with water has been studied previously in basic media, pH > 11,[2] and results can be summarized by (1).

$$k_{obsd} = k_a + k_b[OH^-] \quad (1)$$

Under more acidic conditions the exchange properties can be assessed by studying the rapid complexing of the oxyanion with substitution-inert metal complexes. Taylor[3] has previously reported studies on the complexing of MoO_4^{2-} with Co-

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(1) (a) Montanuniversität. (b) The University, Leeds.
(2) von Felten, H.; Wernli, B.; Gamsjäger, H.; Baertschi, P. *J. Chem. Soc., Dalton Trans.* **1978**, 496.
(3) Taylor, R. S. *Inorg. Chem.* **1977**, *16*, 116.

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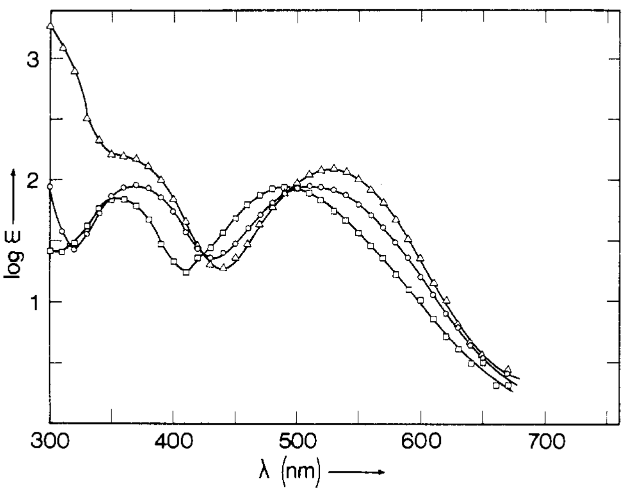

Figure 1. Spectra of *cis*-$Co(en)_2(OH)_2^+$ (○), *cis*-$Co(en)_2(H_2O)(OH)^{2+}$ (□), and *cis*-$Co(en)_2(OH)(WO_4)$ (△) at 25 °C.

$(NH_3)_5(H_2O)^{3+}$ at pH 7.1–8.0 and concluded that reaction paths $Co(NH_3)_5(OH)^{2+} + HMoO_4^-$ and $Co(NH_3)_5(H_2O)^{3+} + HMoO_4^-$ are effective. Attempts to study the corresponding reaction of WO_4^{2-} with $Co(NH_3)_5(H_2O)^{3+}$ gave precipitates. Instead we report here a study of the reaction of WO_4^{2-} with *cis*-$Co(en)_2(H_2O)_2^{3+}$ at pH 8.0–9.0. Protonation constants as defined in (2) and (3) have been determined[4,5] and are $K_1 = 1.55 \times 10^8$ M^{-1} and $K_2 = 1.15 \times 10^6$ M^{-1} at 25 °C and $I = 1.0$ M ($NaNO_3$). The dominant species over the pH range

$$Co(en)_2(OH)_2^+ + H^+ \rightleftarrows Co(en)_2(OH)(H_2O)^{2+} \quad (2)$$

$$Co(en)_2(OH)(H_2O)^{2+} + H^+ \rightleftarrows Co(en)_2(H_2O)_2^{3+} \quad (3)$$

8.0–9.0 are therefore $Co(en)_2(OH)_2^+$ and $Co(en)_2(OH)(H_2O)^{2+}$. The protonation constant for WO_4^{2-} (see eq 4), $K_W = 3.16 \times 10^3$ M^{-1} at 20 °C and $I = 0.10$ M ($NaClO_4$),[6]

$$WO_4^{2-} + H^+ \rightleftarrows HWO_4^- \quad (4)$$

is also relevant. Formation of isopolytungstates occurs at pHs in the 7–8 range and below.[7]

Experimental Section

Materials. *cis*-Diaquobis(ethylenediamine)cobalt(III) perchlorate, $[Co(en)_2(H_2O)_2](ClO_4)_3$, was prepared according to a literature procedure.[8] *Caution*! The complex when dry was found to be shock sensitive. Sodium tungstate, $Na_2WO_4\cdot 2H_2O$, perchloric acid, and sodium perchlorate (p.a., Merck) were used. The sodium perchlorate was recrystallized by dissolving in water to 8–10 M, heating at ca. 140 °C to decrease the volume, and then cooling to ca. 60 °C. Crystals of $NaClO_4\cdot H_2O$ were filtered off. Tris(hydroxymethyl)aminomethane (hereafter Tris) (p.a., Merck) was dried at 100 °C.

