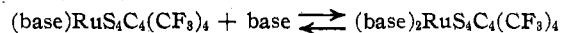


Figure 2.—Electronic spectra of  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  in dichloromethane solution in the presence of  $(\text{C}_6\text{H}_5)_3\text{As}$ . Concentration of  $((\text{C}_6\text{H}_5)_3\text{As})_2\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  is  $7.52 \times 10^{-6} F$  throughout. Concentrations of  $(\text{C}_6\text{H}_5)_3\text{As}$ :  $\cdots$ , no excess added;  $\cdots\cdots$ ,  $5.18 \times 10^{-4} M$ ;  $-\cdot-\cdot-$ ,  $2.64 \times 10^{-3} M$ ;  $—$ ,  $\geq 1.00 \times 10^{-1} M$ .

rium constants for the reaction



These equilibrium constants decrease, as is generally the case with group V donors, down the following series:  $(\text{C}_6\text{H}_5)_3\text{P}$  ( $K = 153 \pm 7 \text{ l. mol}^{-1}$ )  $>$   $(\text{C}_6\text{H}_5)_3\text{As}$  ( $K = 68 \pm 3$ )  $>$   $(\text{C}_6\text{H}_5)_3\text{Sb}$  ( $K = 9 \pm 2$ ).

The great similarity in chemical and physical properties between  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$  and  $(\text{base})\text{FeS}_4\text{C}_4(\text{CF}_3)_4$  suggests that they have very similar structures. X-Ray crystallographic study of  $(\text{C}_6\text{H}_5)_3\text{AsFeS}_4\text{C}_4(\text{CF}_3)_4$  reveals that it is a square pyramid with triphenylarsine in the axial position;<sup>18</sup> a similar geometry is proposed for  $(\text{base})\text{RuS}_4\text{C}_4(\text{CF}_3)_4$ . The bisadducts probably have a pseudooctahedral structure with the bases in trans positions; a five-coordinate structure with a nonchelating dithiolene appears most unlikely.

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(18) E. F. Epstein and I. Bernal, *Inorg. Chem.*, in press.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WESTERN ILLINOIS UNIVERSITY, MACOMB, ILLINOIS 61455, AND NORTH CAROLINA STATE UNIVERSITY, RALEIGH, NORTH CAROLINA 26707

## Kinetics of the Acid and Base Hydrolysis of Di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) Cation<sup>1</sup>

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The acid hydrolysis of di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) cation (hereafter called dimer) was studied using spectrophotometry and the base hydrolysis of this same complex was investigated using a pH-Stat method. The data were found to be well fitted by the assumption of two successive first-order reactions. The apparent first-order rate constants for the acid hydrolysis show a complex dependence on hydrogen ion concentration of the following form:  $k_1(\text{apparent}) = (C_{10} + C_{11}(\text{H}^+))/(1 + K_1(\text{H}^+))$  and  $k_2(\text{apparent}) = (C_{21}(\text{H}^+) + C_{22}(\text{H}^+)^2)/(1 + K_2(\text{H}^+))$ . For the base hydrolysis, the apparent rate constant for the first step as a function of pH was satisfactorily fitted by the equation  $k_3(\text{apparent}) = (C_{30} + C_{31}(\text{OH}^-))/(1 + K_3(\text{OH}^-))$ , while the value of  $k_4$  showed but slight change with pH. A mechanism is proposed in which a singly bridged species acts as an intermediate in the course of the reaction. The acid hydrolysis was studied at nine wavelengths, six hydrogen ion concentrations, and two temperatures, *viz.*,  $25.00 \pm 0.02$  and  $35.00 \pm 0.05^\circ$ , while the base hydrolysis was studied at  $25.00 \pm 0.01^\circ$  and over the pH range 9.3–10.4. At  $25.00^\circ$  and  $0.1127 F \text{ HClO}_4$  ( $\mu = 1.0 M$ ,  $\text{NaClO}_4$ ) the rate constants for the acid hydrolysis are  $k_1(\text{apparent}) = (11.82 \pm 0.08) \times 10^{-4} \text{ sec}^{-1}$  and  $k_2(\text{apparent}) = (3.76 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$ . For the base hydrolysis at  $25.00^\circ$  and  $2.43 \times 10^{-4} F \text{ NaOH}$  ( $\mu = 1.0 M$ ,  $\text{NaNO}_3$ ) the values for the rate constants are  $k_3 = (3.53 \pm 0.08) \times 10^{-3} \text{ sec}^{-1}$  and  $k_4 = (0.373 \pm 0.01) \times 10^{-4} \text{ sec}^{-1}$ . Values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the various kinetic parameters in the acid hydrolysis are reported.

### Introduction

The doubly bridged cobalt(III) dimeric species  $\text{Co}_2(\text{en})_4(\text{OH})_2^{4+}$  decomposes in acid solutions to give the diaquo ion  $\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+}$  and in basic solutions to give the dihydroxo ion  $\text{Co}(\text{en})_2(\text{OH})_2^+$ .

Rasmussen and Bjerrum<sup>2</sup> studied these reactions spectrophotometrically. They indicated that the accuracy in the case of the basic hydrolysis is rather low due to the similarity of the visible and near-ultraviolet spectra of the dimer to those of the dihydroxo ion. No final results nor detailed study of the basic hydrolysis was given by them.

