

The positive entropy change indicates a greater degree of disorder in the activated complex than in the reactants. Such a result would be expected if a stretching and loosening of bonds occur in forming the activated complex.<sup>7</sup> The lack of a deuterium isotope effect, the insensitivity to changes in ionic strength, and the pseudo-first-order kinetics are all compatible with such an activation process.

Acid catalysis is frequently observed when the displaced ligand is the anion of a weak acid or has a strong tendency to form hydrogen bonds.<sup>8</sup> In the case of nitro complexes, the mechanism is believed to involve the rapid protonation of an oxygen atom of the coor-

(7) J. P. Hunt, "Metal Ions in Aqueous Solution," W. A. Benjamin, Inc., New York, N. Y., 1963, p 93.

(8) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

ordinated nitro group followed by the slower displacement of HNO<sub>2</sub> by water.<sup>9,10</sup>

The absence of an acid-catalyzed pathway in our system may indicate that the nitro ligands are not protonated. The oxygen atoms of the acetylacetonate rings are known to be bridged in the structures of (Ni(acac)<sub>2</sub>)<sub>3</sub><sup>11</sup> and (Co(acac)<sub>2</sub>)<sub>4</sub><sup>12</sup> and in the adducts of Co(acac)<sub>3</sub> with silver nitrate.<sup>13</sup> Therefore, these basic sites may be preferred to the oxygen atoms of the nitro ligand in forming bonds to the protons.

(9) M. L. Tobe, *J. Chem. Soc.*, 3776 (1959).

(10) D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A211**, 254 (1952).

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## Steric Effects in Chelation Kinetics. II. Role of Alcoholic Oxygen as a Donor Atom and the Internal Conjugate Base Effect in Cobalt(II)-Poly(amino alcohol) Reactions<sup>1</sup>

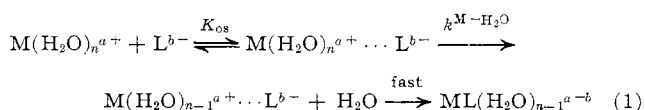
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The kinetics of the aquocobalt(II) ion reacting with two branched poly(amino alcohol) ligands, N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (THPED), have been studied at 25°,  $\mu = 0.1$ , over the pH range from 5.7 to 7.2 using the stopped-flow technique. The reaction rates are slower than would be predicted for a simple dissociative mechanism and the kinetic behavior is found to conform to a mechanism in which first-bond formation involves an alcoholic oxygen donor atom followed by second-bond formation to a nitrogen donor atom as the rate-determining step. The data permit an estimation of the rate constant for cobalt(II)-alcoholic oxygen bond rupture equal to  $6 \times 10^8 \text{ sec}^{-1}$ . In addition, the first evidence is found for an internal conjugate base effect for the aquocobalt(II) ion.

### Introduction

For complexation reactions involving an aquometal ion,  $M(\text{H}_2\text{O})_n^{a+}$ , and a unidentate ligand,  $L^{b-}$ , the general dissociative mechanism<sup>2</sup>



(involving formation of an equilibrated outer-sphere complex,  $M(\text{H}_2\text{O})_n^{a+} \cdots L^{b-}$ , preceding metal-water bond rupture,  $k^{M-H_2O}$ , as the rate-determining step) has been thoroughly tested and found to be applicable almost without exception.<sup>3</sup> Even for multidentate

ligand reactions, where the formation of multiple coordinate bonds to a single metal ion raises the possibility of a more complicated mechanistic behavior, there is much supportive evidence for the applicability of the simple dissociative mechanism. In fact, conformance in the mechanism described by eq 1 can be tested readily by comparing the observed overall second-order rate constant,  $k_M^L$  ( $M^{-1} \text{ sec}^{-1}$ ), to the value predicted by

$$k_M^L = K_{os} k^{M-H_2O} \quad (2)$$

where  $K_{os}$  ( $M^{-1}$ ) represents the diffusion-controlled equilibrium constant for formation of the outer-sphere complex and  $k^{M-H_2O}$  ( $\text{sec}^{-1}$ ) represents the first-order rate constant for unaided metal-water bond rupture from the aquated metal ions.

Recent studies on multidentate ligand reactions with aquonickel ion, however, have shown evidence of modified behavior resulting in observed rate constants

(1) Paper I: D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969).