Measurement of pH. A Beckman 4500 digital pH meter fitted with Pt–H_2 and Ag–AgCl electrodes were used. The reference electrode system consisted of a Wilhelm-type salt bridge.[9] Care was taken that test and reference solutions were at the same ionic strength of 1.0 M ($NaClO_4$).

Buffer. Solutions of 0.10 M Tris with $HClO_4$ (as required) were used as buffer. The pK_a of Tris at 25 °C and $I = 1.0$ M ($NaClO_4$) was determined by titration of Tris in excess $HClO_4$ with NaOH while the emf was monitored between the hydrogen and reference electrodes.

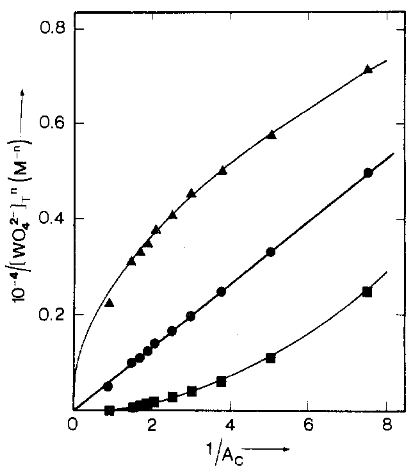

Figure 2. Plot of $[WO_4^{2-}]_T^{-n}$ against inverse absorbance according to eq 6. Key: ▲, $n = 0.5$; ●, $n = 1.0$; ■, $n = 2.0$. The straight line for $n = 1$ implies a 1:1 ratio of Co(III):WO_4^{2-} in the complex formed. $[Co(III)]_T = 1.58 \times 10^{-2}$ M.

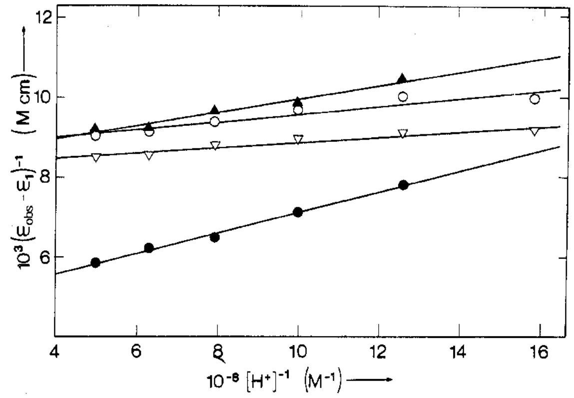

Figure 3. Benesi–Hildebrand plot for the determination of the stability constant, K_C, according to the reaction $Co(en)_2(OH)(H_2O)^{2+} + WO_4^{2-} \rightleftarrows Co(en)_2(OH)(WO_4) + H_2O$ at 25 °C and $I = 1.0$ M ($NaClO_4$). $[WO_4^{2-}]_T = 0.010$ M (●), 0.025 M (▲), 0.050 M (○), and 0.075 M (▽); $[Co(III)]_T = 2.4 \times 10^{-3}$ M.

Readings were treated by the Gran[10] method, giving pK_a = 8.250 ± 0.015.

Spectra. A Zeiss DMR 10 spectrophotometer was used for absorbance measurements. Spectra were recorded for the following: $Co(en)_2(H_2O)_2^{3+}$ in 0.01 M $HClO_4$, $Co(en)_2(OH)_2^+$ in Tris buffer at pH 10.5, $Co(en)_2(OH)(H_2O)^{2+}$ in Tris buffer at pH 7.0, and $Co(en)_2(OH)(WO_4)$ in Tris buffer at pH 9.0 (tungstate in large excess as in kinetic runs), all at $I = 1.0$ M ($NaClO_4$). Spectra (Figure 1) for $Co(en)_2(OH)(H_2O)^{2+}$ and $Co(en)_2(OH)(WO_4)$ were corrected for (small) contributions from other species.

Stoichiometry. The stoichiometric composition of the reaction product was determined by the straight-line method of Asmus.[11] At pH 9.0 $[WO_4^{2-}]_T$ was varied with total Co(III) concentration, $[Co(III)]_T = 1.58 \times 10^{-2}$ and 2.80×10^{-3} M, and the absorbance was measured at λ = 320 nm immediately after mixing the reactants. This is important since a second slower stage was apparent, especially at lower pH. For the first stage, an equilibrium constant K can be defined (see eq 5). For the condition $[Co(III)]_T \gg [WO_4^{2-}]_T$, (6) is obtained,

$$Co^{III}(WO_4)_n \overset{K}{\rightleftarrows} Co(III) + nWO_4^{2-} \quad (5)$$

$$\frac{1}{[WO_4^{2-}]_T^n} = \frac{[Co(III)]_T\epsilon_C}{K}\frac{1}{A_C} - \frac{1}{K} \quad (6)$$

where ϵ_C is the absorption coefficient for $Co^{III}(WO_4)_n$ at λ = 320 nm, i.e., $Co(en)_2(OH)(WO_4)$ in Figure 1. Measured absorbance values

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(4) Bjerrum, J.; Rasmussen, S. A. *Acta Chem. Scand.* **1952**, *6*, 1265.