Although a detailed study and a mechanism were

given for the acid hydrolysis, it was observed that a representative run given in ref 2 has the first experimental point taken after 1 hr from the time of mixing the reactants. It was also observed that their experiments were done at only three wavelengths, *viz.*, 560, 540, 520 nm, all in the visible region. This indicated that a repetition of the study of Rasmussen and Bjerrum was desirable.

### Experimental Section

**Materials.**—All chemical reagents used were analytical reagent grade. The water was first deionized by passing it through a mixed-bed cation-anion-exchange resin and then distilled from very dilute potassium permanganate-sodium hydroxide solution. Sodium hydroxide stock solutions were prepared from carbonate-free concentrated NaOH.<sup>3</sup> Sodium perchlorate was pre-

(1) Based on the Ph.D. thesis of A. A. El-Awady, University of Minnesota, Minneapolis, Minn. 55455.

(2) S. E. Rasmussen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 735 (1955).

(3) I. M. Kolthoff and E. B. Sandell, "Text Book of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1952.

pared by neutralization of reagent grade 70% perchloric acid with reagent grade sodium carbonate and recrystallized three times from hot distilled water.

**Preparation of Complexes.**—With minor modifications the complex salts used were prepared according to methods described in the literature. *cis*-Diaquobis(ethylenediamine)cobalt(III) perchlorate was prepared from the carbonate salt according to the method described by Linhard and Stirn.<sup>4</sup> *Anal.* Calcd for  $[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_3$ : Co 11.48. Found: Co, 11.52.

Di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) nitrate was prepared from the corresponding bromide,<sup>5-7</sup> which in turn was prepared from the dithionate salt. The dithionate salt was prepared by heating *cis*-hydroxo-aquobis(ethylenediamine)cobalt(III) dithionate<sup>8,9</sup> in an electric oven at 110° until constant weight was obtained. *Anal.* Calcd for  $[(\text{en})_4\text{Co}_2(\text{OH})_2](\text{NO}_3)_4 \cdot 0.5\text{H}_2\text{O}$ : Co, 18.16. Found: Co, 18.14.

Di- $\mu$ -hydroxo-tetrakis(ethylenediamine)dnicobalt(III) perchlorate was prepared from the corresponding bromide by dissolving in water and precipitating the perchlorate salt with excess  $\text{NaClO}_4$ . A solution of the perchlorate salt gave no precipitate with  $\text{AgNO}_3$ , indicating the absence of bromide ions. *Anal.* Calcd for  $[(\text{en})_4\text{Co}_2(\text{OH})_2](\text{ClO}_4)_4$ : Co, 14.92;  $\text{ClO}_4$ , 50.35. Found: Co, 14.89;  $\text{ClO}_4$ , 49.98.

**Kinetic Runs.**—The kinetic runs for the acid hydrolysis were followed spectrophotometrically by recording the change in absorbance at fixed wavelength as a function of time. To begin a run, a weighed sample of the perchlorate salt was added to a volumetric flask containing an  $\text{NaClO}_4$ - $\text{HClO}_4$  solution at the temperature of the run. The solution was diluted to the mark and mixed thoroughly, and a sample was transferred to a cell contained in the thermostated cell compartment of the Cary Model 14 spectrophotometer. Measurements were made at some or all of nine wavelengths and six different hydrogen ion concentrations at each of two temperatures. The wavelengths used were 275, 290, 350, 365, 380, 400, 520, 540, and 560 nm. The two temperatures used were  $25.00 \pm 0.02$  and  $35.00 \pm 0.05^\circ$ .

The kinetic data for the base hydrolysis were obtained using the pH-Stat method.<sup>10,11</sup> This method is primarily suitable for recording as a function of time the volume of base required to keep a sample at a constant pH. Thus, complete reaction rate curves were obtained by maintaining the pH fixed at a pre-selected value, with continuous correction for the base used up during the reaction. A recorded plot, then, of milliequivalents (or volume) of base *vs.* time provides a reaction rate curve.

The experimental data were obtained using a Radiometer recording pH-Stat obtained from Radiometer, Copenhagen NV, Denmark.

The chart paper scale of the syringe recorder was calibrated by titration of the standard sodium hydroxide stock solution, used in all experiments, with a standard solution of potassium hydrogen phthalate. Experimentally the solutions for the kinetic runs were prepared by adding a known weight of the dimer nitrate to an  $\text{NaNO}_3$  solution in a volumetric flask maintained at  $25.00 \pm 0.01^\circ$ . The mixture was then diluted to the mark and mixed thoroughly. Thirty milliliters of this solution was then transferred to the thermostated reaction vessel. The pH-Stat was set to the desired pH, and the volume of standard sodium hydroxide required to keep the pH at the set value was traced by the recorder. No corrections for the volume of the added  $\text{NaOH}$  solution were needed since these volumes did not exceed 1.0 ml in any of the experiments performed. The final pH of the solution was determined by measuring the pH of the solution immediately after the reaction was over using a Radiometer pH meter, Model 4.

