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Trimethylenediamine Complexes. IV.* Kinetics and Mechanism of Acid and Base Hydrolysis of Tetranitro(ethylenediamine)- and Tetranitro(trimethylenediamine)cobaltates(III)

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Hydrolysis of $Co(NO_2)_4(AA)^-$ (AA=en or tn) was studied in acidic and basic aqueous solutions by the spectrophotometric method. In faintly acidic solution ($6>pH>4$) the aquation proceeds reversibly to attain an equilibrium with $Co(NO_2)_3(H_2O)(AA)$, K_{eq} being $(1.71\pm0.03)\times10^{-2}$ and $(3.55\pm0.06)\times10^{-2}$ mol·l^{-1} for AA=en and tn, respectively, at 25.0 °C and $\mu=0.1$. With increasing concentration of hydrogen ion the acid-catalyzed pathway becomes increasingly important. In basic solution ($12.2>pH>9.5$) $Co(NO_2)_3(OH)(AA)^-$ was formed irreversibly as the first product. Kinetic data of these hydrolysis reactions are interpreted in terms of the dissociative mechanism involving a five-coordinate intermediate $Co(NO_2)_3(AA)$. The rates of nitrite release from $Co(NO_2)_4(tn)^-$ ($(9.27\pm0.03)\times10^{-4}$ s^{-1}) and deaquation from $Co(NO_2)_3(H_2O)(tn)$ ($(3.95\pm0.12)\times10^{-4}$ s^{-1}) are several times greater than those for the corresponding ethylenediamine complexes ($(2.08\pm0.01)\times10^{-4}$ and $(5.46\pm0.10)\times10^{-5}$ s^{-1}, respectively.

Although the trans structure of Erdmann's salt $NH_4[Co(NO_2)_4(NH_3)_2]$ was confirmed by X-ray analysis,[1] two geometrical isomers are expected to exist in equilibrium in solution. Kyuno prepared analogous Erdmann-type complexes by replacing the ammine ligands with ethylenediamine and propylenediamine.[2a] The tetranitrodiammine- and tetranitro(ethylenediamine)cobaltates(III) were further used for preparation of dinitrodianionodiammine and related cobalt(III) complexes.[2b] Usually *cis*-dinitrobis(ethylenediamine)cobalt(III) nitrite is prepared by the reaction of hexanitrocobaltate(III) with ethylenediamine,[3] intermediacy of the tetranitro(ethylenediamine)cobaltate(III) complex in the series of reaction being postulated by Kettle.[4] The reaction of sodium hexanitrocobaltate(III) with diamine afforded $[Co(NO_2)_2(AA)_2][Co(NO_2)_4(AA)]$, where AA stands for ethylenediamine or trimethylenediamine.

Tetranitro(diamine)cobaltate(III) anions are interesting complexes in preparative coordination chemistry. Kinetic and equilibrium studies of the nitrite displacement have been performed in order to clarify the reaction mechanism. The effect of ring size in the ethylenediamine and trimethylenediamine chelates on the rates and equilibria has also been investigated. The acid-catalyzed aquation of the tetranitrodiamminecobaltate(III) ion was reported by Malik and McAuley.[5]

Experimental

Preparation of Complexes. *Dinitrobis(diamine)cobalt(III) Tetranitro(diamine)cobaltate(III), $[Co(NO_2)_2(AA)_2][Co(NO_2)_4(AA)]$*: To a cold solution (100 ml) of sodium hexanitrocobaltate(III) (20 g, 49.5 mmol) was added with stirring a 50% aqueous solution of an equimolar amount of ethylenediamine(en) or trimethylenediamine(tn). Orange yellow crystallites separated were washed with water and dried over silica gel in a desiccator. The yield was 20% (*ca.* 6 g). The results of elemental analysis correspond to the composition of $Co_2(NO_2)_6(AA)_3$, suggesting that they are complex salts of the type $[Co(NO_2)_2(AA)_2][Co(NO_2)_4(AA)]$. The ethylenediamine complex was obtained by Kyuno by the reaction of $Co(NO_2)_4(NH_3)_2^-$ with ethylenediamine and identified as a less soluble trans isomer.[2a] Found: C, 12.34; H, 4.56; N, 27.76; Co, 20.58%. Calcd for $Co_2(NO_2)_6(en)_3$: $C_6H_{24}N_{12}O_{12}Co_2$: C, 12.55; H, 4.21; N, 29.27; Co, 20.53%. Found: C, 17.38; H, 5.05; N, 26.53; Co, 19.10%. Calcd for $Co_2(NO_2)_6(tn)_3$: $C_9H_{30}N_{12}O_{12}Co_2$: C, 17.54; H, 4.91; N, 27.28; Co, 19.12%.

Potassium Tetranitro(ethylenediamine)cobaltate(III), $K[Co(NO_2)_4(en)]$ and Potassium Tetranitro(trimethylenediamine)cobaltate(III) Hemihydrate, $K[Co(NO_2)_4(tn)]\cdot1/2H_2O$: These compounds were prepared with a solution of potassium tricarbonatocobaltate(III) as the starting material,[6] and recrystallized twice from methanol–water (1 : 1 by volume). The yields were 40 and 46%, respectively. Found: C, 7.30; H, 2.67; N, 23.41%. Calcd for $K[Co(NO_2)_4(en)]$: $C_2H_8N_6O_8CoK$: C, 7.02; H, 2.36; N, 24.56%. Found: C, 9.95; H, 3.36; N, 22.74%. Calcd for $K[Co(NO_2)_4(tn)]\cdot1/2H_2O$: $C_3H_{11}N_6O_{8.5}CoK$: C, 9.87; H, 3.04; N, 23.01%.