(5) Cannon, R. D.; Earley, J. O. *J. Am. Chem. Soc.* **1966**, *88*, 1872.

(6) Schwarzenbach, G.; Geier, G.; Littler, J. *Helv. Chim. Acta* **1962**, *45*, 2603.

(7) Kepert, D. L. *Prog. Inorg. Chem.*, **1967**, *4*, 199.

(8) Linhard, M.; Stirn, G. *Z. Anorg. Allg. Chem.* **1952**, *268*, 105.

(9) Rosotti, F. J. C.; Rosotti, H. "Determination of Stability Constants"; McGraw-Hill: New York; p 146.

(10) Gran, G. *Analyst* (*London*) **1952**, *77*, 661.

(11) Asmus, E. *Fresenius' Z. Anal. Chem.* **1960**, *178*, 104.

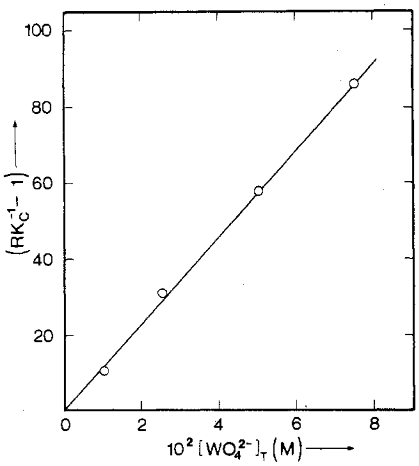

Figure 4. Stability constant of $Co(en)_2(OH)(WO_4)$. According to eq 9, the slope of the straight line gives K_C.

A_C were corrected for the absorbance of excess $[Co(III)]_T$. Plots of $[WO_4^{2-}]_T^{-n}$ against A_C^{-1} are shown in Figure 2, with $n = 0.5$, 1, and 2. The linear plot for $n = 1$ implies a 1:1 ratio of $Co(III):WO_4^{2-}$ in the complex formed.

Determination of Formation Constant. Absorbance measurements ($\lambda = 320$ nm) in the pH range 8.70–9.30 were carried out at $[WO_4^{2-}]_T \gg [Co(III)]_T$ in order to determine K_C (25 °C) for (7) by the Benesi–Hildebrand method.[3,12] Equation 8 can be derived, where ϵ_1

$$Co(en)_2(OH)(H_2O)^{2+} + WO_4^{2-} \xrightleftharpoons{K_C} Co(en)_2(OH)(WO_4) + H_2O \qquad (7)$$

$$\frac{1}{\epsilon_{obsd} - \epsilon_1} = \frac{K_1^{-1}[H^+]^{-1} + 1 + K_C[WO_4^{2-}]_T}{\epsilon_2 + \epsilon_C K_C[WO_4^{2-}]_T - \epsilon_1 - \epsilon_1 K_C[WO_4^{2-}]_T} \qquad (8)$$

and ϵ_2 are absorption coefficients for $Co(en)_2(OH)_2^+$ and $Co(en)_2(OH)(H_2O)^{2+}$, respectively. Linear plots of $(\epsilon_{obsd} - \epsilon_1)^{-1}$ against $[H^+]^{-1}$ with $[WO_4^{2-}]_T$ in the range 0.01–0.075 M are shown in Figure 3. From (8) the ratio R of intercept/slope is given by (9). Figure 4

$$R = (1 + K_C[WO_4^{2-}]_T)K_1 \qquad (9)$$

is a plot of $(R/K_1) - 1$ against $[WO_4^{2-}]_T$, the slope of which gives $K_C = 1160 \pm 10\ M^{-1}$.

Kinetics. Stopped-flow measurements were performed on a Durrum-Gibson D-110 spectrophotometer by using at least a 10-fold excess of $[WO_4^{2-}]_T$, pH 8.0–9.0, and $\lambda = 580$ nm. Rate constants (25.0 °C) listed in Table I are the average of three or four determinations. With 0.10 M Tris the pH changes were <0.03 unit on completion of the reaction at pH 9.0, $[Co(III)]_T = 8.0 \times 10^{-4}$ M, and <0.02 unit at pH 8.0, $[Co(III)]_T = 1.0 \times 10^{-3}$ M. Traces of absorbance changes were stored by using a Tektronix Model 5103 N storage oscilloscope. The experimental traces were simulated by a Philips function generator with the aid of an resistance–capacitance element. From the time constant of the RC element k_{obsd} was calculated. Under the conditions described, one stage only occurred, and all traces were good exponential curves.