## Results

**Acid Hydrolysis.**—The visible and ultraviolet spectra of the dimer as well as those of *cis*-( $\text{en}$ )<sub>2</sub>Co(OH)<sub>2</sub><sup>3+</sup> are

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

(5) A. Werner and J. Rapiport, *Justus Liebigs Ann. Chem.*, **375**, 84 (1910).

(6) J. Dubsky, *J. Prakt. Chem.*, [2] **90**, 70, 85-89 (1914).

(7) R. J. Meyer, Ed., "Gmelin's Handbuch der anorganischen Chemie," Vol. 58, Part B, 1930, pp 346-347.

(8) J. Dubsky, *J. Prakt. Chem.*, [2] **90**, 84 (1914).

(9) A. Werner, *Ber.*, **40**, 284 (1907).

(10) C. F. Jacobsen and J. Leonis, "Methods of Biochemical Analysis," Vol. IV, Interscience, New York, N. Y., 1957, pp 171-210.

(11) H. V. Malmstadt and E. H. Piepmeier, *Anal. Chem.*, **37**, 34 (1965).

reported in several places.<sup>12-14</sup> The spectra of these two compounds differ widely in the visible and ultraviolet regions with two isosbestic points at  $443 \pm 2$  and  $464 \pm 2$  nm with molar absorptivity indices of  $62.0 \pm 1$  and  $46.5 \pm 0.5 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. Figures 1 and 2 display the spectral changes during a typical hydrolysis run.

An overall look at the spectra given in Figures 1 and 2 shows two major points of interest, namely, the region

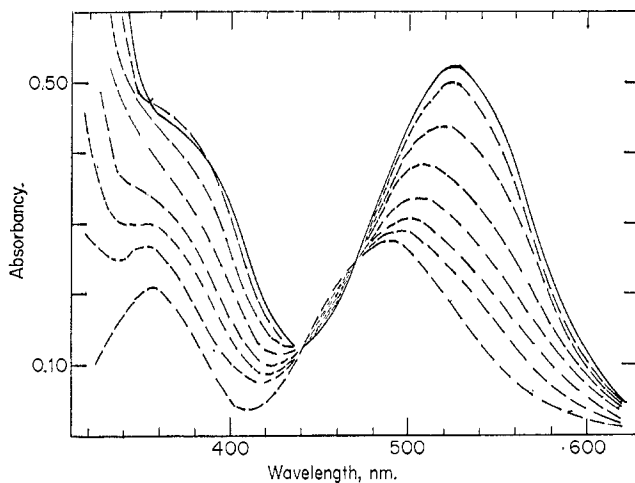


Figure 1.—Change in absorption spectrum of the dimer ( $C_0 = 0.355 \text{ mF}$ ) in  $0.0305 \text{ F HClO}_4$  ( $\mu = 1.00 \text{ M}$ ,  $\text{NaClO}_4$ ) with time at  $25.00^\circ$ ; reading downward at 520 nm, reaction times are 7, 40, 126, 215, 304, 398, and 518 min and 1 week later.

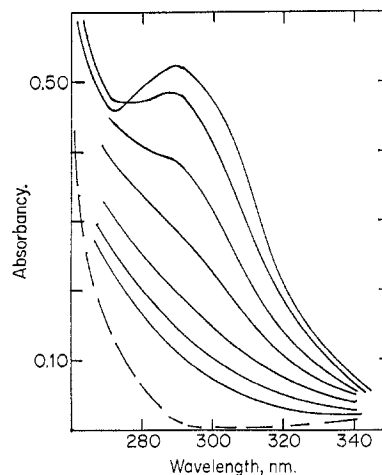


Figure 2.—Change in absorption spectrum of the dimer ( $C_0 = 0.36 \text{ mF}$ ) in  $0.030 \text{ F HClO}_4$  ( $\mu = 1.00 \text{ M}$ ,  $\text{NaClO}_4$ ) with time at  $25.00^\circ$ ; reading downward at 300 nm, reaction times are 12, 46, 133, 221, 309, 402, and 423 min and 1 week later.

between 360 and 380 nm and that in the vicinity of 270 nm. If the conversion of the dimer to the diaquo species was a one-step process or if no appreciable concentration of an intermediate was formed in a more complicated scheme, a monotonic change of optical density from that of the dimer to that of the diaquo species would have been observed in all regions of the spectrum. This, however, is not the state of affairs, and a noticeable increase in optical density is observed

(12) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

(13) F. Basolo, *J. Amer. Chem. Soc.*, **72**, 4393 (1950).

(14) Y. Inamura and Y. Kondo, *Nippon Kagaku Zasshi*, **74**, 627 (1953); *Chem. Abstr.*, **48**, 2476 (1954).

at 270 nm and between 360 and 380 nm in the early stages of reaction. This feature indicates that at least one intermediate is formed in appreciable concentration in the course of the reaction.

The maximum number of species that could be present in the reaction mixture was determined using a statistical method<sup>15,16</sup> which utilizes the Beer-Lambert law for a multicomponent system. The results of such an analysis indicated that a maximum of three species occurs in all cases.