Isolation in Solution of Trinitroaqua(diamine)cobalt(III), $Co(NO_2)_3(H_2O)(AA)$: About 0.3 g of potassium tetranitro(diamine)cobaltate(III) was dissolved in 20 ml of water. To the resulting solution was added 15 ml of 0.04 mol·l^{-1} sodium hydroxide and the mixture was stirred for about 30 min at 40—50 °C (AA=en) or room temperature (AA=tn). The solution was then acidified to pH 2—3 with perchloric acid, and poured into a 20 cm column of 2 cm diameter containing a mixture of equal amounts of a sodium type cation exchange resin (Dowex 50WX8, 50—100 mesh) and a perchlorate type anion exchanger (Dowex 1X8, 50—100 mesh). The column was kept cold with ice water. The trinitro complex, the product of hydrolysis, is electrically neutral, running through the column. The effluent was kept cold with ice–water and protected against light. The solution was subjected to determination of the acid dissociation constant, the cobalt(III) content being determined by the photochemical reduction to cobalt(II) followed by photometric analysis of the latter as a tetraisothiocyanatocobaltate(II) complex.[7] In order to confirm the reproducibility, the isolation and determination of the trinitroaqua(diamine) complexes were repeated three times, respectively.

Measurements. The hydrogen ion activity in solution was determined with a Beckman "Century" SS-1 pH meter with a Beckman 39301 glass electrode and a Beckman 39400 calomel electrode, and converted into the hydrogen ion concentration by virtue of the activity coefficient $f_H=0.83$ at 25 °C and $\mu=0.1$.[8] The method is applicable to solutions in which

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*Part III: H. Kawaguchi and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **46**, 3453 (1973).

10^{-3} mol·l^{-1}>[H$^+$]>10^{-11} mol·l^{-1}, and the hydrogen ion concentration in more acidic solutions was determined by titration. Absorption spectra were recorded on Hitachi EPS-3T and 139 spectrophotometers.

Determination of the Acid Dissociation Constants of the Trinitroaqua(diamine)cobalt(III) Complexes: Buffer solutions were prepared with use of potassium dihydrogen phosphate–sodium hydroxide (pH 5.68—7.16), borax–perchloric acid (pH 7.97—9.28) and borax–sodium hydroxide (pH 9.47—10.29) systems. A given quantity of the effluent solution of the trinitroaqua(diamine)cobalt(III) complex was poured into a measuring flask containing a buffer solution, and the ionic strength was adjusted to $\mu=0.1$ with a solution of sodium perchlorate. Thus solutions with various pH were prepared at 0 °C and the spectra were recorded promptly at 2 °C.

Kinetic Studies: The desired amount of a buffer solution was placed in a dark measuring flask and kept in a thermostat. Solid $K[Co(NO_2)_4(en)]$ (0.040 g) or $K[Co(NO_2)_4(tn)]\cdot 1/2H_2O$ (0.050 g) was poured into the solution by means of thermostated pure water to make up 100 ml of the reaction mixture. The complex was readily dissolved by agitation, and the reaction started. Aliquots were pipetted at appropriate time intervals and subjected to specrtal measurement. Perchloric acid was used for the preparation of acidic solutions. Since hydrolysis was very fast in acidic solutions where [H$^+$]≥0.65 mol·l^{-1}, a Union Giken Stopped-flow, Rapid-Scan Spectrophotometer RA 1300 was used for measuring spectra in the 355—505 nm region.

Results

Acid Dissociation Constants of the Trinitroaqua(diamine)-cobalt(III) Complexes. The spectra of $Co(NO_2)_3(H_2O)(AA)$ complexes in aqueous solution change with pH showing an isosbestic point at 502 nm (AA=en) or 506 nm (AA=tn). The following dissociation equilibria (Eq. 1) are responsible for the spectral behavior, the limiting spectra (Fig. 1) being assigned to aqua and hydroxo complexes.

$$\underset{\mathbf{2}}{Co(NO_2)_3(H_2O)(AA)} \rightleftarrows H^+ + \underset{\mathbf{3}}{Co(NO_2)_3(OH)(AA)^-} \tag{1}$$

The spectra at various hydrogen ion concentrations were analyzed by means of the equation

$$\log\{(A-\varepsilon_3 c_M)/(\varepsilon_2 c_M - A)\} = pK_a + \log[H^+], \tag{2}$$

where c_M is the total concentration of the cobalt(III) complexes, A is the optical density of a solution at a given wave length, and ε_2 and ε_3 denote the molar extinction coefficients at the same wave length of the aqua (**2**) and hydroxo (**3**) complexes, respectively. For the ethylenediamine complexes ε_2 and ε_3 are 328 and 204 l·mol^{-1}·cm^{-1}, respectively, at 410 nm where the separation of spectra is the highest, and $\varepsilon_2=279$ and $\varepsilon_3=146$ l·mol^{-1}·cm^{-1} at 420 nm in the case of the trimethylenediamine complexes.

The plots of $\log\{(A-\varepsilon_3 c_M)/(\varepsilon_2 c_M - A)\}$ against pH gave straight lines with a slope of −1.0 in either case, the pK_a values being 8.40±0.04 and 8.21±0.03 for the ethylenediamine and trimethylenediamine complexes, respectively, at 2 °C and $\mu=0.1$.