(2) M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 373.

(3) M. Eigen and R. G. Wilkins in "Mechanisms of Inorganic Reactions," *Advances in Chemistry Series*, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

which are both faster<sup>4,5</sup> and slower<sup>1</sup> than values predicted by eq 2. In both cases the kinetic behavior can be explained in terms of the basic and steric properties of the multidentate ligands involved.

In the current study we have extended our investigation to include reactions of the aquacobalt(II) ion in order to compare the influence of the electronic structure of the metal ion and to eliminate the possibility of "uniqueness" for the aquonickel ion in exhibiting the previously observed "anomalous" rate behavior. Two poly(amino alcohols), N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (THPED), were selected as the reacting ligands since our previous work indicated that these ligands possess properties tending to promote both enhanced and depressed rate behavior. In addition, the structural similarity between these ligands and ethylenediaminetetraacetic acid (EDTA) permits the resultant conclusions to be applied to explain the behavior of EDTA as well.

Whereas two alternative mechanisms were previously proposed to explain the kinetic behavior observed for the aquonickel ion reacting with these poly(amino alcohols), a comparison with the aquacobalt(II) data permits the conclusion that the dominant reaction path involves a shift of the rate-determining step to the point of second coordinate bond formation following a prior equilibrium involving the formation and dissociation of a weak metal ion-alcoholic oxygen bond. The data thus permit an estimate to be made for the dissociation rate constant of this latter bond. In addition, the results indicate that the internal conjugate base (ICB) effect, previously reported only for aquonickel ion, is also operative in the aquacobalt(II) reactions.

### Experimental Section

**Reagents.**—TKED (a gift of ICI Organics, Inc.) and THPED (a gift of Wyandotte Chemical Corp.) were purified as previously described<sup>1</sup> with the following modifications. Initial treatment with activated charcoal was used to effect removal of colored impurities. The methanol solution of impure ligand was cooled in Dry Ice, and 73.6% HClO<sub>4</sub> (G. F. Smith Chemical Co.) was added dropwise while stirring. When 2 equiv of acid had been added, the white crystalline salts, TKED·2HClO<sub>4</sub> or THPED·2HClO<sub>4</sub>, precipitated. The salts were recrystallized from absolute methanol and the excess acid removed by repeatedly suspending the salt in ether until the ethereal layer was neutral to litmus after which the salts were dried. Solutions were prepared and standardized by potentiometric titration with base.

Cobalt(II) perchlorate was prepared by suspending ~100 g of reagent grade CoCO<sub>3</sub> in 400 ml of water and adding 140 ml of 73.6% HClO<sub>4</sub> dropwise with stirring. A small amount of black precipitate, presumably the oxide, was removed by filtration. After evaporating to about half-volume, the solution was cooled slowly precipitating out Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O crystals. The salt was washed with ether until the washings were neutral to litmus and allowed to air dry. Stock cobalt(II) solutions were prepared and standardized by EDTA titration.

The sodium perchlorate (G. F. Smith Chemical Co.) used for ionic strength control was purified by dissolving in water, filter-

ing, and recrystallizing. All other chemicals used were reagent grade and were used without further purification.

**Kinetic Measurements.**—The Co(II) complex formation reactions were followed spectrophotometrically at 240 nm using the stopped-flow technique. The TKED study utilized a Durum stopped-flow spectrometer while the THPED investigation was carried out using an Aminco-Morrow stopped-flow mixing chamber mounted in place of the cell compartment on a Beckman DU-2 spectrophotometer. For the latter instrument, the photomultiplier output was fed directly to a Tektronix Type 549 storage oscilloscope, without further signal modification, and recorded photographically. The solutions used in both instruments were thermostated at 25.0 ± 0.4°. The pH was controlled with a borate-mannitol buffer<sup>5</sup> and ionic strength was maintained at 0.1 M using NaClO<sub>4</sub>. Molar absorptivity values determined for 240 nm are:  $\epsilon_{\text{Co}^{2+}}$  0.30,  $\epsilon_{\text{TKED}}$  93,  $\epsilon_{\text{HTKED}}$  20,  $\epsilon_{\text{CoTKED}}$  395,  $\epsilon_{\text{THPED}}$  285,  $\epsilon_{\text{HTHPED}}$  25,  $\epsilon_{\text{CoTHPED}^{2+}}$  419.