**Treatment of Data.**—The data for the acid hydrolysis were found to be well fitted by an empirical equation of the form

$$D_t - D_\infty = Ae^{-k_1t} + Be^{-k_2t} \quad (1)$$

where  $D_t$  is the absorbance of the reaction mixture at time  $t$ ,  $D_\infty$  is the absorbance at infinite time,  $A$  and  $B$  are two constants, and  $k_1$  and  $k_2$  are rate constants.

Equation 1 suggests that the reaction occurs by two successive first-order steps of the form



where R, I, and P represent the dimer, an intermediate, and the diaquo product, respectively. The concentration of each of these species given as functions of the initial concentration of the dimer  $[R_0]$  and time  $t$  are given by

$$[R] = [R_0]e^{-k_1t} \quad (3)$$

$$[I] = ([R_0]k_1/(k_2 - k_1))(e^{-k_1t} - e^{-k_2t}) \quad (4)$$

$$[P] = [R_0] \left\{ 1 + \frac{1}{k_1 - k_2} (k_2e^{-k_1t} - k_1e^{-k_2t}) \right\} \quad (5)$$

In a solution having an optical path length of 1 cm, the absorbance at any time is given by

$$D = \epsilon_R[R] + \epsilon_I[I] + \epsilon_P[P] \quad (6)$$

where  $\epsilon_R$ ,  $\epsilon_I$ , and  $\epsilon_P$  are the molar absorbances of R, I,

and P, respectively. Initial values of  $k_1$  and  $k_2$  were obtained graphically by this method, and these were used to get the final values using an iterative least-squares treatment. A computer program was written for this purpose and the final results were obtained using a Control Data Corp. 1604 computer. The final least-squares values for  $k_1$  and  $k_2$  are given in Table I.

The apparent first-order rate constants  $k_1$  and  $k_2$

TABLE I  
LEAST-SQUARES VALUES OF THE RATE CONSTANTS  
FOR THE ACID HYDROLYSIS<sup>a</sup>

Temp, °C	(H <sup>+</sup> ), M	10 <sup>4</sup> k <sub>1</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k <sub>2</sub> , sec <sup>-1</sup>
25.00	0.0042	1.06 ± 0.05	0.62 ± 0.04
25.00	0.0101	2.02 ± 0.05	0.86 ± 0.03
25.00	0.0201	3.52 ± 0.07	1.15 ± 0.02
25.00	0.0301	4.87 ± 0.05	1.38 ± 0.01
25.00	0.0416	6.15 ± 0.08	1.69 ± 0.01
25.00	0.1127	11.82 ± 0.08	3.76 ± 0.01
35.00	0.0046	3.68 ± 0.05	1.59 ± 0.02
35.00	0.0113	6.00 ± 0.12	2.52 ± 0.01
35.00	0.0226	9.48 ± 0.15	3.52 ± 0.03
35.00	0.0342	13.25 ± 0.15	4.45 ± 0.02
35.00	0.0457	16.83 ± 0.18	5.18 ± 0.03
35.00	0.1127	26.53 ± 0.25	9.73 ± 0.05

<sup>a</sup> Ionic strength was adjusted to 1.0 using sodium perchlorate.

exhibit hydrogen ion dependences that were satisfactorily fitted by the empirical relationships

$$k_1(\text{apparent}) = \frac{C_{10} + C_{11}(\text{H}^+)}{1 + K_1(\text{H}^+)} \quad (8)$$

$$k_2(\text{apparent}) = \frac{C_{21}(\text{H}^+) + C_{22}(\text{H}^+)^2}{1 + K_2(\text{H}^+)} \quad (9)$$

Least-squares fitting of the data to these forms gave the values listed in Table II. Recalculation of  $k_1$  and  $k_2$  using the parameters obtained from eq 8 and 9 gave values that are in good agreement with experimental values.

TABLE II  
PARAMETERS FOR DEPENDENCE OF THE RATE CONSTANTS  $k_1$  AND  $k_2$  ON HYDROGEN ION  
CONCENTRATION CALCULATED BY LEAST-SQUARES TREATMENT OF DATA IN TABLE I

Temp, °C	10 <sup>4</sup> C <sub>10</sub> , sec <sup>-1</sup>	10 <sup>2</sup> C <sub>11</sub> , M <sup>-1</sup> sec <sup>-1</sup>	K <sub>1</sub> , M <sup>-1</sup>	10 <sup>2</sup> C <sub>21</sub> , M <sup>-1</sup> sec <sup>-1</sup>	C <sub>22</sub> , M <sup>-2</sup> sec <sup>-1</sup>	K <sub>2</sub> , M <sup>-1</sup>
25.00	0.33 ± 0.02	1.83 ± 0.02	6.87 ± 0.1	5.87 ± 0.33	28.2 ± 0.7	1000 ± ?
35.00	1.72 ± 0.33	4.50 ± 0.33	8.47 ± 1.6	6.67 ± 0.50	13.3 ± 2.0	248 ± 23

and P, respectively. Substituting (3), (4), and (5) into (6) and rearranging we get

$$D - D_2 = \left\{ D_0 + \frac{D_1 k_1}{k_2 - k_1} + \frac{D_2 k_2}{k_1 - k_2} \right\} e^{-k_1 t} + \left\{ \frac{D_1 k_1}{k_1 - k_2} - \frac{D_2 k_1}{k_1 - k_2} \right\} e^{-k_2 t} \quad (7)$$

where  $D_0$ ,  $D_1$ , and  $D_2$  are absorbances corresponding to solutions made of pure dimer, pure intermediate, and pure diaquo complexes, respectively.  $D_2$  will, thus, be the same as the absorbance of the reaction mixture at infinite time. Equation 7 reduces to eq 1 with  $A$  and  $B$  representing the preexponential factors.