Analysis of Data. Least-squares analyses were performed on kinetic and equilibrium constant data with an RC 3600 computer.

Results

Rate constants k_{obsd} were independent of $[Co(III)]_T$ in the range $(0.88–2.4) \times 10^{-3}$ M. A first-order dependence of $[WO_4^{2-}]_T$ was observed (Figure 5), as well as a dependence on $[H^+]$. Concentrations of $[WO_4^{2-}]_T$ were such that the reaction goes essentially to completion ($K_C = 1160\ M^{-1}$; see above), and no intercepts were obtained in Figure 5. A small but significant dependence of k_{obsd} on buffer concentration was observed (Figure 6) and interpreted as a medium effect rather than as a direct participation of the buffer in the reaction. The same explanation was given by Taylor[3] for an effect of similar magnitude. The $[H^+]$ dependence is consistent with (10) and (11). Alternative paths are considered below. Reactions 10 and 11 give (12), which can be simplified by substituting

Table I. k_{obsd} and k_{calcd} for the Reaction of *cis*-$Co(en)_2(OH)(H_2O)^{2+}$ with WO_4^{2-} at 25 °C and $I = 1.0$ M ($NaClO_4$) with [Tris] = 0.1 M

pH	$[WO_4^{2-}]_T$, M	$10^3[Co(III)]_T$, M	k_{obsd}, s^{-1}	k_{calcd}, s^{-1}
9.00	0.100	2.44	8.56	9.25
9.00	0.080	0.80	6.40	7.40
9.00	0.080	2.40	6.60	7.40
9.00	0.060	0.80	4.70	5.55
9.00	0.060	2.40	4.90	5.55
9.00	0.040	2.40	3.10	3.70
8.50	0.095	1.00	26.30	23.70
8.50	0.085	1.00	24.30	21.21
8.50	0.075	1.00	21.00	18.71
8.50	0.060	1.00	16.00	14.97
8.50	0.050	1.00	13.20	12.48
8.50	0.040	1.00	9.50	9.98
8.50	0.025	1.00	6.60	6.24
8.50	0.015	1.00	4.30	3.74
8.50	0.010	1.00	2.40	2.50
8.50	0.010	1.00	2.50	2.50
8.40	0.100	1.00	28.00	29.95
8.30	0.010	1.00	3.17	3.57
8.22	0.100	1.00	40.20	41.04
8.22	0.080	1.00	36.80	32.83
8.22	0.060	1.00	26.80	24.62
8.22	0.040	1.00	17.20	16.41
8.22	0.020	1.00	9.48	8.21
8.22	0.010	1.00	4.96	4.10
8.10	0.010	1.00	4.56	5.02
8.00	0.080	1.00	42.30	47.41
8.00	0.070	1.00	39.90	41.49
8.00	0.060	1.00	35.40	35.56
8.00	0.050	1.00	32.70	29.63
8.00	0.045	1.00	24.60	26.67
8.00	0.040	1.00	21.90	23.71
8.00	0.030	1.00	17.50	17.78
8.00	0.020	1.00	11.00	11.85
8.00	0.010	1.00	4.70	5.93

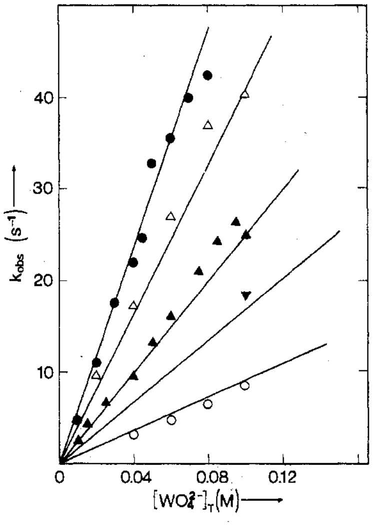

Figure 5. Dependence of pseudo-first-order rate constants, k_{obsd}, for the reaction of *cis*-$Co(en)_2(H_2O)_2^{3+}$ with WO_4^{2-} on $[WO_4^{2-}]_T$ at 25 °C and $I = 1.0$ M ($NaClO_4$) with [Tris] = 0.1 M. pH = 9.00 (○), 8.70 (▼), 8.50 (▲), 8.22 (△) and 8.00 (●); $[Co(III)]_T = 1.00 \times 10^{-3}$ M. The straight lines have been plotted with $k_1 = 3.22 \times 10^7\ M^{-1}\ s^{-1}$, $k_2 = 1.03 \times 10^7\ M^{-1}\ s^{-1}$, $K_1 = 1.55 \times 10^8\ M^{-1}$, $K_2 = 1.15 \times 10^6\ M^{-1}$, and $K_w = 3.16 \times 10^3\ M^{-1}$, respectively.

