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Trimethylenediamine Complexes. VI.[1] Kinetic and Equilibrium Studies of Ligand Substitution Reactions of the *trans*-Aquabis(diamine)sulfito- and *trans*-Bis(diamine)-hydroxosulfitocobalt(III) Complexes

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Substitution reactions of the *trans*-$CoSO_3$ (H_2O or OH) (en or tn)$_2$ complex with Cl^-, Br^-, CH_3COO^-, N_3^-, NO_2^-, NCS^-, CN^-, and SO_3^{2-} have been studied by the spectrophotometric method. The equilibrium constant of anation $K^{X}_{H_2O}$ spans many orders of magnitude, *e.g.* from 1.24 for bromide to 1.23×10^7 M^{-1} for cyanide in the case of the en complex, and is correlated to the electron donor constant E_n which was defined by Edwards. The kinetics of the substitution reactions is adequately interpreted by virtue of the reversible **D** mechanism *via* a five-coordinate intermediate $CoSO_3(AA)_2^+$. Release of the ligand X^{n-} from *trans*-$CoSO_3(X)(tn)_2^{(1-n)+}$ proceeds 10—25 times faster than from the corresponding bis(ethylenediamine) complex, and the kinetic ring-size effect is attributed to the larger stability of the en complex as compared with the tn complex at the ground state.

Although cobalt(III) complexes are usually inert,[2] two groups of complexes are known to perform rapid ligand substitution. One is those containing unsaturated macrocyclic(N_4) ligands, which have been shown to enhance the rate of ligand substitution at the metal center by many orders of magnitude.[3] The increasing degree of unsaturation in the encircling macrocycle is considered to enhance softness of the central metal ion, thus stabilizing five-coordinate intermediates and increasing the rates of ligand displacement.[4]

The other group of rather labile cobalt(III) complexes contain S-bonded ligands such as sulfite[5] and sulfinate,[6] σ-bonded organo ligands,[7] and P-bonded phosphonate ligands[8] which exert a significant labilizing effect on the trans ligand. By comparing activation enthalpies, Stranks and Yandell[9] concluded that the labilizing effect of the sulfite ligand in the *trans*-aqua(or hydroxo)-bis(ethylenediamine)sulfitocobalt(III) complex arises from stabilization of the five-coordinate intermediate in the dissociative (**D**) reaction pathway. On the other hand Palmer and Deutsch attributed the trans labilizing effect of the sulfinate ligand in *trans*-bis(dimethylglyoximato)methanol(*p*-toluenesulfinato)cobalt(III) to its trans influence, that is a ground-state weakening of the trans bond.[6]

The present paper is concerned with the reactions of *trans*-$CoSO_3(Y)(AA)_2^{(1-m)+}$ with various nucleophiles X^{n-}, where AA=ethylenediamine(en) or trimethylenediamine(tn), $Y^{m-}=OH^-$ or H_2O, and $X^{n-}=Cl^-$, Br^-, CH_3COO^-, NO_2^-, N_3^-, NCS^-, SO_3^{2-}, or CN^-. The equilibrium and kinetic studies of these reactions have revealed that they proceed *via* the **D** mechanism, and afforded a quantitative relationship between the electron-donating properties of X^{n-} and the formation constants of *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$.

Experimental

Preparation of Complexes. trans-*Aquabis(ethylenediamine)-sulfitocobalt(III) Perchlorate Monohydrate,* $[CoSO_3(H_2O)(en)_2]ClO_4\cdot H_2O$, was prepared by the method of Baldwin[10] and recrystallized twice from water containing sodium perchlorate and a trace amount of perchloric acid. It contained one molecule of crystalline water contrary to Baldwin's anhydrous compound. Found: C, 12.17; H, 5.10; N, 14.55%. Calcd for $C_4H_{20}N_4O_9SClCo$: C, 12.17; H, 5.11; N, 14.20%.

trans-*Aquasulfitobis(trimethylenediamine)cobalt(III) Perchlorate Monohydrate,* $[CoSO_3(H_2O)(tn)_2]ClO_4\cdot H_2O$, was prepared by a similar method. The compound $CoCl(SO_3)(tn)_2\cdot H_2O$[11] (14 g) was dissolved in a dilute perchloric acid solution (pH=4) and a trace amount of insoluble material was filtered off. About three times molar amount of sodium perchlorate was added to this solution and the mixture was kept standing at 0 °C in the dark to give light brown thin crystals. The precipitate was filtered off, washed with ethanol and acetone successively, and dried over silica gel. The yield was 43% (7.4 g), and the compound was recrystallized twice from water containing sodium perchlorate and a trace amount of perchloric acid. Found: C, 16.91; H, 5.65; N, 13.22%. Calcd for $C_6H_{24}N_4O_9SClCo$: C, 17.05; H, 5.72; N, 13.25%.

trans-*Aquasulfitobis(trimethylenediamine)cobalt(III) Nitrate Hemihydrate,* $[CoSO_3(H_2O)(tn)_2]NO_3\cdot 1/2H_2O$, was derived from the perchlorate. The perchlorate (1 g) was dissolved in cold water (7 ml), and treated with a slightly excess amount of pulverized silver nitrate. After filtration of silver chloride, two drops of concentrated nitric acid, 0.3 g of ammonium nitrate and 50 ml of ethanol were added to the solution and the mixture was kept in a refrigerator. A light brown precipitate was recrystallized twice from ethanol–water (5: 1 by volume), washed with ethanol and acetone successively, and then air-dried. The yield was 18% (0.2 g). Found: C, 19.06; H, 6.27; N, 18.62%. Calcd for $C_6H_{23}N_5O_{7.5}SCo$: C, 19.15; H, 6.16; N, 18.61%.