On the assumption that  $k_1$  is larger than  $k_2$ , a plot of log  $(D - D_2)$  vs. time should give a straight line at long times; a plot of log  $((D - D_2) - Be^{-k_2t})$  vs. time should also give a straight line in the early stages of the reac-

The parameters of  $k_2$ , however, are interdependent and as such were not very well determined, particularly at 25°. It was, thus, decided to fix the value of the parameter  $K_2$  and determine the best values for  $C_{21}$  and  $C_{22}$  subject to that restriction. The results for such an analysis for different assumed values of  $K_2$  are given in Table III.

An overall look at Table III, especially with reference to the quotients  $C_{21}/K_2$  and  $C_{22}/K_2$ , would indicate

TABLE III  
PARAMETERS OF THE HYDROGEN  
ION DEPENDENCE OF  $K_2$  AT 25°

K <sub>2</sub> , M <sup>-1</sup>	10 <sup>2</sup> C <sub>21</sub> , M <sup>-1</sup> sec <sup>-1</sup>	C <sub>22</sub> , M <sup>-2</sup> sec <sup>-1</sup>	10 <sup>2</sup> C <sub>21</sub> /K <sub>2</sub> , sec <sup>-1</sup>	C <sub>22</sub> /K <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup>
500	3.22 ± 0.20	14.0 ± 0.4	0.644	0.0280
1000	5.87 ± 0.30	28.2 ± 0.6	0.587	0.0282
1500	8.53 ± 0.40	42.5 ± 0.8	0.568	0.0283
2000	11.18 ± 0.50	56.8 ± 1.0	0.559	0.0284
2500	13.83 ± 0.65	71.0 ± 1.3	0.553	0.0284
3000	16.48 ± 0.90	85.3 ± 1.5	0.549	0.0284

(15) R. M. Wallace, *J. Phys. Chem.*, **64**, 899 (1960).

(16) A more careful analysis was done by us and is to be published.

that these quotients vary but slightly with the assumed values of  $K_2$ . A consideration of the energetics of what we interpret to be a protonation reaction, whose equilibrium constant is  $K_2$  (see the 35° value for  $K_2$ ), would impose an upper limit on the 25° value. We feel that the value of 1000 chosen is about as large as is reasonable. This value corresponds to  $\Delta H^\ddagger = -25$  kcal/mol and  $\Delta S^\ddagger = -72$  cal/deg mol, and larger values of  $K_2$  at 25° would increase the magnitude of each of these quantities.

**Base Hydrolysis.**—The data for the base hydrolysis of the dimer (the dimer nitrate was used for solubility reasons) were well fitted by the assumption that the reaction takes place by two consecutive first-order steps. A similar treatment to that discussed for the acid hydrolysis was developed and least-squares fit to an equation of the form

$$C_\infty - C_t = A'e^{-k_3t} + B'e^{-k_4t} \quad (10)$$

where  $C_\infty$  and  $C_t$  represent the concentration of the  $\text{OH}^-$  ions consumed during the reaction at infinite time and at time  $t$ , respectively, given in arbitrary concentration units. The values of the rate constants  $k_3$  and  $k_4$  obtained from a least-squares treatment are given in Table IV.

TABLE IV  
LEAST-SQUARES VALUES OF THE FIRST-ORDER RATE  
CONSTANTS OF THE BASIC HYDROLYSIS<sup>a</sup> AT 25.00°

pH	$10^4(\text{OH}^-), M$	$10^4k_3, \text{sec}^{-1}$	$10^4k_4, \text{sec}^{-1}$
10.385	2.427	$3.53 \pm 0.08$	$3.73 \pm 0.10$
10.300	1.995	$2.95 \pm 0.10$	$3.48 \pm 0.17$
10.280	1.905	$2.77 \pm 0.05$	$3.68 \pm 0.28$
10.140	1.380	$2.16 \pm 0.03$	$3.82 \pm 0.12$
10.130	1.349	$2.18 \pm 0.08$	$3.10 \pm 0.18$
10.090	1.230	$1.94 \pm 0.01$	$3.33 \pm 0.22$
9.940	0.871	$1.39 \pm 0.02$	$4.32 \pm 0.17$
9.915	0.822	$1.42 \pm 0.02$	$3.42 \pm 0.10$
9.905	0.804	$1.36 \pm 0.03$	$3.87 \pm 0.17$
9.900	0.794	$1.37 \pm 0.04$	$3.40 \pm 0.18$
9.730	0.537	$0.98 \pm 0.04$	$4.07 \pm 0.12$
9.660	0.457	$0.80 \pm 0.01$	$3.57 \pm 0.20$
9.580	0.380	$0.63 \pm 0.01$	$4.50 \pm 0.20$
9.513	0.320	$0.59 \pm 0.02$	$3.88 \pm 0.21$
9.450	0.280	$0.54 \pm 0.02$	$2.85 \pm 0.21$
9.300	0.200	$0.39 \pm 0.01$	$3.40 \pm 0.15$

<sup>a</sup> Ionic strength adjusted to 1.0 *M* with  $\text{NaNO}_3$ .