### Results

The stability constant for Co<sup>II</sup>TKED was determined potentiometrically by titrating the ligand in the presence of a fourfold excess of cobalt(II) perchlorate.<sup>6</sup> For Co<sup>II</sup>THPED the stability constant was determined simultaneously with the molar absorptivity of the complex by iterating absorbance data taken at several pH values. In the course of obtaining these values, the protonation constants of the ligands were redetermined by means of potentiometric titrations of the perchlorate salts with standard base. The pertinent constants are listed in Table I where they are compared with previously determined values and the stability constants calculated from the kinetic data.

TABLE I  
PROTONATION CONSTANTS AND COBALT COMPLEX  
STABILITY CONSTANTS FOR TKED AND THPED AT 25°

Ionic strength, M	Log K <sub>H1</sub>	Log K <sub>H2</sub>	Log K <sub>CoL</sub>	Ref
TKED				
0.1 (NaClO <sub>4</sub> )	8.35	4.29	5.13 (titrim)	a
	...	...	4.9 (kinetic)	
0.1 (NaClO <sub>4</sub> )	8.38	4.37	...	b
0.5 (KNO <sub>3</sub> )	...	...	5.04	c
THPED				
0.1 (NaClO <sub>4</sub> )	8.70	4.12	6.1 (spectro)	a
0.1 (NaClO <sub>4</sub> )	8.75	4.24	...	b
0.5 (KNO <sub>3</sub> )	...	...	6.33	c
0.05 (KNO <sub>3</sub> )	...	...	5.7	d

<sup>a</sup> This work. <sup>b</sup> Reference 1. <sup>c</sup> J. L. Hall, W. E. Dean, and E. A. Pacofsky, *J. Am. Chem. Soc.*, **82**, 3303 (1960). <sup>d</sup> D. A. Keyworth, *Talanta*, **2**, 383 (1959).

The kinetics of the complex formation reactions were found to obey the reversible mixed second- and first-order rate equation

$$-\frac{d[\text{Co}^{2+}]}{dt} = k_f[\text{Co}^{2+}][\Sigma\text{L}] - k_d[\text{CoL}^{2+}] \quad (3)$$

where  $k_f$  and  $k_d$  represent the observed formation and dissociation rate constants, respectively, for each pH studied and  $[\Sigma\text{L}]$  represents the total concentration of uncomplexed ligand. The method for the resolution of the kinetic data was identical with that previously

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(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

TABLE II  
EXPERIMENTAL RATE CONSTANTS FOR THE REACTION OF  
Co<sup>2+</sup> WITH TKED AT 25°, μ = 0.1 (NaClO<sub>4</sub>), [Co<sup>2+</sup>] =  
2.335 × 10<sup>-3</sup> M, AND [TKED] = 3.115 × 10<sup>-4</sup> M

pH	10 <sup>3</sup> k <sub>f</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>d</sub> , sec <sup>-1</sup>	Kinetic log K <sub>CoL</sub>
7.55	6.56	1.47	4.51
7.33	4.44	0.924	4.73
7.00	2.41	1.02	4.74
6.92	2.60	0.639	5.06
6.55	1.72	1.05	5.02
6.50	1.67	1.01	5.08
6.26	1.25	1.13	5.14
6.23 <sup>a</sup>	1.26	1.33	5.10
6.15	1.16	0.771	5.39
6.06	1.03	1.56	5.11
6.03 <sup>b</sup>	1.07	1.54	5.16
6.01	1.04	1.63	5.15
5.94	0.889	1.79	5.11
5.92	0.859	1.73	5.14
5.85	0.721	1.92	5.09
5.77	0.703	2.17	5.10

<sup>a</sup> [Co<sup>2+</sup>] = 4.67 × 10<sup>-3</sup> M. <sup>b</sup> [Co<sup>2+</sup>] = 1.86 × 10<sup>-3</sup> M.