Aquation of the Tetranitro(diamine)cobaltate(III) Complexes. In weakly acidic solutions (6>pH>4) the tetranitro complex is hydrolyzed to produce the trinitroaqua complex. The reaction is reversible, the backward anation being effected by addition of excess nitrite ions.

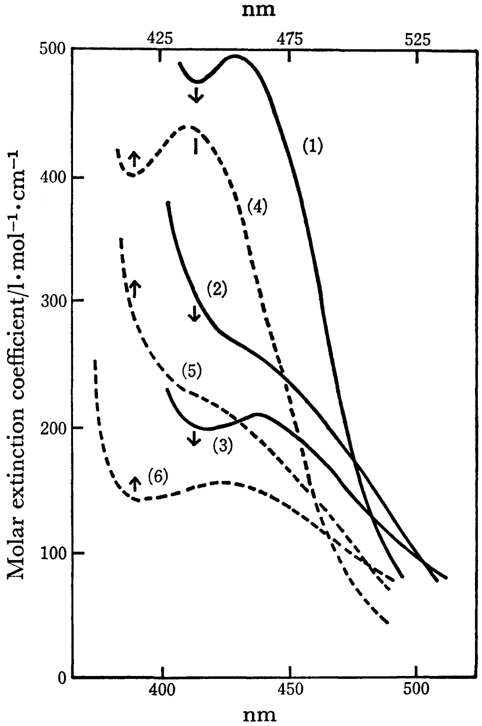

Fig. 1. Absorption spectra in the 400—500 nm region of $Co(NO_2)_4(en)^-$ (1), $Co(NO_2)_3(H_2O)(en)$ (2), $Co(NO_2)_3(OH)(en)^-$ (3), $Co(NO_2)_4(tn)^-$ (4), $Co(NO_2)_3(H_2O)(tn)$ (5), and $Co(NO_2)_3(OH)(tn)^-$ (6) in aqueous solution.

$$\underset{\mathbf{1}}{Co(NO_2)_4(AA)^-} + H_2O \rightleftarrows \underset{\mathbf{2}}{Co(NO_2)_3(H_2O)(AA)} + NO_2^- \tag{3}$$

In the presence of more than ten times excess of sodium nitrite, aquation of the tetranitro complex proceeds as a pseudo first order reaction to attain an equilibrium, revealing an isosbestic point at 480 (AA=en) or 487 nm (AA=tn).

$$-d\ln([Co(NO_2)_4(AA)^-]_t - [Co(NO_2)_4(AA)^-]_{eq})/dt = k_{obsd}$$
$$\ln\{(A_0-A_{eq})/(A_t-A_{eq})\} = k_{obsd}t \tag{4}$$

Subscripts 0, t, and eq refer to the time zero, t, and the equilibrium state, respectively. The reaction was followed by measuring the absorbance A at 430 (AA=en) or 440 nm (AA=tn). The plot $\ln\{(A_0-A_{eq})/(A_t-A_{eq})\}$ *vs.* t gave straight lines over two to three half lives. The values of the pseudo first order rate constant k_{obsd} at various hydrogen and nitrite ion concentrations are summarized in Table 1.

The equilibrium constant of Reaction 3 is related to the nitrite concentration by

$$K = [Co(NO_2)_3(H_2O)(AA)]_{eq}[NO_2^-]_{eq}/[Co(NO_2)_4(AA)^-]_{eq} = [\mathbf{2}]_{eq}[NO_2^-]_{eq}/[\mathbf{1}]_{eq}$$
$$(A_{eq}-A_2)/(A_1-A_{eq}) = [NO_2^-]_{eq}/K, \tag{5}$$

Table 1. Pseudo first order rate constants of aquation of the tetranitro(diamine)cobaltate(III) complexes at 25.0 °C and $\mu=0.1$, c_M being 1.169×10^{-3} and 1.369×10^{-3} mol·l^{-1} for the ethylenediamine and trimethylenediamine complexes, respectively

pH	$10^3\,c_{NO_2}$ / mol·l^{-1}	$10^5\,k_{obsd}$ / s^{-1}
	Ethylenediamine complex	
5.42	11.99	8.19
5.52	12.00	7.33
5.60	19.99	6.65
5.77	39.98	6.39
5.81	40.00	6.21
5.68	59.97	5.88
5.72	59.97	5.85
5.71	79.96	5.95
5.77	79.96	6.01
5.71	99.95	5.88
5.72	100.0	5.46
5.36	20.00	6.55
5.28	20.00	6.53
5.22	20.00	6.81
5.14	20.00	6.99
5.01	20.00	6.59
4.92	20.00	6.74
	Trimethylenediamine complex	
5.52	19.99	63.8
5.62	20.00	65.7
5.62	29.98	58.3
5.72	39.98	56.4
5.88	40.00	54.7
5.68	39.98	52.7
5.76	59.97	51.4
5.81	60.00	52.0
5.92	80.00	47.3
5.92	80.00	51.3
5.82	99.95	51.4
5.73	40.00	55.7
5.59	40.00	57.0
5.49	40.00	56.7
5.38	40.00	56.0
5.02	40.00	58.0
4.72	40.00	56.0