$$Co(en)_2(OH)_2^+ + HWO_4^- \xrightarrow{k_1} Co(en)_2(OH)(WO_4) + H_2O \qquad (10)$$

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(12) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

$$\mathrm{Co(en)_2(OH)(H_2O)^{2+} + HWO_4^-} \xrightarrow{k_2} \mathrm{Co(en)_2(OH)(WO_4) + H^+ + H_2O} \quad (11)$$

$$k_{\mathrm{obsd}} = \frac{k_1 K_{\mathrm{W}}[\mathrm{H^+}][\mathrm{WO_4^{2-}}]_{\mathrm{T}} + k_2 K_{\mathrm{W}} K_1 [\mathrm{H^+}]^2 [\mathrm{WO_4^{2-}}]_{\mathrm{T}}}{1 + K_1[\mathrm{H^+}] + K_1 K_2 [\mathrm{H^+}]^2} \quad (12)$$

(13)–(15) to give (16). A multiple linear regression analysis

$$x = [\mathrm{WO_4^{2-}}]_{\mathrm{T}} \quad (13)$$

$$y = [\mathrm{H^+}][\mathrm{WO_4^{2-}}]_{\mathrm{T}} \quad (14)$$

$$z = k_{\mathrm{obsd}}(1 + K_1[\mathrm{H^+}] + K_1 K_2 [\mathrm{H^+}]^2)/K_{\mathrm{W}}[\mathrm{H^+}] \quad (15)$$

$$z = k_1 x + k_2 K_1 y \quad (16)$$

performed on all data (k_{obsd}, $[\mathrm{H^+}]$, $[\mathrm{WO_4^{2-}}]_{\mathrm{T}}$) yielded $k_1 = (3.22 \pm 0.14) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ and $k_2 = (1.03 \pm 0.16) \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, and these values have been used to plot the straight lines in Figure 5.

Discussion

The complexing of substitution-inert *cis*-$\mathrm{Co(en)_2(H_2O)_2^{3+}}$ with $\mathrm{WO_4^{2-}}$ was studied under conditions of pH 8.0–9.0, where $\mathrm{Co(en)_2(OH)_2^+}$ and $\mathrm{Co(en)_2(OH)(H_2O)^{2+}}$ are the dominant species. Complexing is rapid and is assumed therefore to occur by substitution at the W(VI), the dominant form of which is $\mathrm{WO_4^{2-}}$; see eq 4. Results complement those obtained previously for the $\mathrm{H_2{}^{18}O}$ exchange with $\mathrm{WO_4^{2-}}$ at pH >11.[2] It was not possible to extend the present studies to acidic pHs because of precipitation. Two paths, (10) and (11), are defined involving reaction of $\mathrm{Co(en)_2(OH)_2^+}$ with $\mathrm{HWO_4^-}$ (k_1) and $\mathrm{Co(en)_2(OH)(H_2O)^{2+}}$ with $\mathrm{HWO_4^-}$ (k_2). Proton ambiguities exist, and contributions from (17) and (18), to k_1 and k_2,

$$\mathrm{Co(en)_2(OH)(H_2O)^{2+} + WO_4^{2-}} \xrightarrow{k_3} \mathrm{Co(en)_2(OH)(WO_4) + H_2O} \quad (17)$$

$$\mathrm{Co(en)_2(H_2O)_2^{3+} + WO_4^{2-}} \xrightarrow{k_4} \mathrm{Co(en)_2(OH)(WO_4) + H_2O + H^+} \quad (18)$$

respectively, have also to be considered. Consistency with $\mathrm{H_2{}^{18}O}$-exchange studies is necessary, where the rate constant k_a (eq 1), for the reaction of $\mathrm{WO_4^{2-}}$ with $\mathrm{H_2O}$ of 0.44 $\mathrm{s^{-1}}$ at 25 °C and $I = 1.0$ M ($\mathrm{NaClO_4}$), is particularly relevant. Maximum values (corresponding to 100% contributions) from k_3 ($=k_1K_{\mathrm{W}}/K_1$) and k_4 ($=k_2K_{\mathrm{W}}/K_2$) are 660 $\mathrm{M^{-1}\ s^{-1}}$ and $2.8 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$, respectively. An allowance for outer-sphere association (K_{OS}) is required before a direct comparison with the water-exchange rate constant can be made. At $I = 1.0$ M, estimates of K_{OS} based on electrostatics alone are <10 $\mathrm{M^{-1}}$ for the $\mathrm{Co(en)_2(OH)(H_2O)^{2+}}$ and $\mathrm{WO_4^{2-}}$ (i.e., 2+,2– interaction), so that k_3/K_{OS} is >66 $\mathrm{s^{-1}}$. For the 3+,2– interaction $K_{\mathrm{OS}} < 50\ \mathrm{M^{-1}}$, giving $k_4/K_{\mathrm{OS}} > 560\ \mathrm{s^{-1}}$. Both these values seem unrealistic in comparison to k_a, and at most small contributions are expected.