Sodium Disulfitobis(trimethylenediamine)cobaltate(III) Trihydrate, $Na[Co(SO_3)_2(tn)_2]\cdot 3H_2O$, was prepared by a previous method.[11] Found: C, 16.06; H, 6.09; N, 12.48%. Calcd for $C_6H_{26}N_4O_9S_2CoNa$: C, 16.22; H, 5.90; N, 12.61%.

All the nucleophilic reagents are sodium salts of A. R. grade.

Measurements. The ionic strength was adjusted with sodium perchlorate to 1.00 M. The hydrogen ion concentration was determined by means of a Beckman "Century" SS-1 pH meter with a Beckman 39301 glass electrode and a Beckman 39402 B-4U calomel electrode. A saturated solution of sodium chloride was employed in place of potassium chloride for the calomel electrode in order to prevent precipitation of potassium perchlorate, and a 4.302×10^{-3} M solution of perchloric acid ($\mu=1.00$ M) was used as a reference solution.

Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer and NMR spectra on a JOEL C-60 HL spectrometer. IR spectra were measured in Nujol with JASCO IR-E (4000—600 cm^{-1}) and Hitachi EPI-L (700—200 cm^{-1}) Infrared Spectrophotometers. Reactions were followed by the stopped-flow method with a Union Stopped-Flow, Rapid-Scan Spectrophotometer RA-1300.

Results

Characterization of the Aqua Sulfitobis(trimethylenediamine)-cobalt(III) Complex. The IR spectrum of $[CoSO_3(H_2O)(tn)_2]ClO_4\cdot H_2O$ in Nujol shows a single sharp band at 899 cm^{-1} which is assigned to the CH_2 rocking vibration, suggesting a trans structure.[12] The proton NMR spectrum in a 0.3 M D_2SO_4–D_2O solution at 25 °C displays three signals at 1.73 (4H), 2.59 (8H), and 3.67 (8H) ppm from DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate). They are assigned to the β-CH_2, α-CH_2, and NH_2 protons, respectively, of the trimethylenediamine ligands $NH_2CH_2(\alpha)CH_2(\beta)CH_2(\alpha)NH_2$. Usually the amine protons in a *trans*-bis(diamine)cobalt(III) complex resonate as a single peak, whereas those in a *cis* isomer exhibit two bands.[13,14] The trans structure of $CoSO_3(H_2O)(tn)_2^+$ is thus supported by the NMR data, too.

In order to inspect IR spectra in the 1200—1000 cm^{-1} region, the perchlorate anion in the outer sphere, which has absorption in this region, was replaced by the nitrate ion. $[CoSO_3(H_2O)(tn)_2]NO_3\cdot 1/2H_2O$ shows absorption bands assignable to the sulfite ligand at 1120(s), 1092(s, br), 980(vs), 628(vs, br), and 524(sh) cm^{-1}. The frequencies are higher as compared with those of free sulfite ion, suggesting S-bonding to the cobalt atom.[15] The S-bonding of the sulfite ligands has been ascertained by X-ray analysis for $[CoSO_3(NH_3)_5]Cl\cdot H_2O$,[16] *trans*-$[CoSO_3(H_2O)(en)_2]ClO_4\cdot H_2O$,[17] *trans*-$[CoSO_3(H_2O)$(quarterpyridine)$]NO_3\cdot H_2O$,[18] and *trans*-$[CoSO_3(NCS)(en)_2]\cdot 2H_2O$.[19]

Equilibrium Studies. The pK_a value of *trans*-$CoSO_3(H_2O)(en)_2^+$ was reported by Stranks and Yandell to be 9.45 at 25 °C.[9] Now pK_a of *trans*-$CoSO_3(H_2O)(tn)_2^+$ was determined to be 9.10 ± 0.05 at 25.0 °C and $\mu=1.00$ M from the customary acid-base titration curve using 0.05 M NaOH as the base titrant.

$$\textit{trans-}CoSO_3(H_2O)(AA)_2^+ \rightleftarrows \textit{trans-}CoSO_3(OH)(AA)_2 + H^+ \qquad (1)$$

Equilibrium constants of the anation reactions of $CoSO_3(H_2O)(AA)_2^+$ with various ligands (X^{n-}) spanned many orders of magnitude, and were measured by the following three methods at 25.0 °C and $\mu=1.00$ M. The complex concentration was kept much smaller as compared with $[X^{n-}]$ in the case of (i) and (ii), and with $[OH^-]$ in (ii) and (iii).

(i) Substitution with Chloride, Bromide and Acetate Ions: Anation reactions of *trans*-$CoSO_3(H_2O)(en)_2^+$ with chloride at pH 3.46, bromide at pH 3.45 and acetate ions at pH 3.19—5.01,[20] and of *trans*-$CoSO_3(H_2O)(tn)_2^+$ with these anions at pH 3.40, 4.45, and 3.84—4.90,[20] respectively, proceed to attain equilibria

$$\textit{trans-}CoSO_3(H_2O)(AA)_2^+ + X^{n-} \rightleftarrows \textit{trans-}CoSO_3(X)(AA)_2^{(1-n)+} + H_2O. \qquad (2)$$

The spectral change in either case exhibits isosbestic points at 223, 247, and 276 nm (Cl^-); 255 and 286 nm (Br^-); 241 and 269 nm (CH_3COO^-) in the case of the en complex, and at 236, 257, and 283 nm (Cl^-); 265 and 290 nm (Br^-); 242, 254, and 274 nm (CH_3COO^-) for the tn complex.