where **2** and **1** denote the trinitroaqua and tetranitro complexes, respectively, and $A_2=\varepsilon_2 c_M$ and $A_1=\varepsilon_1 c_M$. The molar extinction coefficients were determined as $\varepsilon_2=268$ and $\varepsilon_1=483$ l·mol^{-1}·cm^{-1} at 430 nm in the case of AA=en, and $\varepsilon_2=233$ and $\varepsilon_1=432$ l·mol^{-1}·cm^{-1} at 440 nm for AA=tn. Since the pK_a of nitrous acid lies around 2.95(μ=0.25)—3.15(μ=0) at 25 °C[9] and protonation of the nitrite ion is negligible at the present conditions (pH=4.7—6.0), the value of $[NO_2^-]_{eq}$ was calculated by

$$[NO_2^-]_{eq} = c_{NO_2} + c_M(A_1-A_{eq})/(A_1-A_2), \qquad (6)$$

where c_{NO_2} denotes the concentration of nitrite ions added.

As shown in Fig. 2 the plots of the left side term of Eq. 5 against $[NO_2^-]_{eq}$ give straight lines through the origin. From the slope of each straight line the equilibrium constant of aquation of the tetranitro complex (Eq. 3) at 25.0 °C and μ=0.1 was determined to be $(1.71\pm0.03)\times10^{-2}$ and $(3.55\pm0.06)\times10^{-2}$ mol·l^{-1} for AA=en and tn, respectively.

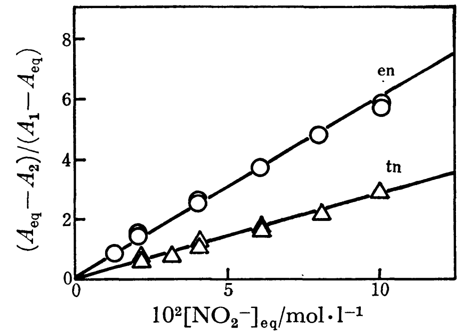

Fig. 2. The linear plot of Eq. 5 in order to determine the equilibrium constant of aquation of $Co(NO_2)_4$(AA)$^-$ at 25.0 °C and μ=0.1. The absorbance was determined at 430 nm (AA=en) or 440 nm (AA=tn).

Acid-Catalyzed Aquation of Tetranitro(diamine)cobaltate(III) Complexes. In more acidic solutions, aquation of the tetranitro(diamine)cobaltate(III) complexes becomes fast with increasing hydrogen ion concentration. In the 2.5>pH>1.0 region, the first-order rate law holds for about two half lives. After this the spectra begin to deviate from the isosbestic point indicating the contribution of the succeeding aquation step. The observed pseudo first order rate constants are plotted against the hydrogen ion concentration in Fig. 3 to afford straight lines in line with Eq. 7.

$$k_{obsd} = k_0 + k_a[H^+] \qquad (7)$$

At 25.0 °C and μ=0.1, $k_0=(2.8\pm0.4)\times10^{-4}$ s^{-1} and $k_a=(2.2\pm0.1)\times10^{-2}$ l·mol^{-1}·s^{-1} for $Co(NO_2)_4$(en)$^-$ and $k_0=(8.6\pm1.0)\times10^{-4}$ s^{-1} and $k_a=(5.5\pm0.2)\times10^{-2}$ l·mol^{-1}·s^{-1} for $Co(NO_2)_4$(tn)$^-$.

In order to gain insight into the acid-catalyzed aquation (the second term in Eq. 7), rapid reactions in more acidic solutions (1.0 mol·l^{-1}>[H$^+$]>0.65 mol·l^{-1})

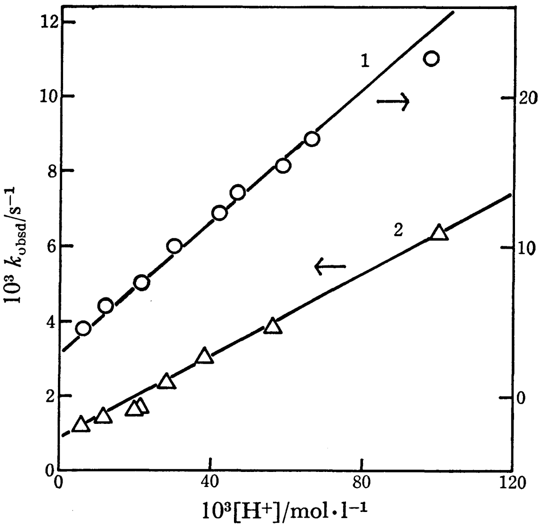

Fig. 3. The pseudo first order rate constants of aquation of $Co(NO_2)_4$(AA)$^-$ at various hydrogen ion concentrations (AA=en (1) and tn (2)).

were examined by following the spectral change in the 355—505 nm region with a rapid-scan spectrophotometer. For either of the ethylenediamine and trimethylenediamine complexes, the isosbestic point was maintained up to 50 s after commencement of the reaction. The pseudo first order rate constant was obtained by the Guggenheim method.[10] The result shows a linear dependence on the hydrogen ion concentration even in these highly acidic solutions, giving $k_a = 1.9\times10^{-2}$ and 3.6×10^{-2} l·mol^{-1}·s^{-1} for AA=en and tn, respectively, at 25.0 °C, $\mu = 2.0$ mol·l^{-1} (NaClO$_4$). These values are less accurate than but close to those obtained in the $2.5 > \text{pH} > 1.0$ region at $\mu = 0.1$.