TABLE III  
EXPERIMENTAL RATE CONSTANTS FOR THE REACTION OF Co<sup>2+</sup>  
WITH THPED AT 25°, μ = 0.1 (NaClO<sub>4</sub>), [Co<sup>2+</sup>] = 1.785 ×  
10<sup>-3</sup> M, AND [THPED] = 2.14 × 10<sup>-4</sup> M

pH	10 <sup>3</sup> k <sub>f</sub> , M <sup>-1</sup> sec <sup>-1</sup>	k <sub>d</sub> , sec <sup>-1</sup>	Kinetic log K <sub>CoL</sub>
7.69	11.9		
7.29	6.60		
7.06 <sup>a</sup>	5.16		
6.98	6.08	0.018	6.21
6.73	4.44	0.010	6.34
6.73 <sup>a</sup>	5.00		
6.53	3.85	0.039	6.21
6.48 <sup>a</sup>	3.89		
6.39	3.68	0.090	5.94
6.30	3.49	0.077	6.06
6.29 <sup>a</sup>	3.98		
6.19	3.15	0.140	5.89
6.15	3.47	0.104	6.08
6.11	3.47	0.102	6.09
6.09 <sup>a</sup>	3.55		
6.00	2.79	0.148	6.02
5.98	2.70	0.109	6.17
5.94 <sup>a</sup>	2.83		
5.94 <sup>b</sup>	3.10	0.162	6.00-6.08
5.90	2.62	0.171	6.04

<sup>a</sup> [Co<sup>2+</sup>] = 1.428 × 10<sup>-2</sup> M, [THPED] = 2.675 × 10<sup>-4</sup> M.

<sup>b</sup> [Co<sup>2+</sup>] = 1.07 × 10<sup>-2</sup> M, [THPED] = 2.14 × 10<sup>-4</sup> M.

described.<sup>1</sup> The values of *k<sub>f</sub>* and *k<sub>d</sub>* for all runs are listed in Tables II and III.

Since only the unprotonated and monoprotonated ligand species are capable of reacting with the aquo-metal ion, eq 3 can be expanded to the form

$$\frac{-d[\text{Co}^{2+}]}{dt} = k_{\text{CoL}}[\text{Co}^{2+}][\text{L}] + k_{\text{CoHL}}[\text{Co}^{2+}][\text{HL}^+] - k_{\text{CoL}}[\text{CoL}^{2+}] - k_{\text{HCoL}}[\text{H}^+][\text{CoL}^{2+}] \quad (4)$$

Combining eq 3 and 4, the individual rate constants can be resolved by plotting the equations

$$k_f \frac{[\Sigma \text{L}]}{[\text{L}]} = k_{\text{CoL}} + k_{\text{CoHL}} K_{\text{H1}} [\text{H}^+] \quad (5)$$

$$k_d = k_{\text{CoL}} + k_{\text{HCoL}} [\text{H}^+] \quad (6)$$

Plots of eq 5 for both ligand studies are shown in Figure 1. Kinetic runs at pH values above 6.9 invariably

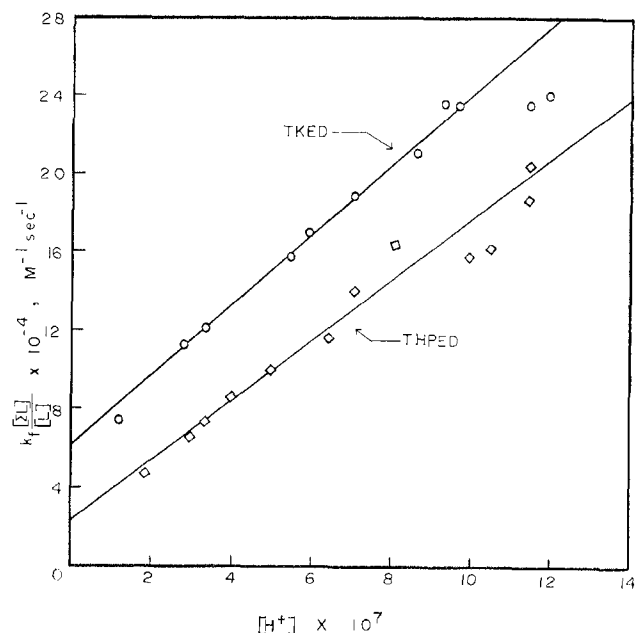


Figure 1.—Resolution of the formation rate constants for aquocobalt(II) ion reacting with the unprotonated and monoprotonated ligand species. Plot of eq 5: O, TKED data; □, THPED data.

resulted in *k<sub>f</sub>* values which were too low, presumably due to the formation of cobalt hydroxide, and these values were omitted from the data resolution.