The equilibrium constant of each reaction is expressed by

$$K^{X}_{H_2O} = \frac{[RX]}{[ROH_2][X^{n-}]} = \left(\frac{A-A_{ROH_2}}{A_{RX}-A}\right)\frac{1}{[X^{n-}]}, \qquad (3)$$

where RX and ROH_2 denote *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$ and *trans*-$CoSO_3(H_2O)(AA)_2^+$, respectively, and A is the absorbance of a solution equilibrated at given concentrations of the complex (c_M) and X^{n-}(c_X), and $A_{ROH_2}=\varepsilon_{ROH_2}c_M$, $A_{RX}=\varepsilon_{RX}c_M$. All quantities except $K^X_{H_2O}$ and ε_{RX} are observable, since $[X^{n-}]=c_X$ when $c_X\gg c_M$. Eq. 3 is transformed into

$$\frac{1}{A-A_{ROH_2}} = \frac{1}{A_{RX}-A_{ROH_2}} + \frac{1}{(A_{RX}-A_{ROH_2})K^X_{H_2O}}\cdot\frac{1}{[X^{n-}]}. \qquad (4)$$

By plotting the left side tem against $[X^{n-}]^{-1}$, a straight line is obtained for each reaction (Eq. 2), and values of the equilibrium constant $K^X_{H_2O}$ and the molar extinction coefficient ε_{RX} of the anation product are calculated from the slope and intercept of the straight line. The results are included in Table 1.

(ii) Substitution with Azide, Nitrite, Thiocyanate, and Sulfite Ions: Basic solutions are suitable for investigation of these reactions, which are reversible and exhibit the following isosbestic points: 455 nm(NO_2^-), 486 and 556 nm (NCS^-) for AA=en and 474 nm (NO_2^-), 391, 402, and 507 nm (NCS^-), 498 nm(SO_3^{2-}) for AA=tn. In the reactions with azide ions no isosbestic points were observed in the 340—700 nm region.

$$\textit{trans-}CoSO_3(OH)(AA)_2 + X^{n-} \rightleftarrows \textit{trans-}CoSO_3(X)(AA)_2^{(1-n)+} + OH^- \qquad (5)$$

The equilibrium constant K^X_{OH} of Reaction 5 is defined by

$$K^X_{OH} = [RX][OH^-]/[ROH][X^{n-}], \qquad (6)$$

where ROH stands for *trans*-$CoSO_3(OH)(AA)_2$. In a similar manner to Eq. 4, the spectral data are related to K^X_{OH} and ε_{RX} by Eq. 7, of which values are included in Table 1.

$$\frac{1}{A-A_{ROH}} = \frac{1}{A_{RX}-A_{ROH}} + \frac{1}{(A_{RX}-A_{ROH})K^X_{OH}}\cdot\frac{[OH^-]}{[X^{n-}]} \qquad (7)$$

(iii) Substitution with Cyanide Ion: In a basic solution, the reversible replacement by the cyanide ion also proceeds according to Eq. 5, and the spectral change displays isosbestic points at 364, 380 and 440 nm in the case of the en complex and at 366, 396 and 456 nm for the tn complex. Since the values of K^{CN}_{OH} are large enough to complete reactions in the presence of excessive cyanide, the molar extinction coefficients ε_{RX} of *trans*-$CoSO_3(CN)(AA)_2$ were determined under these conditions. Then the equilibrium constant K^X_{OH} was calculated by Eq. 6 using

$$[RX] = (A-\varepsilon_{ROH}c_M)/(\varepsilon_{RX}-\varepsilon_{ROH}),$$

$$[ROH] = (\varepsilon_{RX}c_M-A)/(\varepsilon_{RX}-\varepsilon_{ROH}),$$

$$[X^{n-}] = c_X - [RX],$$

TABLE 1. EQUILIBRIUM CONSTANTS FOR THE SUBSTITUTION REACTIONS OF *trans*-$CoSO_3(H_2O)(AA)_2^+$ AND *trans*-$CoSO_3(OH)(AA)_2$ WITH NUCLEOPHILES X^{n-} AT 25.0 °C AND μ=1.00 M ($NaClO_4$)

X^{n-}	E_n a) / V	$\log K^{X}_{H_2O}$	$\log K^{X}_{OH}$	ε b) / $cm^{-1}\cdot M^{-1}$	Wavelength / nm
		AA = en			
Cl^-	1.24	0.171±0.034	−4.18±0.09	$(9.64\pm0.40)\times10^3$	300
Br^-	1.51	0.093±0.040	−4.26±0.10	$(4.36\pm0.75)\times10^3$	310
CH_3COO^-	0.95	1.65 ±0.01	−2.70±0.07	$(1.50\pm0.01)\times10^4$	290
N_3^-	1.58	2.56 ±0.09	−1.79±0.03	$(3.98\pm0.13)\times10^2$	470
NO_2^-	1.73	3.59 ±0.07	−0.758±0.007	$(2.15\pm0.01)\times10^2$	430
NCS^-	1.83	3.38 ±0.07	−0.975±0.012	$(2.37\pm0.02)\times10^2$	458
CN^-	2.79	7.09 ±0.09	2.74 ±0.03	$(5.26\pm0.05)\times10$	470
SO_3^{2-}	2.57	3.92 c)	−0.434 c)	$(3.88\pm0.09)\times10^{2}$ c)	432 c)
OH^-	1.65	4.35 ±0.06	0	—	—
		AA = tn			
Cl^-	1.24	−0.044±0.019	−4.74 ±0.08	$(9.19\pm0.47)\times10^3$	310
Br^-	1.51	1.18 ±0.09	−3.53 ±0.15	$(1.55\pm0.01)\times10^4$	280
CH_3COO^-	0.95	1.58 ±0.01	−3.12 ±0.07	$(1.88\pm0.01)\times10^4$	290
N_3^-	1.58	3.26 ±0.09	−1.44 ±0.03	$(5.42\pm0.17)\times10^2$	490
NO_2^-	1.73	4.29 ±0.06	−0.409±0.003	$(2.32\pm0.01)\times10^2$	450
NCS^-	1.83	4.39 ±0.065	−0.313±0.005	$(2.72\pm0.01)\times10^2$	474
CN^-	2.79	6.75 ±0.07	2.05 ±0.01	$(5.14\pm0.05)\times10$	490
SO_3^{2-}	2.57	3.76 ±0.07	−0.939±0.006	$(4.04\pm0.06)\times10^2$	430
OH^-	1.65	4.70 ±0.06	0	—	—

a) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); S. Yamada and M. Tanaka, *J. Inorg. Nucl. Chem.*, **37**, 587 (1975). b) Molar extinction coefficient of *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$ at the indicated wavelength. c) Ref. 9.

where c_X is the total concentration of cyanide ions.

The equilibrium constants $K^{X}_{H_2O}$ and K^{X}_{OH} can be converted into each other by virtue of the interrelation

$$\log K^{X}_{H_2O} = \log K^{X}_{OH} - pK_a - \log K_w, \qquad (8)$$

and are collected in Table 1. Here, $\log K_w = -13.80$ at 25.0 °C and μ=1.00 M($NaClO_4$).[21]

Kinetic Studies. The substitution Reaction 5 was followed spectrophotometrically by the stopped-flow method. Azide, nitrite, thiocyanate, sulfite and cyanide ions were used as the nucleophile X^{n-}, and the reaction with sulfite ion was studied only with the trimethylenediamine complex, since the corresponding reaction with the ethylenediamine complex was previously reported by Stranks and Yandell.[9]

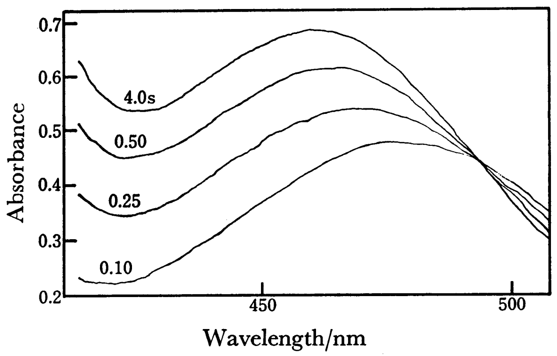

Fig. 1. The spectral change in the course of reaction between *trans*-$CoSO_3(OH)(tn)_2$ and SO_3^{2-} at 23.0 °C and μ=1.00 M ($NaClO_4$) with $c_M=2.990\times10^{-3}$ M, $c_{Na_2SO_3}=0.116$ M and $c_{OH}=33.59\times10^{-3}$ M. The reaction is in equilibrium after 4 s.

As an example of the results, the spectral change during the reaction of *trans*-$CoSO_3(OH)(tn)_2$ with sulfite is displayed in Fig. 1. The reaction attains an equilibrium 4 s after the commencement and an isosbestic point is observed at 494 nm which nearly coincides with that observed in the equilibrium study (498 nm). Concentrations of sulfite and hydroxide ions were both varied in the region of large excess over the complex. In the case of other nucleophiles, on the other hand, $[OH^-]$ was kept constant and only $[X^{n-}]$ was changed. In either case the plot of $\log|A_\infty - A_t|$ against time gave a straight line over about 90% conversion.

Figures 2 and 3 show that the pseudo first order rate constant k_{obsd} increases linearly with $[X^{n-}]/[OH^-]$ in conformity with the equation

$$k_{obsd} = k_f([X^{n-}]/[OH^-]) + k_r. \qquad (9)$$

Ligand substitution reactions of several cobalt(III) sulfite complexes have been reported to proceed *via* the **D** mechanism,[5,9] and the present rate Eq. 9 is also compatible with the following reversible **D** mechanism.

$$trans\text{-}CoSO_3(OH)(AA)_2 \underset{k_{OH}}{\overset{k_{-OH}}{\rightleftarrows}} CoSO_3(AA)_2^+ + OH^- \qquad (10)$$

$$CoSO_3(AA)_2^+ + X^{n-} \underset{k_{-X}}{\overset{k_X}{\rightleftarrows}} trans\text{-}CoSO_3(X)(AA)_2^{(1-n)+} \qquad (11)$$

Assuming that the stationary state approximation is applicable to the five-coordinate intermediate $CoSO_3(AA)_2^+$, then

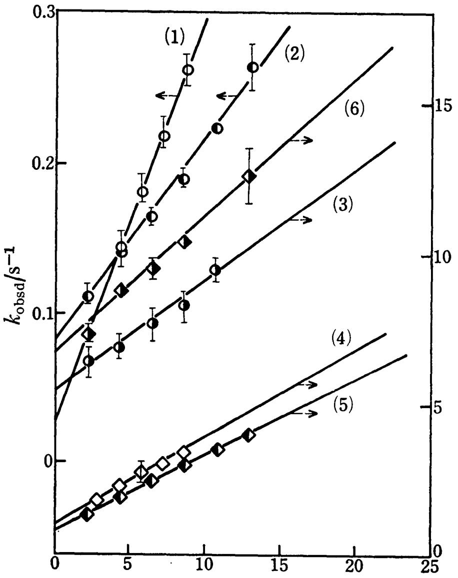

Fig. 2. Linear plots of the pseudo first order rate constants k_{obsd} for attaining the equilibrium, *trans*-$CoSO_3(OH)(AA)_2 + X^{n-} \rightleftharpoons$ *trans*-$CoSO_3(X)(AA)_2{}^{(1-n)+} + OH^-$ at 25.0 °C and $\mu = 1.00$ M ($NaClO_4$) against $c_X/[OH^-]$. Lines 1 (NCS^-), 2 (NO_2^-) and 3 (N_3^-) are for the en complex, and 4 (NCS^-), 5 (NO_2^-) and 6 (N_3^-) are for the tn complex. $[OH^-] = 0.0353$ M and $c_M = (1.500$—$1.657) \times 10^{-3}$ M.