The apparent first-order rate constant  $k_3$  exhibits a hydroxide ion dependence that was satisfactorily fitted by the equation

$$k_3(\text{apparent}) = \frac{C_{30} + C_{31}(\text{OH}^-)}{1 + K_3(\text{OH}^-)} \quad (11)$$

Least-squares fitting of the data in this form resulted in the values  $C_{30} = (3.78 \pm 1.7) \times 10^{-5} \text{ sec}^{-1}$ ,  $C_{31} = 180 \pm 7 \text{ M}^{-1} \text{ sec}^{-1}$ , and  $K_3 = 1150 \pm 300 \text{ M}^{-1}$ . The rate constant  $k_4$  showed but a slight change with pH.

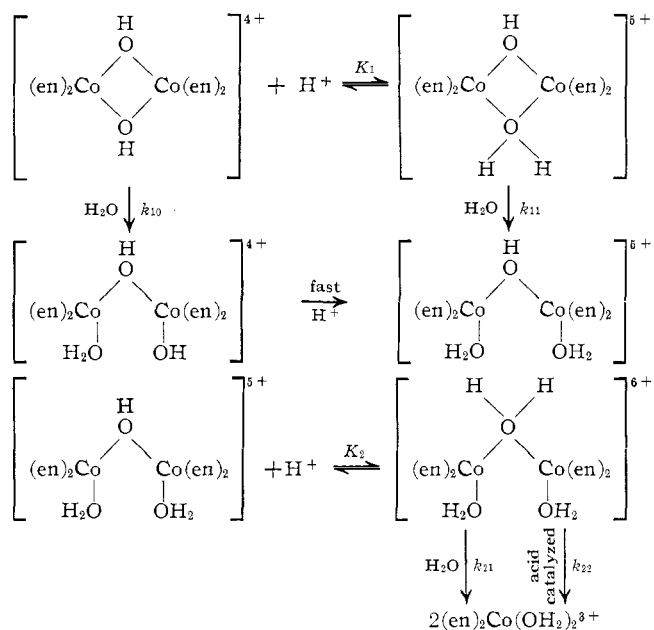
### Discussion

As was noted in the previous sections, the data for the hydrolysis of the dimer are well fitted by an empirical relation given by eq 1. The two exponential parts in eq 1, as well as those in eq 7, could be interchanged without affecting the calculations nor the results.

Consequently, the apparent first-order rate constants  $k_1$  and  $k_2$ , as well as  $k_3$  and  $k_4$ , do not necessarily represent  $k_1$  and  $k_2$ , respectively, in eq 2. We are, thus, inclined to believe that the type of mechanism suggested and the hydrogen ion dependences derived from these mechanisms will correlate our experimental rate constants to various reactions in going from the dimer to the final products.

The interpretation of the experimental rate law could very likely be done using a variety of mechanisms, each involving a quite different chemistry for the reaction. We propose, however, that any mechanism should involve the formation of a single hydroxo-bridged dimeric species as an intermediate. This is very likely since simultaneous cleavage of the two hydroxo bridges is improbable.

In the following, we will concern ourselves with two types of mechanisms, each of which involves a different chemistry for the reaction. Thus, consider the series of reactions for the acid cleavage of the dimer



These chemical reactions lead to the rate laws

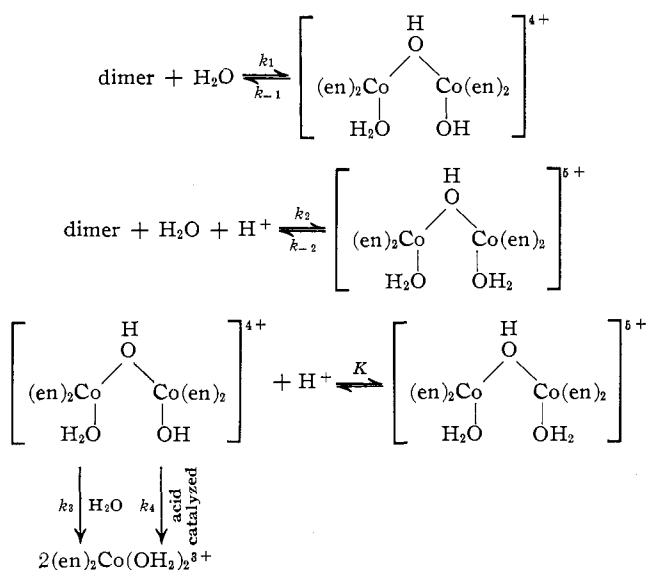
$$-\frac{d(\text{dimer})}{dt} = k_A(\text{dimer}) = \left[ \frac{k_{10} + k_{11}(\text{H}^+)}{1 + K_1(\text{H}^+)} \right] (\text{dimer}) \quad (12)$$

and

$$\frac{d(\text{product})}{dt} = k_B(\text{intermediate}) = \frac{k_{21}K_2(\text{H}^+) + k_{22}K_2(\text{H}^+)^2}{1 + K_2(\text{H}^+)} (\text{intermediate}) \quad (13)$$

In this mechanism,  $k_A$  has the same hydrogen ion dependence as our experimental  $k_1$ , and  $k_B$  has the dependence of the experimental  $k_2$ . One of the major assumptions of this mechanism is the protonation of the dimer and the intermediate in a fast reversible step. Unfortunately, we do not have any substantial experimental evidence for this assumption.