## Discussion

**Reaction Mechanism.**—The reactions between the poly(amino alcohols) and the aquonickel(II) ion were previously found to proceed at an anomalously slow rate.<sup>1</sup> To account for this behavior two alternate reaction paths were considered: mechanism I, involving direct bond formation between the metal ion and a nitrogen donor atom, wherein steric hindrance must be invoked to account for the decreased reaction rate; and mechanism II, in which first-bond formation involves an alcoholic oxygen donor atom to form a metastable complex which is then followed by second-bond formation to a nitrogen donor atom as the rate-determining step (Figure 2).

In view of the accumulated evidence relating to the weak bonding ability of alcoholic oxygen, it was concluded that mechanism II would become the preferential reaction route only in the event that the approach of the aquonickel ion to a nitrogen donor atom were severely hindered, thereby making the formation of intermediate I in Figure 2 unfavorable.

From the results of the nickel study alone it was not possible to distinguish which mechanism was operative. However, the results of the aquocobalt(II) study provide additional information permitting a definitive decision to be made.

On the basis of arguments previously presented,<sup>1,4</sup> the experimental rate constants for aquocobalt(II) ion reacting with ammonia and monoprotonated ethylenediamine, Hen<sup>+</sup>, may be taken as representing the theoretical rate constants predicted by eq 2 for the reactions of monoprotonated and unprotonated poly-

(amino alcohol) species, respectively. Unfortunately, no experimental rate constant for the  $\text{Co(II)}\text{-Hen}^+$  reaction has been reported. However, the excellent agreement obtained between the calculated and experimental rate constants for the  $\text{Ni(II)}\text{-Hen}^+$  reaction lends confidence that a similarly accurate value may be calculated for the  $\text{Co(II)}$  reaction as well.<sup>7</sup> These values are listed in Table IV along with the resolved rate constants for the poly(amino alcohol) reactions.

TABLE IV  
COMPARISON OF RATE CONSTANTS FOR COBALT(II) COMPLEXES  
IN AQUEOUS SOLUTION AT 25° AND  $\mu = 0.1$

Ligand	$k_{\text{Co}^{\text{L}}}$ , $M^{-1} \text{sec}^{-1}$	$k_{\text{Co}^{\text{HL}}}$ , $M^{-1} \text{sec}^{-1}$	$k_{\text{Co}^{\text{L}}}$ , $\text{sec}^{-1}$	$k_{\text{H}^{\text{Co}^{\text{L}}}$ , $M^{-1} \text{sec}^{-1}$
$\text{NH}_3$	$1.1 \times 10^6$ <sup>a</sup>			
en		$1.4 \times 10^4$ <sup>b</sup>		
TKED	$6.2 \times 10^4$	$7.5 \times 10^2$	0.77	$8.5 \times 10^5$
THPED	$2.3 \times 10^4$	$2.7 \times 10^2$	(0.05?)	$(1.3 \times 10^5)$

<sup>a</sup> Reference 4. <sup>b</sup> Calculated value.<sup>7</sup>

It is obvious from Table IV that the experimental rate constants for the aquacobalt(II) ion reacting with  $\text{HTKED}^+$  and  $\text{HTHPED}^+$  are significantly smaller than the calculated value for  $\text{Hen}^+$ . Since the mono-protonated species are incapable of exhibiting an ICB effect,<sup>1</sup> this comparison provides the most reliable evidence that some other perturbing influence is affecting the poly(amino alcohol) reaction rates. This is in qualitative agreement with the results of the aquonickel ion study.<sup>1</sup>

**Consideration of Mechanism I.**—If mechanism I represents the operative reaction path, the difference between the "theoretical" rate constants and those determined experimentally for  $\text{HTKED}^+$  and  $\text{HTHPED}^+$  in this study may be attributed directly to steric blocking of the metal ion as it approaches the available nitrogen donor atom. In accord with the treatment applied to the corresponding nickel data,<sup>1</sup> the magnitude of this apparent steric effect may be calculated as the logarithmic ratio,  $E_s$

$$E_s = \log(k/k_0) \quad (7)$$

where  $k$  represents the rate constant for the "sterically hindered" reaction and  $k_0$  represents a reference rate constant for a corresponding system presumed to be free of steric effects.