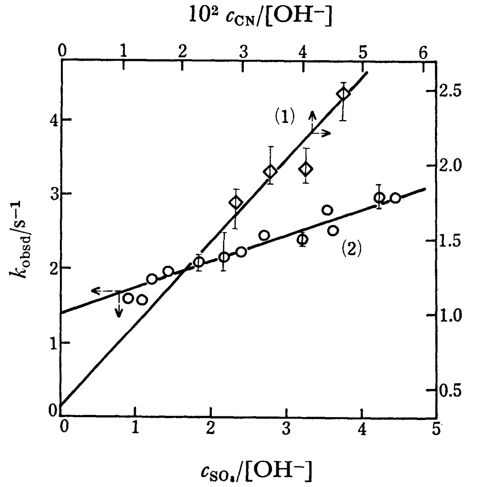

Fig. 3. Linear plots of the pseudo first order rate constants k_{obsd} for attaining the equilibrium, *trans*-$CoSO_3(OH)(tn)_2 + X^{n-} \rightleftharpoons$ *trans*-$CoSO_3(X)(tn)_2{}^{(1-n)+} +$ OH^- at 25.0 °C and $\mu = 1.00$ M ($NaClO_4$) against $c_X/[OH^-]$, 1: $X^{n-} = CN^-$, $[OH^-] = 0.03530$ M and $c_M = 2.08 \times 10^{-5}$ M; 2: $X^{n-} = SO_3^{2-}$, $[OH^-] = 0.02203$—0.08089 M, and $c_M = 1.500 \times 10^{-3}$ M. Each point represents an average of at least five measurements.

$$k_{\text{obsd}} = \frac{k_X k_{-OH}[X^{n-}] + k_{OH} k_{-X}[OH^-]}{k_{OH}[OH^-] + k_X[X^{n-}]}. \tag{12}$$

If $k_{OH}[OH^-] \gg k_X[X^{n-}]$ over the concentration range employed, Eq. 12 is reduced to

$$k_{\text{obsd}} = \frac{k_X k_{-OH}}{k_{OH}} \frac{[X^{n-}]}{[OH^-]} + k_{-X}, \tag{13}$$

which is of the same form as Eq. 9, leading to

$$k_f = k_X k_{-OH}/k_{OH}, \quad k_r = k_{-X}. \tag{14}$$

In Table 2 are listed values of k_f, k_r, and the equilibrium constant for Reaction 5 which is calculated by

$$(K_{OH}^X)_{\text{kin}} = k_f/k_r,$$

and is to be compared with K_{OH}^X determined at the equilibrium state.

The reaction of *trans*-$CoSO_3(OH)(tn)_2$ with sulfite was studied at several temperatures other than 25.0 °C to obtain the rate data listed in Table 3. Eyring plots of k_f and k_r afforded good straight lines leading to $\Delta H^{\neq} = 16.7 \pm 0.4$ kcal·mol^{-1} and $\Delta S^{\neq} = -2.1 \pm 1.2$ cal·K^{-1}·mol^{-1} for the dissociation of a sulfite ion from *trans*-$Co(SO_3)_2(tn)_2{}^-$.

For the reaction of *trans*-$CoSO_3(OH)(en)_2$ with cyanide, the equilibrium constant is so large and the rate is so small that determination of the forward and

Table 2. Rate and equilibrium data for the reactions *trans*-$CoSO_3(OH)(AA)_2 + X^{n-} \rightleftharpoons$ *trans*-$CoSO_3(X)(AA)_2{}^{(1-n)+} + OH^-$ at 25.0 °C and $\mu = 1.00$ M ($NaClO_4$)

X^{n-}	Wavelength[a)] nm	k_f/s^{-1}	k_r/s^{-1}	$(K_{OH}^X)_{\text{kin}}$	K_{OH}^X
			AA = en		
N_3^-	470	$(3.62 \pm 0.23) \times 10^{-2}$	$(5.56 \pm 0.16) \times 10^{-1}$	$(6.51 \pm 0.60) \times 10^{-2}$	$(1.61 \pm 0.09) \times 10^{-2}$
NO_2^-	430	$(1.34 \pm 0.05) \times 10^{-2}$	$(8.21 \pm 0.41) \times 10^{-2}$	$(1.63 \pm 0.14) \times 10^{-1}$	$(1.75 \pm 0.03) \times 10^{-1}$
NCS^-	458	$(2.53 \pm 0.14) \times 10^{-2}$	$(4.00 \pm 0.89) \times 10^{-2}$	$(6.3 \pm 1.8) \times 10^{-1}$	$(1.06 \pm 0.03) \times 10^{-1}$
CN^-	470	$(1.33 \pm 0.05) \times 10^{-2}$ b)	$(2.41 \pm 0.23) \times 10^{-5}$	—	552 ± 29
SO_3^{2-}	432	$(4.09 \pm 0.05) \times 10^{-2}$ c)	$(1.11 \pm 0.05) \times 10^{-1}$ c)	$(3.68 \pm 0.21) \times 10^{-1}$ c)	$3.6_8 \times 10^{-1}$ c)
			AA = tn		
N_3^-	490	$(4.55 \pm 0.20) \times 10^{-1}$	6.75 ± 0.15	$(6.74 \pm 0.45) \times 10^{-2}$	$(3.63 \pm 0.19) \times 10^{-2}$
NO_2^-	450	$(2.51 \pm 0.03) \times 10^{-1}$	$(8.10 \pm 0.20) \times 10^{-1}$	$(3.10 \pm 0.11) \times 10^{-1}$	$(3.90 \pm 0.03) \times 10^{-1}$
NCS^-	474	$(2.89 \pm 0.12) \times 10^{-1}$	1.00 ± 0.07	$(2.89 \pm 0.32) \times 10^{-1}$	$(4.86 \pm 0.05) \times 10^{-1}$
CN^-	290	$(4.48 \pm 0.44) \times 10^{-1}$	$(3.6 \pm 1.6) \times 10^{-3}$	124 ± 67	112 ± 2
SO_3^{2-}	430	$(3.31 \pm 0.20) \times 10^{-1}$	1.41 ± 0.05	$(2.35 \pm 0.23) \times 10^{-1}$	$(1.15 \pm 0.06) \times 10^{-1}$