An alternate mechanism can be suggested using a generalized formulation of the mechanism by Hoffman and Taube<sup>17</sup> for the acid cleavage of the closely related

octaammine system  $(\text{H}_3\text{N})_8\text{Co}_2(\text{OH})_2^{4+}$ 

This mechanism leads to the steady-state rate law

$$-\frac{d \ln (\text{dimer})}{dt} = k_A' = \frac{k_1 k_3 + (k_1 k_4 + k_2 k_3)(\text{H}^+) + k_2 k_4 (\text{H}^+)^2}{(k_{-1} + k_3) + (k_{-2} K + k_4)(\text{H}^+)} \quad (14)$$

$k_A'$  resembles the experimental  $k_2$ . It predicts that  $k_2$  should have a finite intercept. Since both  $k_1$  and  $k_3$  represent water reactions, their value will be small relative to the specific rate constants of acid reactions. The product  $k_1 k_3$  could, thus, be very small compared to other terms in the numerator to warrant its neglect. If, however, we make the assumption that  $k_3$  alone is very small, we can write

$$k_A' = \frac{(k_1 k_4 / k_{-1})(\text{H}^+) + (k_2 k_4 / k_{-1})(\text{H}^+)^2}{1 + ((k_{-2} K + k_4) / k_{-1})(\text{H}^+)} \quad (15)$$

This gives the same hydrogen ion dependence as the experimental  $k_2$ . In addition, we could write the rate law

$$\frac{d(\text{product})}{dt} = k_B'(\text{intermediate}) = \frac{k_3 + k_4(\text{H}^+)}{1 + K(\text{H}^+)}(\text{intermediate}) \quad (16)$$

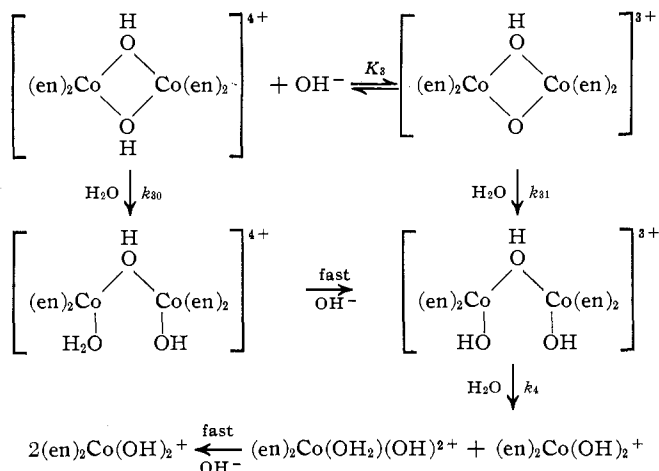
This predicts that  $k_B'$  has the same hydrogen ion dependence as our experimental rate constant  $k_1$ . The activation parameters for some of the specific rate constants in these mechanisms are given in Table V.

TABLE V  
ACTIVATION PARAMETERS FOR THE  
ACID HYDROLYSIS RATE CONSTANTS

	$E_a$ , kcal/mol	$\Delta H^\ddagger(298^\circ\text{K})$ , kcal/mol	$\Delta S^\ddagger(298^\circ\text{K})$ , eu
$k_{10}, k_3$	30.5	29.9	5.7
$k_{11}, k_4$	16.5	15.9	-1.7
$k_{21}$	28.0	27.4	4.1
$k_{22}$	15.50	14.9	-3.3

The base hydrolysis of the dimer can be interpreted by mechanisms similar to those discussed for the acid

hydrolysis. Consider, for example, the mechanism



This mechanism leads to the rate law

$$\frac{d(\text{intermediate})}{dt} = k_o(\text{dimer}) - k_d(\text{intermediate}) \quad (17)$$

where

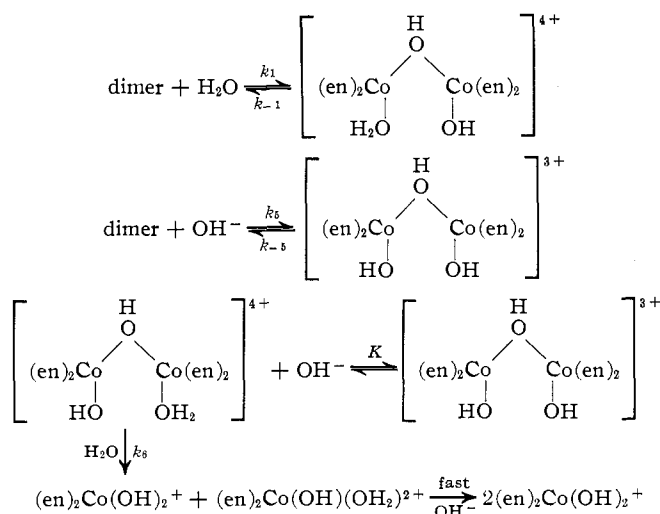
$$k_o = \frac{k_{30} + k_{31}K_3(\text{OH}^-)}{1 + K_3(\text{OH}^-)} \quad (18)$$

and

$$k_d = k_4 \quad (19)$$

This mechanism predicts that the rate constant  $k_o$  given in (18) has the same hydroxide ion dependence as the experimental  $k_3$ ;  $k_d$  given in (19) has the dependence of experimental  $k_4$ .