For reaction paths involving $\mathrm{Co(en)_2(OH)(H_2O)^{2+}}$, it is possible for the $\mathrm{OH^-}$ or $\mathrm{H_2O}$ to substitute into the W(VI) coordination sphere. First inclinations would be to assume that $\mathrm{OH^-}$ is the more effective, with a coordinated $\mathrm{H_2O}$ not able to match either a coordinated $\mathrm{OH^-}$ or free $\mathrm{H_2O}$ in ease of exchange. This is not the case however, as previous studies have also shown. Thus the reaction of $\mathrm{Co(NH_3)_5(H_2O)^{3+} + HMoO_4^-}$ ($3.2 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$) is faster than that of $\mathrm{Co(NH_3)_5(OH)^{2+} + HMoO_4^-}$ ($6.6 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$);[3] similar observations apply in the complexing of aquo- and hydroxocobalt(III) complexes to $\mathrm{HSeO_3^-}$,[13,14] and complexing of Co(III) and Cr(III) complexes with $\mathrm{HSeO_3^-}$ and $\mathrm{HIO_3}$ occurs ca. 6 and 7 times more readily than the $\mathrm{H_2O}$-exchange reactions.[13-15] Clearly the oxygen of a coordinated $\mathrm{H_2O}$, even though it is already bonded to three other atoms, can substitute into the coordination sphere of the second reactant with enhanced reactivity. This unexpected behavior is accounted for by a mechanism involving H bonding of the $\mathrm{H_2O}$ to the oxyanion in the activated complex,[13-16] a process which is believed to facilitate an association process. In the present study the relative ease of substitution of coordinated $\mathrm{H_2O}$ and $\mathrm{OH^-}$ into the W(VI) coordination sphere appears to be not too different with $k_1 = 3.22 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$ and $k_2 = 1.03 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$. This may be in part the result of the $\mathrm{OH^-}$ and $\mathrm{H_2O}$ being in cis positions so that H bonding can be achieved whichever group substitutes in the W(VI).

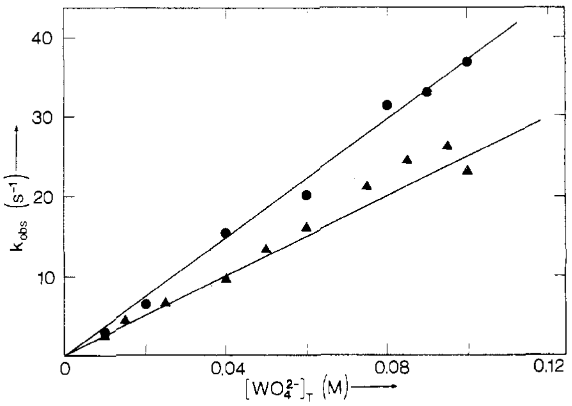

Figure 6. Dependence of pseudo-first-order rate constants, k_{obsd}, for the reaction of *cis*-$\mathrm{Co(en)_2(H_2O)_2^{3+}}$ with $\mathrm{WO_4^{2-}}$ on $[\mathrm{WO_4^{2-}}]_{\mathrm{T}}$ at pH 8.50, 25 °C, and $I = 1.0$ M ($\mathrm{NaClO_4}$) with [Tris] = 0.1 M (▲) and 0.3 M (●); $[\mathrm{Co(III)}]_{\mathrm{T}} = 1.00 \times 10^{-3}$ M.

The rate constants k_1 and k_2 for substitution into $\mathrm{HWO_4^-}$ (k_c) provide an interesting comparison with rate constants obtained for the $\mathrm{H_2{}^{18}O}$-exchange studies (k_a and k_b)[2] as follows:

$\mathrm{WO_4^{2-} + H_2O}$, $k_a = 0.44\ \mathrm{s^{-1}}$
$\mathrm{WO_4^{2-} + OH^-}$, $k_b = 273\ \mathrm{M^{-1}\ s^{-1}}$
$\mathrm{HWO_4^-}$ + complex, $k_c =$ ca. $10^7\ \mathrm{M^{-1}\ s^{-1}}$