a) Wavelength utilized for the kinetic measurement. b) Determined at the irreversible condition (see text).
c) Ref. 9.

TABLE 3. RATE DATA FOR THE REACTION *trans*-$CoSO_3(OH)(tn)_2 + SO_3^{2-} \rightleftharpoons$ *trans*-$Co(SO_3)_2(tn)_2^- + OH^-$ AT VARIOUS TEMPERATURES AND $\mu = 1.00$ M ($NaClO_4$)

Temp/°C	k_f/s^{-1}	k_r/s^{-1}
10.0	0.083±0.009	0.275±0.015
15.0	0.123±0.003	0.490±0.018
20.0	0.216±0.013	0.780±0.043
25.0	0.331±0.020	1.41 ±0.05
29.9	0.533±0.034	2.02 ±0.13
35.0	0.790±0.091	3.42 ±0.29

backward rates in the above manner was difficult. Alternatively the cyanide concentration was kept in large excess to render the reaction irreversible. In this case the pseudo first order rate constant is expressed by

$$k_{obsd} = k_{CN}k_{-OH}[CN^-]/(k_{OH}[OH^-]+k_{CN}[CN^-]), \qquad (15)$$

which is transformed into

$$\frac{1}{k_{obsd}} = \frac{1}{k_{-OH}} + \frac{k_{OH}}{k_{CN}k_{-OH}}\left(\frac{[OH^-]}{[CN^-]}\right). \qquad (16)$$

A plot of the observed rate data according to Eq. 16 gave a straight line displayed in Fig. 4, which also contains another plot for the reaction of *trans*-$CoSO_3(OH)(tn)_2$ performed in a similar condition for the sake of comparison. The intercepts and slopes of these straight lines gave the following constants: $k_{-OH} = 1.19 \pm 0.81\ s^{-1}$(AA=en) and $13.9 \pm 2.7\ s^{-1}$(AA=tn), $k_{CN}/k_{OH} = (1.12 \pm 0.80) \times 10^{-2}$(AA=en) and $(2.02 \pm 0.42) \times 10^{-2}$(AA=tn) at 25.0 °C and $\mu = 1.00$ M. Furthermore, by combining the value of slope $k_{OH}/k_{CN}k_{-OH}$ with that of the equilibrium constant K_{OH}^{CN} listed in Table 1, k_{-CN} was calculated to be $(2.41 \pm 0.23) \times 10^{-5}\ s^{-1}$ for the en complex. The value of $k_f = k_{CN}k_{-OH}/k_{OH} = 0.280 \pm 0.004\ s^{-1}$ for the tn complex, which was calculated from the slope of the straight line (2) in Fig. 4, nearly coincides with that obtained in the reversible condition (Table 2).

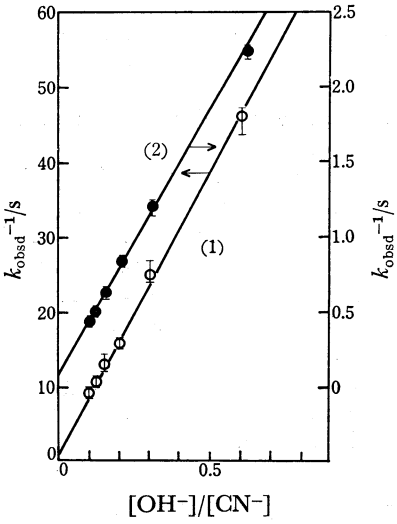

Fig. 4. The plot of $1/k_{obsd}$ *vs.* $[OH^-]/[CN^-]$ for the reaction *trans*-$CoSO_3(OH)(AA)_2 + CN^- \rightarrow$ *trans*-$CoSO_3(CN)(AA)_2 + OH^-$ at 25.0 °C and $\mu = 1.00$ M ($NaClO_4$). 1: AA=en, $[OH^-] = 0.03656$ M and $c_M = 4.485 \times 10^{-4}$ M. 2: AA=tn, $[OH^-] = 0.03657$ M and $c_M = 4.400 \times 10^{-4}$ M.

Division of the k_f value in Table 2 by $k_{-OH} = 1.19 \pm 0.81$ (AA=en) or 13.9 ± 2.7 (AA=tn) s^{-1} affords k_X/k_{OH} (*cf.* Eq. 14) which is shown in Table 4. The ratio indicates that the nucleophilic reactivity of hydroxide ion toward $CoSO_3(AA)_2^+$ is 30—90 times larger than that of other nucleophiles examined. The hydroxide ion was also reported to be at least 4×10^5 times more reactive than H_2O toward $CoSO_3(en)_2^+$,[9] and 8×10^3 times more reactive than NH_3 toward $CoSO_3(NH_3)_4^+$.[22] It was suggested[5a] that the high reactivity of OH^- might reflect a Grotthus-type mechanism.