Base Hydrolysis of the Tetranitro(diamine)cobaltate(III) Complexes. The base hydrolysis reaction of the tetranitro complex proceeds irreversibly to produce the trinitrohydroxo complex.

$$\underset{\mathbf{1}}{\mathrm{Co(NO_2)_4(AA)^-}} + \mathrm{OH^-} \longrightarrow \underset{\mathbf{3}}{\mathrm{Co(NO_2)_3(OH)(AA)^-}} + \mathrm{NO_2^-} \qquad (8)$$

When a buffer solution was employed to maintain a constant hydroxide ion concentration, the reaction followed the first order rate law (Eq. 9) during the course of two half lives.

$$\ln\{(A_0 - A_\infty)/(A_t - A_\infty)\} = k'_{\text{obsd}}t, \qquad (9)$$

where $A_\infty = \varepsilon_3 c_M$, the absorbance being determined at 430 and 440 nm for AA=en and tn, respectively.

Beyond this the plot of the left side term of Eq. 9 against time begins to deviate from the straight line. Concurrently the absorption spectra begin to deviate from the isosbestic point (Fig. 4). The successive base hydrolysis of the trinitrohydroxo complex seems to contribute to the overall kinetics.

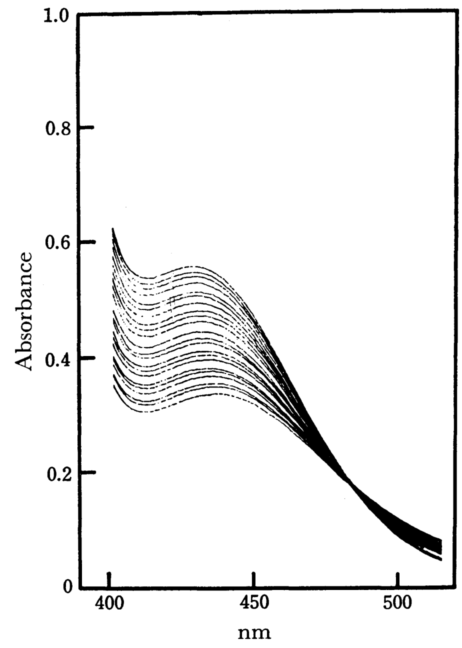

Fig. 4. The spectral change during the initial 100 min (about two half-lives) in the base hydrolysis of Co(NO$_2$)$_4$(en)$^-$ at 25.0 °C, $\mu = 0.1$ and pH=11.94 with $c_M = 1.169$ mmol·l^{-1}.

TABLE 2. PSEUDO FIRST ORDER RATE CONSTANTS OF THE BASE HYDROLYSIS OF THE TETRANITRO(DIAMINE)COBALTATE(III) COMPLEXES AT 25.0 °C AND $\mu = 0.1$, c_M BEING 1.169×10^{-3} AND 1.369×10^{-3} mol·l^{-1} FOR THE ETHYLENEDIAMINE AND TRIMETHYLENEDIAMINE COMPLEXES, RESPECTIVELY

pH	$\frac{10^3\, c_{NO_2}}{\text{mol·l}^{-1}}$	$\frac{10^4\, k'_{\text{obsd}}}{\text{s}^{-1}}$	Buffer solution
	Ethylenediamine complex		
9.76	0	2.03	Borax–NaOH
10.00	0	2.03	
10.65	0	2.06	
11.34	0	2.05	Na$_2$HPO$_4$–NaOH
11.80	0	2.04	
11.94	0	2.07	
10.67	20.00	2.11	Borax–NaOH
10.64	28.00	2.19	
10.67	40.00	2.10	
10.66	50.00	2.07	
	Trimethylenediamine complex		
9.55	0	9.37	Borax–NaOH
9.76	0	9.48	
9.98	9.985	9.19	
10.03	20.00	9.25	
10.03	30.00	8.98	
10.04	0	9.37	
10.08	40.01	8.98	
10.38	0	9.37	
11.32	0	9.40	Na$_2$HPO$_4$–NaOH
11.39	0	9.17	Borax–NaOH
11.79	0	9.14	Na$_2$HPO$_4$–NaOH
11.94	0	9.29	
12.23	20.00	9.48	NaOH

TABLE 3. PSEUDO FIRST ORDER RATE CONSTANTS OF THE BASE HYDROLYSIS OF THE TETRANITRO(DIAMINE)COBALTATE(III) COMPLEXES AT SEVERAL TEMPERATURE AT 25.0 °C, $\mu = 0.1$, pH=9.77 (BORAX–NaOH), $c_{NO_2} = 0$, $c_M = 1.181\times10^{-3}$ (en) AND 1.369×10^{-3} (tn) mol·l^{-1}

$\frac{\text{Temp}}{\text{°C}}$	$\frac{10^4\, k'_{\text{obsd}}}{\text{s}^{-1}}$	$\frac{\Delta H^{\ddagger}}{\text{kcal·mol}^{-1}}$	$\frac{\Delta S^{\ddagger}}{\text{cal·deg}^{-1}\text{·mol}^{-1}}$
	Ethylenediamine complex		
19.8	0.875±0.022	27.2±0.7	15.9±2.0
25.0	2.08 ±0.01		
30.1	4.41 ±0.04		
35.2	9.52 ±0.16		
	Trimethylenediamine complex		
15.1	1.97 ±0.04	26.0±0.4	14.9±1.2
20.1	4.45 ±0.05		
25.0	9.27 ±0.03		
30.1	18.0 ±0.08		

The pseudo first order rate constants k'_{obsd} of Reaction 8 at 25.0 °C and other temperatures are given in Tables 2 and 3, respectively. The Eyring plots of these data give the following activation parameters: $\Delta H^{\ddagger} = 27.2\pm0.7$ (en) and 26.0 ± 0.4 (tn) kcal·mol^{-1}, and $\Delta S^{\ddagger} = 15.9\pm2.0$ (en) and 14.9 ± 1.2 (tn) cal·deg^{-1}·mol^{-1}.