A similar comparison exists for molybdate which from $\mathrm{H_2{}^{18}O}$-exchange studies[2] and studies[3] on the complexing with $\mathrm{Co(NH_3)_5(H_2O)^{3+}}$ provides the following information:

$\mathrm{MoO_4^{2-} + H_2O}$, $k_a = 0.33\ \mathrm{s^{-1}}$
$\mathrm{MoO_4^{2-} + OH^-}$, $k_b = 2.22\ \mathrm{M^{-1}\ s^{-1}}$
$\mathrm{HMoO_4^-}$ + complex, $k_c =$ ca. $10^5\ \mathrm{M^{-1}\ s^{-1}}$

The effects of protonation are more significant than with selenite, where for a range of Co(III) complexes $\mathrm{SeO_3^{2-}}$ reacts 6–24 times slower than does $\mathrm{HSeO_3^-}$.[14] First- and second-protonation constants for both $\mathrm{WO_4^{2-}}$ ($K_{\mathrm{W}} = 3.16 \times 10^3\ \mathrm{M^{-1}}$; $K_{\mathrm{HW}} = 3.98 \times 10^4\ \mathrm{M^{-1}}$ at 20 °C and $I = 0.10$ ($\mathrm{NaClO_4}$))[6] and $\mathrm{MoO_4^{2-}}$ ($K_{\mathrm{Mo}} = 2.95 \times 10^3\ \mathrm{M^{-1}}$; $K_{\mathrm{HMo}} = 5.50 \times 10^3\ \mathrm{M^{-1}}$ at 25 °C and $I = 1.0$ M (NaCl))[17] are the reverse of normal expected behavior (cf. K_1 and K_2 for eq 2 and 3). It has been suggested that the first-protonation constant is anomalous and corresponds to a change in coordination number.[18] However, recently, additional molybdate studies[17] suggest that it is the second-protonation constant which is anomalous and that the change in coordination number (4 ⟶ 6) occurs with addition of the second proton. Whichever of these viewpoints is correct,

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(13) Fowless, A. D.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 1276.
(14) Fowless, A. D.; Stranks, D. R. *Inorg. Chem.* **1977**, *16*, 1282.
(15) Wharton, R. K.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 33.
(16) Beach, T. A.; Lawrence, N. C.; Lincoln, S. F. *Aust. J. Chem.* **1973**, *26*, 1877.
(17) Cruywagen, J. J.; Rohwer, E. F. C. H. *Inorg. Chem.* **1975**, *14*, 3136.
(18) Rohwer, E. F. C. H.; Cruywagen, J. J. *J. S. Afr. Chem. Inst.* **1963**, *16*, 26.

the labilizing effect of the proton is clear-cut in the present case. Other studies of Mo(VI), in particular those with 8-hydroxyquinoline (and the sulfonate derivative),[19] EDTA,[20] and catechol,[21] in which $HMoO_4^-$ is believed to be the reactant, involve rapid addition processes with increase in coordination number of the Mo(VI) (4 → 6). The first protonation has the effect of labilizing the tetrahedral W and Mo oxyanions *and* promoting a change in coordination number.

The second slower stage in the complexing of W(VI) to *cis*-$Co(en)_2(OH)(H_2O)^{2+}$ observed with $[Co(III)]_T \gg [WO_4^{2-}]_T$ was not studied further. This process most likely corresponds to chelation of WO_4^{2-}. There is need for further data for the complexing of monoaquo complexes to further establish the present position. Attempts to study the reaction of $Co(NH_3)_5(H_2O)^{3+}$ with W(VI) resulted in precipitation. Data for the reaction of $Cr(ed3A)(H_2O)$ (ed3A = ethylenediamine-*N*-methyl-*N*,*N*′-,*N*′-triacetate) with W(VI), pH 7.3–8.3, using the triethanolammonium ion as buffer (0.10–0.30 M), gave a strong buffer dependence for the forward reaction.[22] With another buffer this system could provide additional relevant information.

Acknowledgment. A.G.S. was a British Council Academic Interchange visitor to Leoben during 1977. We are grateful to the Austrian Foundation for the Promotion of Scientific Research for support.

Registry No. *cis*-$Co(en)_2(H_2O)_2^{3+}$, 21247-59-6; *cis*-$Co(en)_2(OH)(H_2O)^{2+}$, 21247-60-9; *cis*-$Co(en)_2(OH)_2^+$, 21247-61-0; WO_4^{2-}, 14311-52-5; *cis*-$Co(en)_2(OH)(WO_4)$, 72827-36-2.