Discussion

Linear Free Energy Relations (LFER) have been widely used to sort out the various factors that contribute to the rate and equilibrium of organic[23] and inorganic[24] reactions. On the supposition that nucleophilic character of a reagent is a combination of several factors, Edwards proposed an equation

$$\log (K/K_0) = \alpha E_n + \beta H, \qquad (17)$$

where K and K_0 are the rates or equilibrium constants of reactions of a particular substrate with a nucleophile and water, respectively, α and β are two substrate constants, and E_n and H are electron donor constant and basicity constant, respectively.[25] Recently Tanaka related the formation constant K_{ML}^L of a complex ML with the Edwards' parameters by

$$\log K_{ML}^L = \log K_{os(M,L)} + \alpha E(L) + \beta H(L), \qquad (18)$$

where $K_{os(M,L)}$ denotes the formation constant of an outer-sphere complex [M, L].[26]

Equation 18 was derived on the basis of the Eigen

TABLE 4. THE RATE OF X^{n-} RELEASE (k_{-X}) FROM *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$ AND THE REACTIVITY RATIO OF X^{n-} AND OH^- (k_X/k_{OH}) TOWARD $CoSO_3(AA)_2^+$ AT 25.0 °C AND $\mu = 1.00$ M ($NaClO_4$)

X^{n-}	AA = en		AA = tn		$\frac{k_{-X}(tn)}{k_{-X}(en)}$
	k_{-X}/s^{-1}	k_X/k_{OH}	k_X/s^{-1}	k_X/k_{OH}	
N_3^-	$(5.56 \pm 0.16) \times 10^{-1}$	$(3.0 \pm 2.3) \times 10^{-2}$	6.75 ± 0.15	$(3.28 \pm 0.78) \times 10^{-2}$	12.1 ± 0.6
NO_2^-	$(8.21 \pm 0.41) \times 10^{-2}$	$(1.1 \pm 1.5) \times 10^{-2}$	$(8.1 \pm 0.2) \times 10^{-1}$	$(1.81 \pm 0.37) \times 10^{-2}$	9.87 ± 0.74
NCS^-	$(4.00 \pm 0.89) \times 10^{-2}$	$(2.1 \pm 1.6) \times 10^{-2}$	1.00 ± 0.07	$(2.08 \pm 0.49) \times 10^{-2}$	25.0 ± 7.3
CN^-	$(2.41 \pm 0.23) \times 10^{-5}$	$(1.1 \pm 0.8) \times 10^{-2}$	$(3.6 \pm 1.6) \times 10^{-3}$	$(3.23 \pm 0.94) \times 10^{-2}$	149 ± 80
SO_3^{2-}	$(1.11 \pm 0.05) \times 10^{-1}$ [a]	$(3.4 \pm 2.4) \times 10^{-2}$ [a]	1.41 ± 0.05	$(2.38 \pm 0.61) \times 10^{-2}$	12.7 ± 1.0
OH^-	1.19 ± 0.81	1	13.9 ± 2.7	1	12 ± 10

a) Ref. 9.

(**I**$_d$) mechanism, the rate of dissociation of the ligand L from the complex ML being assumed to be inversely proportional to both the electron donating property and the Brønsted basicity of the leaving group L. The present reactions, on the other hand, are presumed to proceed *via* the **D** mechanism and contribution of the outer-sphere complex as in Eq. 18 need not be considered.

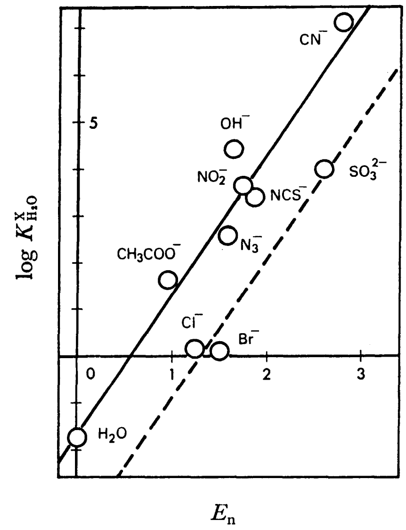

Fig. 5. A plot of log $K^X_{H_2O}$ for Reaction 2 (AA=en) against the electron donor constant E_n of X^{n-}.

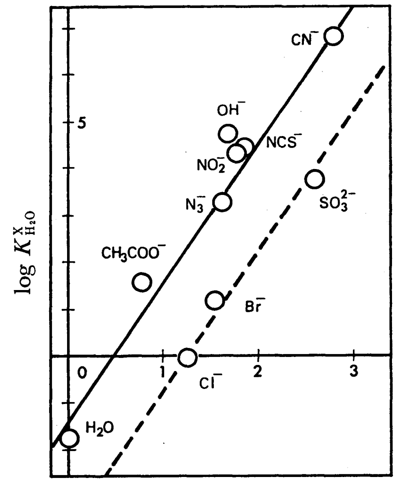

Fig. 6. A plot of log $K^X_{H_2O}$ for Reaction 2 (AA=tn) against the electron donor constant E_n of X^{n-}.