Using the rate constants for the  $\text{NH}_3$  and  $\text{Hen}^+$  reactions as the  $k_0$  values, the resultant  $E_s$  values for the aquacobalt(II) reactions are listed in Table V along with the values previously reported for  $\text{Ni(II)}$ .<sup>1</sup> These figures indicate that  $\text{HTKED}^+$  reacts 16 times slower with  $\text{Co}^{2+}$  and 60 times slower with  $\text{Ni}^{2+}$  than does  $\text{Hen}^+$  while the corresponding values for  $\text{HTHPED}^+$  are 50 and 200 times.

Whereas the threefold difference in the reactivity of  $\text{Ni}^{2+}$  toward  $\text{HTKED}^+$  and  $\text{HTHPED}^+$  could pre-

(7) The  $K_{08}$  value for the reaction between  $\text{Co(H}_2\text{O)}_6^{2+}$  and  $\text{Hen}^+$  may be presumed to be identical with the value calculated for the corresponding reaction with  $\text{Ni(H}_2\text{O)}_6^{2+}$ , i.e.,  $K_{08} = 0.018$  at 25° (ref 1, footnote 13). For  $k^{\text{Co-H}_2\text{O}}$ , a value of  $8 \times 10^6 \text{ sec}^{-1}$  is used preferentially since this value is consistent with the  $\text{Co(II)}\text{-NH}_3$  data.<sup>4</sup> Substituting these values into eq 2 yields  $k_{\text{Co}^{\text{Hen}^+}} = 1.4 \times 10^4 M^{-1} \text{sec}^{-1}$  at 25°.

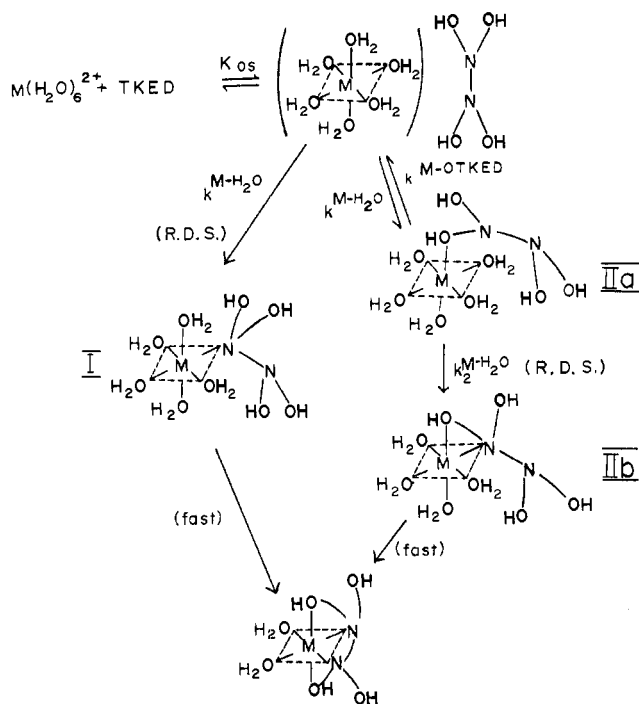


Figure 2.—Schematic representation of the two alternate reaction mechanisms proposed for aquometal ions reacting with the poly(amino alcohols). Intermediate I represents the reaction path designated by mechanism I while mechanism II is represented by intermediates IIa and IIb.