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[19] Knowles, P. F.; Diebler, H. *Trans. Faraday Soc.* **1968**, *64*, 977. Diebler, H.; Timms, R. E. *J. Chem. Soc. A* **1971**, 273.
[20] Honig, D. S.; Kustin, K. *J. Am. Chem. Soc.* **1973**, *95*, 5525.
[21] Kustin, K.; Liu, S. T. *J. Am. Chem. Soc.* **1973**, *95*, 2487.
[22] Taylor, R. S.; Sykes, A. G., unpublished work.

Contribution from the Chemistry Department, Faculty of Military Studies, University of New South Wales, Duntroon, Canberra, A.C.T., Australia 2600, and the Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia 2600

Mechanism of Hydrolysis of Substituted Cobalt(III)–Amine Complexes: Pentacoordinate Intermediates?

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Received September 6, 1979

The nitrate ion competition and rates of nitrosation of $Co(NH_3)_5N_3^{2+}$ have been measured in $NaClO_4/NaNO_3$ solution over the range of nitrate ion concentration 0–1.0 M (25.0 °C, $\mu = 1.0$ M), yielding a rate law $-d[CoN_3^{2+}]/dt = (k_1 + k_2[NO_3^-])[H^+][HNO_2][CoN_3^{2+}]$. One mechanistic model which assumes anion-dependent competition by both the k_1 and k_2 pathways leads to the same competition ratio R for each path ($R = [CoN_3^{2+}]/[CoOH_2^{3+}][NO_3^-] = 0.40_5$ M^{-1}). However it is shown that other models lead to an equally good fit of the data. A similar two-term rate law has been reported for the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ in NO_3^- media,[3] and it is demonstrated that an earlier analysis of this rate and competition data is also not unique. One solution requires a five-coordinate intermediate for the path independent of NO_3^- and direct insertion of NO_3^- by Hg^{2+} ion for the path dependent on NO_3^-. Acceptance of this solution gives the same competition ratio as the nitrosation reaction. Some data are also given which support the direct insertion of anions by the Hg^{2+}-catalyzed path and the problems of interpreting the competition results, and some methods for resolving the ambiguities are discussed.

Introduction

Some years ago Haim and Taube[1] showed that the rapid nitrosation of $Co(NH_3)_5N_3^{2+}$ in water gave $Co(NH_3)_5OH_2^{3+}$ and $N_2 + N_2O$, and in the presence of competing nucleophiles Y^- some anionic product $Co(NH_3)_5Y^{2+}$ was also simultaneously formed. This work followed a similar study of the Hg^{2+}-induced aquation of $Co(NH_3)_5X^{2+}$ (X = I, Br, Cl)[4] where the competition properties of the presumed $Co(NH_3)_5^{3+}$ intermediate appeared to be independent of its source. Other methods to give the supposed intermediates have been developed since, and more accurate techniques[2,3] have led to revised competition numbers which are quite different to the earlier ones.[1,4] Despite this difference the competition results still show a degree of consistency, and the evidence for the intermediate remains.

A second and more fundamental piece of evidence which supports the case for intermediates of reduced coordination number derives from the rate laws in relation to the competition ratios. Earlier data[4] revealed a multiterm rate law for the Hg^{2+}-induced aquations in the presence of SO_4^{2-} ions, i.e.

$$k_0 = k_1 + k_2[SO_4^{2-}] + k_3[SO_4^{2-}]^2$$

and the results suggested that competition arose by the anion-independent as well as the anion-dependent pathways. It was concluded[4] therefore that, at least via the k_1 path, anion entry occurred after the rate-determining step (but before the formation of $Co(NH_3)_5OH_2^{3+}$). The logical inference was the intervention of the $Co(NH_3)_5^{3+}$ intermediate. Following a recent detailed study of the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ in NO_3^- media, this conclusion has been called into question.[3] An examination of the validity of these arguments necessitated a similar analysis of the data for the related nitrosation reaction,[1] which in turn has required a more accurate definition of the rate law and nitrate ion competition, and these results are reported herein.

Results

The kinetic data at 25 °C for the reaction

$$Co(NH_3)_5N_3^{2+} + HNO_2 + H^+ \rightarrow Co(NH_3)_5NO_3^{2+} + Co(NH_3)_5OH_2^{3+} + N_2 + N_2O$$

in the presence of NO_3^- were fitted to the relation (1) by a

$$k_0 = k_1 + k_2[NO_3^-] \qquad (1)$$

standard least-squares analysis yielding $k_1 = (4.14 \pm 0.05) \times 10^{-3}$ s^{-1} and $k_2 = (2.23 \pm 0.09) \times 10^{-3}$ M^{-1} s^{-1} at a fixed

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[1] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
[2] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).
[3] W. L. Reynolds and E. R. Alton, *Inorg. Chem.*, **17**, 3355 (1978).
[4] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

0020-1669/80/1319-1001$01.00/0