Discussion

Although the nitrite ion can coordinate to a metal ion as a unidentate ligand through either the nitrogen or oxygen atom, the N-bonded nitro isomer is usually more stable than the O-bonded nitrito isomer.[11] The *trans*-$Co(NO_2)_4(NH_3)_2^-$ salts[1,12] and $K[Co(NO_2)_4(en)]$[13] were confirmed by X-ray analysis to be nitro complexes. $K[Co(NO_2)_4tn]\cdot 1/2H_2O$ may also be presumed to contain the Co–N bonding.

Two geometrical isomers, facial and meridional, are conceivable for the hydrolysis products $Co(NO_2)_3(H_2O)(AA)$ and $Co(NO_2)_3(OH)(AA)^-$. Distinct isosbestic points were observed in the spectral change during the course of acid and base hydrolysis reactions of $Co(NO_2)_4(AA)^-$. The spectra of $Co(NO_2)_3(H_2O)(AA)$ at various pH's also manifest isosbestic points. The results can be satisfactorily understood on the assumption that only one of the geometrical structures is realized by both of the trinitro complexes. However, no isolation and characterization of the trinitro complexes as solid specimen have been achieved, the stereochemistry of hydrolysis reactions of the tetranitro complexes remaining unclarified.

Mechanism of the Hydrolysis Reactions. The kinetic data of the acid and base hydrolysis of $Co(NO_2)_4(AA)^-$ are satisfactorily explained on the basis of the dissociative (**D**) mechanism including the pentacoordinate intermediate, $Co(NO_2)_3(AA)$.

$$Co(NO_2)_4(AA)^- \underset{k_{NO_2}}{\overset{k_{-NO_2}}{\rightleftharpoons}} Co(NO_2)_3(AA) + NO_2^- \qquad (10)$$

$$Co(NO_2)_3(AA) + H_2O \underset{k_{-H_2O}}{\overset{k_{H_2O}}{\rightleftharpoons}} Co(NO_2)_3(H_2O)(AA) \qquad (11)$$

$$+H^+ \upharpoonleft\downharpoonright -H^+ \ \text{(fast)}$$

$$Co(NO_2)_3(AA) + OH^- \xrightarrow{k_{OH}} Co(NO_2)_3(OH)(AA)^- \qquad (12)$$

In basic solution the reaction proceeds irreversibly to afford the hydroxotrinitro complex, and the reverse anation reaction need not be considered. If we assume a steady state for the pentacoordinate intermediate, the pseudo first order rate constant is given by

$$k'_{obsd} = k_{-NO_2}(k_{H_2O}+k_{OH}[OH^-])/$$
$$(k_{NO_2}[NO_2^-]+k_{H_2O}+k_{OH}[OH^-]). \qquad (13)$$

The observed pseudo first order rate constant is independent of pH in the 9.5—12.2 region and also of the added nitrite concentration (Table 2). The calculated k'_{obsd} in Eq. 13 can be reconciled with the experimental results only when

$$k_{OH}[OH^-] \gg k_{NO_2}[NO_2^-] + k_{H_2O}, \qquad (14)$$

resulting in

$$k'_{obsd} = k_{NO_2}. \qquad (15)$$

Thus the spontaneous dissociation of a nitrite ligand is the rate determining step in the base hydrolysis of $Co(NO_2)_4(AA)^-$.

The base hydrolysis of octahedral metal complexes usually follows the S_N1CB or $\mathbf{D}_{cb}$ mechanism (dissociative mechanism with respect to the conjugate base).[14] If this is the case for $Co(NO_2)_4(AA)^-$, pK_a of the complex should be much smaller than 10 in order for the deprotonation equilibrium (Eq. 16) to be completely shifted to the right rendering the rate of hydrolysis independent of pH.

$$Co(NO_2)_4(AA)^- + OH^- \rightleftharpoons$$
$$Co(NO_2)_4(AA-H)^{2-} + H_2O \qquad (16)$$

Such a high acidity seems unreasonable for the negative diamine complexes even if the electron attracting property of the nitro ligands is taken into account, since pK_a of $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$ is estimated to be larger than 14.[15] Furthermore, if the conjugate base were the predominant species in basic solution of $Co(NO_2)_4(AA)^-$, the spectrum should differ significantly from that in acidic solution. No change with pH was observed in spectra of the tetranitro complexes at 2 °C, denying the appreciable deprotonation of $Co(NO_2)_4(AA)^-$ in basic solution. Thus $\mathbf{D}_{cb}$ mechanism is not operative and **D** mechanism (Eq. 10—12) seems to be favorable for the base hydrolysis of $Co(NO_2)_4(AA)^-$.