In Figs. 5 and 6 are plotted log $K^X_{H_2O}$ (Eq. 3) against E_n of a nucleophile X^{n-}. For both the en and tn complexes LFER holds and data for the ligands containing O, N, or C as donor atom lie on a straight line in conformity with

$$\log K^X_{H_2O} = \alpha E_n + \gamma. \tag{19}$$

The value of substrate constant α is nearly the same for the en(3.0) and tn(2.9) complexes, indicating the similarity of the two complexes in the electron-donor discrimination. The value of intercept γ is -1.6 for the en complex and -1.4 for the tn complex, both being near to log $K^{H_2O}_{H_2O}$=$-$log $[H_2O]$=-1.74 which is obtained by merely substituting X^{n-} in Eq. 3 with H_2O. Thus Eq. 19 coincides with Eq. 17 under the conditions of $\beta=0$, indicating that the $CoSO_3(AA)_2^+$ moiety is soft enough to render the stability constant of *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$ depend not on the Brønsted basicity but on the electron donating property of X^{n-}. In fact the set of values of α and β for $CoSO_3(AA)_2^+$ (3.0, 0) is comparable with those for Ag^+ (3.60, -0.09), Cu^+ (3.92, 0.18), and CH_3Hg^+ (4.21, 0.11)[27] which are typically soft according to Pearson's classification.[28] Usually Co(III) is hard, but in the present compounds the sulfite ion is soft and makes Co(III) prefer a soft ligand at the sixth coordination site trans to SO_3^{2-}. This may be an example of chemical symbiosis proposed by Jørgensen.[29]

In Figs. 5 and 6 Cl^-, Br^-, and SO_3^{2-} remarkably deviate from the straight line established by the other ligands, and lie on another straight line (dotted) paralleling the former. Such a behavior can not be rationalized at the present stage of investigation. Tanaka[26,30] succeeded in estimating the formation constant of a mixed ligand complex MAL and a 1 : n complex ML_n by introducing additional terms $\sum_i\sum_j\delta_{ij}X_i(A)Y_i(L)$ into Eq. 18 in order to take into account the effect of interaction between donor atoms X_i and Y_j in the coexisting ligand and entering one. In the present case effect of the nitrogen atoms in en and tn on the O, N, or C atom in the entering ligand might be similar, but that on the Cl, Br, or S atom might be much larger in the repulsive sense partly because of the larger size of the latter donor atoms (the atomic radius: N=0.74, C=0.772, O=0.74, S=1.04, Cl=0.99, Br=1.14 Å[31]). A similar situation is also noticed when we correlate the equilibrium constants for the substitution of H_2O

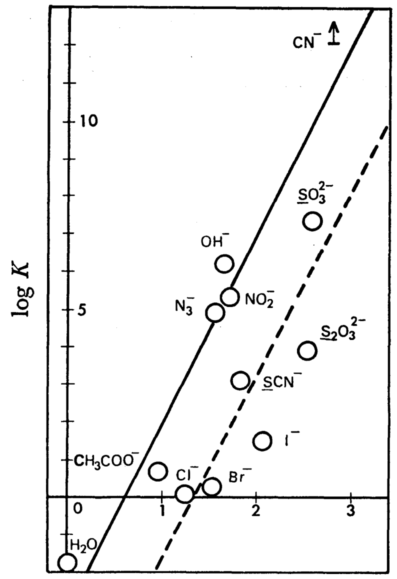

Fig. 7. Relation of the equilibrium constant K for anation of aquacobalamin with the electron donor constant E_n of a nucleophile. Data from Ref. 32 are plotted.

in aquacobalamin which were determined by Pratt and his collaborators[32] with the E_n value of each nucleophile (Fig. 7).

In a previous paper[33] it was reported that the rate of nitrite release from $Co(NO_2)_4(tn)^-$ is 4.5 times and the rate of aqua ligand release from $Co(NO_2)_3(H_2O)(tn)$ is 7.2 times larger than those of the corresponding en complexes. Now Table 4 indicates that the ratio $(k_{-X})_{tn}/(k_{-X})_{en}$ for *trans*-$CoSO_3(X)(AA)_2^{(1-n)+}$ amounts to 10—25 except for the cyano complex. The larger kinetic ring-size effect in the present case may be due to the increase in number of the chelate ring. The enthalpy of activation for the sulfite release from *trans*-$Co(SO_3)_2(en)_2^-$ was reported[9] to be 20.5 ± 0.6 kcal·mol^{-1} and that for the corresponding reaction of *trans*-$Co(SO_3)_2(tn)_2^-$ was now obtained as 16.7 ± 0.4 kcal·mol^{-1}. Holmes and Williams determined the thermodynamic functions of the copper(II) and nickel(II) complexes of en and tn.[34] In either case the en complex is more stable than the tn complex, and the difference in the enthalpy of formation of $M(en)_2(H_2O)_2^{2+}$ and $M(tn)_2(H_2O)_2^{2+}$ amounts to 2.69 kcal·mol^{-1} in the case of the Cu(II) complex and 3.85 kcal·mol^{-1} for Ni(II). A similar amount of excess ground-state stabilization may be offered to *trans*-$Co(SO_3)_2(en)_2^-$ as compared with *trans*-$Co(SO_3)_2(tn)_2^-$ and may be responsible for the excess $\Delta H^{\neq}$ of 3.8 kcal·mol^{-1}. Thus the kinetic ring-size effect seems to stem from the energy difference at the ground state. This is the same conclusion as that drawn in a previous paper.[33]

The cyanide release from *trans*-$CoSO_3(CN)(tn)_2$ is 149 ± 80 times faster than from the corresponding en complex (Table 4). An enormous difference in the aquation rate of the en and tn complexes of the type *trans*-$CoBr_2(AA)_2^+$ and *trans*-$CoCl_2(AA)_2^+$ has previously been reported, $k(tn)/k(en)$ being 680[35] and 1666[36] at 25 °C, respectively. The $k(tn)/k(en)$ for the *trans*→*cis* isomerization of $Co(H_2O)_2(AA)_2^{3+}$ was also recorded as 1450, while the rate ratio for the similar isomerization of $Co(OH)_2(AA)_2^+$ was only 13.[35] Reasonable explanation for these abnormal kinetic ring-size effect is quite difficult.

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