the PDTA case. On the other hand, results obtained on the kinetics of base hydrolysis of the hexadentate complexes suggest that a greater contrast in the behaviors of the two groups of complexes is to be expected when the rate-determining steps are most probably S_N2 in character.[17] From this vantage point, the reactions of the aquo complexes containing pentadentate EDTA and PDTA appear to be associated with relatively strong contributions from the breaking of bonds in proceeding to the transition state. These comments are equally appropriate to the complexes $[Co(Y)H_2O]^-$ and $[Co(HY)H_2O]$.

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CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO

Stereochemistry and Mechanism of the Reactions of Ethylenediamine with Ethylenediaminetetraacetatocobaltate(III) and Propylenediaminetetraacetatocobaltate(III)

BY DARYLE H. BUSCH, K. SWAMINATHAN, AND DEAN W. COOKE

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The kinetics of the reactions of ethylenediamine with $Co(PDTA)^-$ and $Co(EDTA)^-$ have been studied over extensive ranges of *p*H and ethylenediamine concentration. All data were obtained under pseudo first order conditions. At *p*H values greater than 9, the rate constants have the form $k_{obs} = k_1(k_2K/k_{-1})(OH^-)(en)/[1 + (k_2K/k_{-1})(OH^-)]$. This expression is derivable for the series of reactions

$$Co(Y)^- + en \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Co(Y)en^-]^*$$

$$[Co(Y)en^-]^* + OH^- \overset{K}{\rightleftarrows} [Co(Y)(en\text{-}H)^{2-}]^* + H_2O$$

$$[Co(Y)(en\text{-}H)^{2-}]^* \xrightarrow{k_2} \text{5-coördinate intermediate}$$

$$\text{5-coördinate intermediate} \xrightarrow{\text{fast}} Co(Y)(en\text{-}H)^{2-}$$

$$Co(Y)(en\text{-}H)^{2-} + H_2O \rightleftarrows Co(Y)en^- + OH^-$$

where the bracketed and starred formulas imply species containing monodentate en. This scheme involves the intervention of the S_N1cb mechanism after the coördination of the first NH_2 group. All subsequent steps in the displacement of the hexadentate ligand by two additional en molecules are rapid (not rate determining), and $Co(en)_3^{3+}$ is the sole product. The isomer yields and enantiomorphic configurations of the reactants and products are completely explainable in terms of this process. Optically active $Co(EDTA)^-$ reacts to form $Co(en)_3^{3+}$ with partial *retention* of configuration, while $Co(PDTA)^-$ reacts with essentially complete *inversion*. The stereospecificity in the first case arises from statistical effects associated with the low symmetry of the complex. In the second case, $Co(PDTA)^-$, a steric effect produces the observed extreme stereospecificity. The absolute configurations of $Co(EDTA)^-$, $Co(EDTA)Br^{2-}$, $Co(EDTA)Cl^{2-}$, $Co(PDTA)^-$, $Co(PDTA)Br^{2-}$, and $Co(PDTA)Cl^{2-}$ constitute the first examples of unequivocal deduction of configuration from the kinetics and stereochemistry of a reaction of an octahedral ion.

Introduction

The most remarkable reactions observed in the chemistry of the cobalt(III) complexes of ethylenediaminetetraacetic acid (H_4EDTA) and propylenediaminetetraacetic acid (H_4PDTA) are those with ethylenediamine (eq. 1).[1-3] These

$$Co(Y)^- + 3en \longrightarrow Co(en)_3^{3+} + Y^{4-} \qquad (1)$$

reactions proceed with some retention of optical activity when active starting materials are used, even though every bond to the central cobalt(III) ion is replaced. In 50% aqueous ethyl-

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[1] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

[2] F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

[3] S. Kirschner, Y. K. Wei, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 5877 (1957).

enediamine, (−)-$KCo(EDTA)\cdot 2H_2O$ produces 56.6% L-(−)-$Co(en)_3^{3+}$, the remainder being the D-(+)-isomer, while the same reaction in anhydrous ethylenediamine produces 63% of the L-(−)-product. Similarly, the pentadentate complexes $Co(EDTA)Br^{2-}$ and $Co(EDTA)Cl^{2-}$ lead to about 55% of the more abundant isomer of the product.

Recently, investigators in two different laboratories[4,5] have carried out corresponding experiments with (−)-Co((+)-$PDTA)^-$, in both cases observing very nearly a single enantiomer as the product ((+)-$Co(en)_3^{3+}$).