An alternate mechanism is given by the series of reactions



This mechanism leads to the steady-state rate law

$$-\frac{d \ln (\text{dimer})}{dt} = \frac{k_1 k_6 + k_5 k_6 (\text{OH}^-)}{(k_{-1} + k_6) + k_{-5} K (\text{OH}^-)} \quad (20)$$

and

$$\frac{d \ln (\text{product})}{dt} = k_6 \quad (21)$$

The mechanism proposed here for the base hydrolysis is subject to the fact that the experimental data showed some scatter. The experimental rate constant  $k_4$

(apparent) is not very well determined. Its hydroxide ion dependence is, thus, relatively unknown. It is only considering our experimental errors that we suggest its independence of the hydroxide ion concentration.

In addition to the closely related octaammine system<sup>17</sup> discussed previously, a number of other systems have also been reported, particularly those dealing with

chromium analogs.<sup>18,19</sup> In all of these systems, a singly hydroxo-bridged dimer is suggested as an intermediate in the hydrolysis. As far as we know, no base hydrolysis has been reported for these or similar complexes.

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## Bridging and Nonbridging Ligand Effects in Some Reversible Reductions of Macrocyclic Complexes of Cobalt(III)<sup>1</sup>

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The reversible one-electron reductions of *trans*-CoL(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup> (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene or 5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradecane) by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, Cr<sup>2+</sup>, and V<sup>2+</sup> have been examined. The outer-sphere Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reductions are more rapid than similar reductions of Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>3+</sup> and Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> with differences in reactivity being very close to those predicted from variations in the oxidation potentials of the cobalt(II)-cobalt(III) couples. The variations with [H<sup>+</sup>] of reaction rate show the expected qualitative trends for Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> (rate decreases with increasing pH) and Cr<sup>2+</sup> (rate increases with increasing pH). However, the acid dependence of the Cr<sup>2+</sup> reactions is complex in its details and the total chemical behavior is not compatible with the "classical" attribution of an extraordinary electron mediating (or "conducting") capacity to an OH<sup>-</sup> bridging ligand.

Despite the large number of mechanistic studies involving cobalt(III) oxidants,<sup>4</sup> explanations of the range and patterns of reactivity are in many cases controversial or still lacking. It has been particularly difficult to obtain experimental information which reflects on the role played by bridging ligands in inner-sphere electron-transfer reactions.<sup>4</sup> The experimental ambiguities contrast with the considerable interest in theoretical models of possible mediating effects of such bridging ligands.<sup>5-9</sup> Many of the key issues are dramatized by comparisons of the rates of reactions in which hydroxide functions as a bridging group to reactions which are bridged by a water molecule. In the mechanistically clear cases of Cr<sup>2+</sup> reductions of cobalt(III) oxidants,<sup>10-12</sup> an enhancement of about 10<sup>6</sup> has generally been attributed to the hydroxy-bridged path over the aquo-bridged path. There has been a tendency to view this enhancement of rate as the result

of some unique mediating property possessed by OH<sup>-</sup> to a greater extent than by H<sub>2</sub>O. This view has persisted<sup>13</sup> in the face of several considerations which should have raised serious doubts: (1) the hydroxy complexes should be thermodynamically more difficult to reduce (owing to the relative instability of the cobalt(II) hydroxide; this effect apparently dominates in the corresponding outer-sphere reactions<sup>14,15</sup>); (2) OH<sup>-</sup> should have a lower electron affinity than H<sub>2</sub>O; and (3) many stable hydroxy-bridged binuclear species are known in aqueous solution while stable aquo-bridged species are unknown. Relatively recently it has been pointed out that the case of cobalt(III) oxidants may be unique in that the cobalt(III)-bridging ligand bond may be greatly stretched in the activated complex<sup>10a,16</sup> so that the overall reaction energetics could require a relatively great reactivity for the hydroxy-bridged path.<sup>17</sup>

In striking contrast to the very high reactivity of hydroxy complexes in inner-sphere reactions, Co(NH<sub>3</sub>)<sub>5</sub>OH<sup>2+</sup> has been found to be less reactive than Co(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>3+</sup> in outer-sphere reductions with Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup><sup>15</sup> and Cr(bipy)<sub>3</sub><sup>2+</sup>.<sup>14</sup> On the basis of these limited observations it has been proposed<sup>14,15</sup> that the relative reactivities of hydroxy and aquo complexes might be useful criteria for distinguishing inner-sphere from outer-sphere electron-transfer reactions. Such criteria have been used to help clarify reactions of mechanistically ambiguous aquo ions.<sup>13</sup>

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