In weakly acidic solution (6>pH>4) the pseudo first order rate constant of hydrolysis k_{obsd} is smaller than that in basic solution, being independent of pH in this region (Table 1). Since the hydroxide ion concentration is very low in this case ($<10^{-8}$ mol·l^{-1}), path 12 can be neglected to derive the rate equation

$$-d\ln([Co(NO_2)_4(AA)^-]_t - [Co(NO_2)_4(AA)^-]_{eq}) = k_{obsd}$$
$$= (k_{-NO_2}k_{H_2O}+k_{NO_2}k_{-H_2O}[NO_2^-])/(k_{H_2O}+k_{NO_2}[NO_2^-]), \qquad (17)$$

which is transformed into

$$\frac{1}{k_{-NO_2}-k_{obsd}} = \frac{1}{k_{-NO_2}-k_{-H_2O}} + \frac{(k_{H_2O}/k_{NO_2})}{k_{-NO_2}-k_{-H_2O}}\cdot\frac{1}{[NO_2^-]}. \qquad (18)$$

Since k_{-NO_2} is obtained by measurements in basic solutions (Eq. 15), the left side term in Eq. 18 can be calculated for various nitrite concentrations. As is seen in Fig. 5, the plot of $(k_{-NO_2}-k_{obsd})^{-1}$ *vs.* $[NO_2^-]^{-1}$ gives rise to a straight line, the intercept and slope of which afford k_{-H_2O} and k_{H_2O}/k_{NO_2}, thus enabling calculation of the equilibrium constant of aquation (3).

$$K = k_{-NO_2}k_{H_2O}/k_{NO_2}k_{-H_2O} \qquad (19)$$

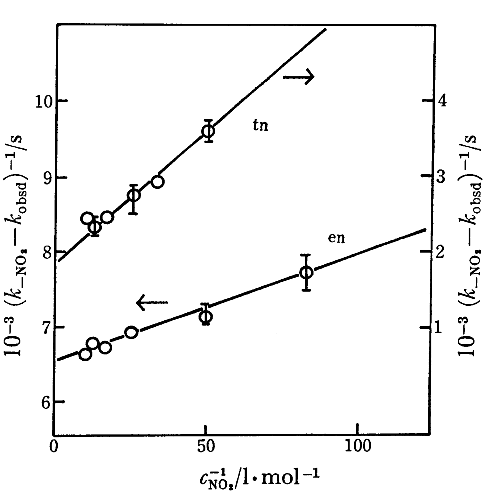

Fig. 5. Linear plots (Eq. 18) of rate data for the aquation of $Co(NO_2)_4(AA)^-$ at 25.0 °C and μ=0.1.

Table 4. Rate and equilibrium data at 25.0 °C and μ=0.1 of the hydrolysis of $Co(NO_2)_4(AA)^-$

AA	en	tn
k_{-NO_2}/s^{-1}	$(2.08\pm0.01)\times10^{-4}$	$(9.27\pm0.03)\times10^{-4}$
k_{OH}/k_{NO_2}	$\gg5\times10^3$	$\gg5\times10^3$
k_{-H_2O}/s^{-1}	$(5.46\pm0.10)\times10^{-5}$	$(3.95\pm0.12)\times10^{-4}$
$\dfrac{k_{H_2O}/k_{NO_2}}{mol\cdot l^{-1}}$	$(2.15\pm0.14)\times10^{-3}$	$(1.79\pm0.13)\times10^{-2}$
$K_{kin}/mol\cdot l^{-1}$ a)	$(8.19\pm0.72)\times10^{-3}$	$(4.20\pm0.45)\times10^{-2}$
$K_{eq}/mol\cdot l^{-1}$ b)	$(1.71\pm0.03)\times10^{-2}$	$(3.55\pm0.06)\times10^{-2}$

a) Calculated by Eq. 19. b) Calculated by Eq. 5.

The spontaneous aquation and anation reactions of cationic cobalt(III) complexes usually follow the dissociative interchange (**I**$_d$) mechanism.[14] However, several anionic cobalt(III) complexes such as $Co(SO_3)_2(en)_2^-$ and $Co(CN)_5(H_2O)^{2-}$ are known to follow the **D** mechanism,[16] $Co(NO_2)_4(AA)^-$ becoming a new example. The rate and equilibrium constants are summarized in Table 4. The values of equilibrium constants calculated by Eq. 19 nearly coincide with those determined directly (Eq. 5). From these data the relative nucleophilicity of H_2O, NO_2^-, and OH^- toward the pentacoordinate intermediate $Co(NO_2)_3(AA)$ is calculated as the ratio $k_{H_2O}/[H_2O]:k_{NO_2}:k_{OH}$, and found to be $1:2.6\times10^4:\gg1.3\times10^8$ for AA=en, and $1:3.1\times10^3:\gg1.6\times10^7$ for AA=tn. The nucleophilicity order coincides with the basicity order of these reagents, reflecting the hard character of $Co(NO_2)_3(AA)$.