TABLE V  
APPARENT STERIC FACTORS FOR THE AQUOCOBLT(II) ION  
REACTING WITH THE POLY(AMINO ALCOHOLS) AT 25°

Ligand species	$-\log k_{\text{Co}^{\text{L}}}$		$E_s$	$\Delta E_s$	Apparent ICB effect
	Theoret	Exptl			
TKED	5.0	4.8	-0.2		
HTKED <sup>+</sup>	4.1	2.9	-1.2	1.0	Tenfold
THPED	5.0	4.4	-0.6		
HTHPED <sup>+</sup>	4.1	2.4	-1.7	1.1	Thirteenfold
Ligand species	$-\log k_{\text{Ni}^{\text{L}}}$		$E_s$	$\Delta E_s$	Apparent ICB effect
	Theoret	Exptl			
TKED	3.6	2.4	-1.2	0.6	Fourfold
HTKED <sup>+</sup>	2.7	0.9	-1.8		
THPED	3.6	2.2	-1.4		
HTHPED <sup>+</sup>	2.7	0.4	-2.3	0.9	Eightfold

<sup>a</sup> Reference 1.

viously be rationalized on the basis of increased steric hindrance toward the latter ligand, the fourfold difference in apparent steric hindrance between the two metal ions,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , with each ligand species is irreconcilable with mechanism I since the two metal ions are of nearly identical dimensions. Therefore, it is concluded that the  $\text{Co}^{2+}$  reactions must be proceeding by mechanism II; this is the presumed mechanism for  $\text{Ni}^{2+}$  as well.<sup>8</sup>

#### Mechanism II. Rate Constant for Cobalt-Alcoholic

(8) Since the  $E_s$  values for the  $\text{Ni}^{2+}$  reactions represent the minimal steric hindrance for mechanism I,<sup>1</sup> the smaller values found for the  $\text{Co}^{2+}$  reactions cannot be representative of this mechanism. However, this does not definitively rule out the possibility that the  $\text{Ni}^{2+}$  reactions are proceeding by mechanism I.

**Oxygen Bond Rupture.**—On the basis of mechanism II the rate constant for the rupture of a cobalt(II)-alcoholic oxygen bond,  $k_{\text{Co-O}^{\text{TKED}}}$ , can be estimated as outlined for nickel in the preceding paper of this series.<sup>1</sup> Utilizing the data for the monoprotonated ligands, to avoid complications arising from the ICB effect, the applicable equation for  $\text{HTKED}^+$  is

$$k_{\text{Co-O}^{\text{HTKED}}} = \frac{K_{\text{os}} k_{\text{Co-H}_2\text{O}} k_2^{\text{Co-H}_2\text{O}}}{k_{\text{Co-O}^{\text{TKED}}}} \quad (8)$$

where  $k_2^{\text{Co-H}_2\text{O}}$  represents the rate constant for water loss modified by the potential energy barrier for rotating the nitrogen donor atom into a position suitable for bonding. Applying values equivalent to those calculated for the nickel study ( $K_{\text{os}} = 0.22 \text{ M}^{-1}$ ,  $k_{\text{Co-H}_2\text{O}} = 8 \times 10^5 \text{ sec}^{-1}$ ,  $k_2^{\text{Co-H}_2\text{O}} = k_{\text{Co-H}_2\text{O}}/30$ ) the value of  $k_{\text{Co-O}^{\text{TKED}}}$  is calculated to be  $6.1 \times 10^6 \text{ sec}^{-1}$ . Similarly for  $\text{HTHPED}^+$  (where  $k_2^{\text{Co-H}_2\text{O}} = k_{\text{Co-H}_2\text{O}}/90$ ) the corresponding value obtained is  $6.4 \times 10^6 \text{ sec}^{-1}$ .

It is interesting to note that this estimated rate constant for the rupture of a cobalt(II)-alcoholic oxygen bond is only 8 times faster than the value for the cobalt(II)-water bond whereas for nickel(II) this factor was 25 times. As shown by the comparison in Table VI, this fact correlates well with the greater

TABLE VI  
RATE CONSTANTS FOR SINGLE BOND RUPTURES AT 25° FOR THE SPECIES  $\text{ML}(\text{H}_2\text{O})_5^{2+}$  (ALL RATE CONSTANTS IN  $\text{SEC}^{-1}$ )

M-L bond	Co(II)	Ni(II)
M-NH <sub>3</sub> <sup>a</sup>	$1.5 \times 10^3$	3.6
M-H <sub>2</sub> O <sup>a</sup>	$8 \times 10^5$	$3 \times 10^4$
M-OR <sup>b</sup>	$6 \times 10^6$	$8 \times 10^5$

<sup>a</sup> Reference 4. <sup>b</sup> Metal ion-alcoholic oxygen bond ruptures as estimated from poly(amino alcohol) reactions in aqueous solution (this work and ref 1).

lability noted for Ni-H<sub>2</sub>O bond rupture relative to Ni-NH<sub>3</sub> bond rupture as compared to the corresponding Co(II) values. The greater sensitivity of Ni(II) bond rupture rate constants to ligand strength appears to correlate directly to the greater stabilization predicted by simple crystal field theory for d<sup>8</sup> systems relative to d<sup>7</sup>.