With increasing hydrogen ion concentration the acid-catalyzed aquation of $Co(NO_2)_4(AA)^-$ becomes increasingly important, which may proceed *via* the following two steps.

$$Co(NO_2)_4(AA)^- + H^+ \overset{K_H}{\rightleftarrows} Co(NO_2)_3(HNO_2)(AA) \qquad (20)$$

$$Co(NO_2)_3(HNO_2)(AA) \xrightarrow{k_{-HNO_2}} Co(NO_2)_3(AA) + HNO_2 \qquad (21)$$

In acidic solutions where pH<2, free nitrite ions are mostly protonated and the reverse step of Eq. 10 can be neglected, giving the rate law

$$k_{obsd} = (k_{-NO_2}+k_{-HNO_2}K_H[H^+])/(1+K_H[H^+]). \qquad (22)$$

In the acidity region examined the simple two term rate law (Eq. 7) holds, indicating that $K_H[H^+]\ll1$, giving rise to

$$k_0 = k_{-NO_2} \text{ and } k_a = k_{-HNO_2}K_H. \qquad (23)$$

The values of k_0 obtained from the intercepts of straight lines in Fig. 3 nearly coincide with those of k_{-NO_2} given in Table 4. Thus the doubly protonated species $Co(NO_2)_2(HNO_2)_2(AA)$ need not be considered. The value of k_{-HNO_2} can not be obtained independently of K_H, but seems to be much greater than 10^{-2} s^{-1}.

The acid-catalyzed aquation of nitrocobalt(III) complexes has been investigated,[17] the pseudo first order rate constant of aquation of *trans*-$Co(NO_2)_2(tn)_2^+$ in a 1.09 mol·l^{-1} sulfuric acid solution at 25.0 °C having been reported[18] to be 6.9×10^{-5} s^{-1}. As compared with this the present k_{-HNO_2} value is astonishingly larger. A similar situation is noticed in the rate of spontaneous aquation. Staples[19] stated that no aquation of *cis*- and *trans*-$Co(NO_2)_2(en)_2^+$ occurs in neutral or faintly acidic solutions. On the contrary, $Co(NO_2)_4(en)^-$ is hydrolyzed spontaneously at a fairly fast rate of $(2.08\pm0.01)\times10^{-4}$ s^{-1} at 25.0 °C, indicating that the Co–NO$_2$ bond in the tetranitro(diamine) complexes is remarkably weaker than that in the dinitrobis(diamine) complexes. Similar results were also obtained for $Co(NO_2)_4(NH_3)_2^-$, k_0 being reported[5] to be 1.7×10^{-4} s^{-1} at 25 °C and μ=2.5 mol·l^{-1}.

As to the mechanism of the acid-catalyzed aquation of $CoNO_2(NH_3)_5^{2+}$ in sulfuric acid, Harris *et al.*[20] postulated from the results of ^{18}O tracer experiments that the proton-assisted nitrosonium ion release occurred, leaving $CoOH(NH_3)_5^{2+}$ which maintains one oxygen atom of the nitrite ligand. A similar N–O bond fission mechanism is also suggested for the acid-catalyzed replacement of nitro-ligand from some dinitrodiamine platinum(II) complexes.[21] It is not certain whether an analogous mechanism is operative or a simple release of nitrous acid occurs in the acid-catalyzed aquation of $Co(NO_2)_4(AA)^-$.

Kinetic Chelate Ring Size Effect. The ligand substitution rates of trimethylenediamine complexes have been compared in several instances with those of the corresponding ethylenediamine complexes. Although *trans*-$CoCl_2(tn)_2^+$ and *trans*-$CoBr_2(tn)_2^+$ aquate 1500 times and 680 times as fast as the corresponding en complexes, respectively,[22] the acid-catalyzed aquation of *trans*-$Co(NO_2)_2(tn)_2^+$ is only a few times faster than that of *trans*-$Co(NO_2)_2(en)_2$.$^+$[18,23] The aquation rate of $CoCO_3(tn)_2^+$ is similar to that of $CoCO_3(en)_2$,$^+$ [24] while the rate of carbonate exchange of the tn complex is smaller than that of the en complex.[25] In the present case the rate of nitrite release from $Co(NO_2)_4(tn)^-$ is 4.5 times and the rate of aqua ligand release from $Co(NO_2)_3(H_2O)(tn)$ 7.2 times larger than those of the corresponding en complexes (Table 4).

Trimethylenediamine forms a six-membered chelate ring whose conformation is usually of chair form in crystals.[26] In solution, however, the energy difference between chair and skew-boat conformers is small,[27] and 30% of Δ-$Co(tn)_3^{3+}$ and *ca.* 9% of $Ni(tn)(H_2O)_4^{2+}$ are in the skew-boat form in aqueous solutions at 20 and 27 °C, respectively.[28,29] Couldwell and House[30] presumed that the tn rings of *trans*-$CoCl_2(tn)_2^+$ can adopt the skew-boat configuration and steric interaction between the central methylene protons and the chloro ligands may be responsible for the exceptionally rapid aquation.

Holmes and Williams determined the thermodynamic functions of the copper(II) and nickel(II) complexes of en and tn.[31] The difference in the enthalpy of formation of $M(en)(H_2O)_4^{2+}$ and $M(tn)(H_2O)_4^{2+}$ amounts to 1.43 ± 0.18 kcal·mol^{-1} for Cu(II) and 2.01 ± 0.14 kcal·mol^{-1} for Ni(II). It appears that if the enthalpies of free en and tn are similar to each other, the five-membered en ring has stronger bonds than the six-membered tn ring by 13 and 28% for the Cu(II) and Ni(II) complexes, respectively. The enthalpy of activation for the nitrite release from $Co(NO_2)_4(tn)^-$ is smaller by 1.2 kcal·mol^{-1} than that for $Co(NO_2)_4(en)^-$

(Table 3). The difference seems to stem from the energy difference at the ground state, and both complexes may have similar enthalpies at the transition state where the steric strain is released by dissociation of one nitrite ligand. The positive entropy of activation is also in line with the proposed **D** mechanism.

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