**Evidence of an Internal Conjugate Base Effect for Cobalt(II).**—In establishing the hypothesis that an ICB effect is operative for reactions involving basic ligands reacting with aquonickel ion, the reaction rates for polyamine reactions were compared with rates predicted by eq 2 and found to be anomalously fast.<sup>4</sup> In accordance with the interpretation that this rate enhancement is attributable to hydrogen-bond formation in the outer-sphere complex between a basic donor atom of the ligand and a coordinated water molecule, the magnitude of this effect has been observed only for ligand species with protonation constants on the same order of magnitude as the corresponding constant for the monohydroxymetal ion species; furthermore, the magnitude of the effect appears to parallel the basicity of the ligand.<sup>1</sup>

For metal ions other than aquonickel ion, relevant experimental values are almost totally lacking. However, the reactions of the aquocobalt(II) ion with the poly(amino alcohols) should provide the needed data to establish the existence of such an effect for Co(II) since monohydroxycobalt(II) ion ( $\log K_{\text{H}} < 9$ ) appears to be slightly less basic than the corresponding nickel species ( $\log K_{\text{H}} \approx 9$ )<sup>9</sup> and these ligands have already been shown to exhibit an ICB effect with Ni(II).

If mechanism II represents the reaction mechanism, then, combining eq 2, 7, and 8, the values of  $E_s$  are seen to represent

$$E_s = \log k_2^{\text{Co-H}_2\text{O}}/k_{\text{Co-O}^{\text{TKED}}} \quad (9)$$

in the case of the monoprotonated ligand. For the unprotonated ligand the  $E_s$  values will then be identical except for the inclusion of the ICB term. Therefore, the difference between the  $E_s$  values for the monoprotonated and protonated forms of the same ligand should give a quantitative representation of any ICB effect inherent in the reaction of the unprotonated species with the aquocobalt(II) ion.<sup>10</sup>

As shown by the  $\Delta E_s$  values in Table V there is an apparent ICB rate enhancement of 10-fold for TKED ( $\log K_{\text{H1}} = 8.35$ ) and 13-fold for THPED ( $\log K_{\text{H1}} = 8.70$ ) in their reactions with Co(II). This contrasts with the corresponding values of fourfold and eightfold, respectively, for the same ligand species reacting with Ni(II).

Thus we have obtained the first evidence of the internal conjugate base effect for a metal ion other than Ni(II). Furthermore, the magnitude of this effect appears to parallel the basicity of the corresponding monohydroxymetal ion in the same way as it has been found to parallel the basicity of the ligand. Although more work is needed in this area, it may be possible to establish a quantitative relationship between the magnitude of the ICB effect and the difference in basicities between the ligand and metal ions.

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(9) L. G. Sillén and A. E. Martell, "Stability Constants," 2nd ed, Special Publication No. 17, The Chemical Society, London, 1964.

(10) In calculating the  $E_s$  values, the tentative assumption has been made that the bond rotation, which puts the nitrogen donor atom into a suitable position for bonding, is the same for both unprotonated and monoprotonated poly(amino alcohols). It is conceivable that proton sharing by the two nitrogens of a monoprotonated poly(amino alcohol) occurs to a significant extent and that such a shared proton could affect the bond rotation of the alcoholic substituent group which in turn would affect the  $E_s$  value of the monoprotonated species. Since the ICB effect is calculated as the difference in  $E_s$  of the monoprotonated and unprotonated species, any difference in the two rotational barrier values will be reflected in the calculated ICB effect. However, such a rotational factor would be an inherent property of the ligands and would affect the calculated ICB values of different metal ions by the same amount, thus yielding correct relative values. Therefore, since the ICB effect cannot be less than zero by definition, the fact that the ICB value for Co(II) is larger than Ni(II) indicates that Co(II) definitely exhibits an ICB effect.