As pointed out by Kirschner, Wei, and Bailar,[3] such highly stereospecific reactions as these must occur by a series of stepwise displacement processes. In earlier communications,[5,6] we have shown how the observed stereochemical relationships may be combined with structural considerations to deduce the absolute configurations of all the optically active complexes of cobalt(III) with EDTA and PDTA, and also to fix the orientation of the methyl group on the N–C–C–N chelate ring of the coördinated PDTA as equatorial.

The present report records the kinetic investigation of these reactions. The data obtained provide the basis for a detailed mechanism which serves to further clarify the nature of these uniquely stereospecific substitution reactions.

Experimental

The complexes, $NH_4[Co(EDTA)]\cdot 2H_2O$ and $K[Co(PDTA)]\cdot 3H_2O$, were prepared by the methods of Dwyer and co-workers.[2,7] Stock solutions of ethylenediamine were prepared from reagent quality en and standardized against acid.

The apparatus consisted of a Beckman DU spectrophotometer, a constant temperature bath, and a centrifugal circulating pump.

Aqueous solutions of en were utilized as the buffers. pH was adjusted by the addition of calculated amounts of nitric acid. The concentrations of standard acid and en required to give a particular pH were calculated from the equilibrium constants for en and water.

The equilibrium constants utilized are given in Table I. The constants K_1 and K_2 are defined as

$$K_1 = (\text{enH}^+)(\text{H}^+)/(\text{enH}_2{}^{2+})$$
$$K_2 = (\text{en})(\text{H}^+)/(\text{enH}^+)$$

These constants were obtained by extrapolation of the data of Everett and Pinsent[8] to an ionic strength of 0.8 and interpolation to obtain values for the appropriate temperatures. The ionization constants for water were corrected for salt concentration and temperature.[9]

TABLE I

EQUILIBRIUM CONSTANTS[a] UTILIZED IN CALCULATIONS

T, °C.	K_1	K_2	K_w
34.7	6.03×10^{-8}	1.31×10^{-10}	3.58×10^{-14}
44.3	1.05×10^{-7}	2.43×10^{-10}	7.01×10^{-14}

[a] Corrected to $\mu = 0.8$.

Sodium nitrate, previously calculated to yield an ionic strength of 0.8, was weighed into a volumetric flask. The required amounts of nitric acid and en (from stock solns.) were introduced into the flask and equilibrated at the reaction temperature. Ten ml. of the stock solution of complex was added, and the volume was adjusted with water. Both the solution of the complex and the additional solvent were maintained at the temperature of experiment. The solution was transferred immediately to the Beckman cell (1-cm.) and the optical density was measured at convenient time intervals. The solutions in the cell were replaced every 6 hr.

Rate constants were calculated by plotting log ($OD - OD_\infty$) against time. All measurements were made at 540 mμ. At pH >9.5, OD_∞ was obtained experimentally at long elapsed time, the value corresponding within permissible error to the product, $Co(en)_3^{3+}$. This value of OD_∞ also was used for calculations on experiments conducted below pH 9.5.

Results

The rates of reaction of the hexadentate complexes $Co(PDTA)^-$ and $Co(EDTA)^-$ with ethylenediamine have been measured over extensive ranges of pH (3160-fold) and ethylenediamine concentration (575-fold) in systems maintained at constant ionic strength and constant temperature. Strict pseudo first order conditions were maintained by working with ethylenediamine–nitric acid buffer systems with the total ethylenediamine always representing a swamping excess when compared to the total concentration of the cobalt complex. The observed pseudo first order constants are summarized in Tables II, III, and IV. Most of these constants are the average of two or more (as many as six) identical experiments.

It is particularly significant to note at this point that all studies conducted on the reactions with ethylenediamine above pH 9 clearly satisfy the pseudo first order rate law, proceeding to only a single product, $Co(en)_3^{3+}$. The fact that this single substance is formed in these reactions compels one to assume that the initial reaction is followed by rapid reaction with additional ethylene-

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(4) H. Irving and R. D. Gillard, *J. Chem. Soc.*, 2249 (1961).

(5) D. H. Busch and K. Swaminathan, *J. Inorg. & Nuclear Chem.*, in press.

(6) D. H. Busch and D. W. Cooke, *ibid.*, in press.

(7) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

(8) D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc.* (London), **A215**, 416 (1952).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1954, p. 488.

TABLE II

RATE CONSTANTS FOR THE REACTION OF $Co(PDTA)^-$ WITH ETHYLENEDIAMINE AT 34.7°

$\mu = 0.8$; $[Co(PDTA)^-] = 2.270 \times 10^{-3}$ *M* (time in min.).

*p*H	Total (en), *M*	Free (en), *M*	$k_{en}(en)$	$k_{enH^+}(enH^+)$	k_{calcd}[a]	k_{obsd}[a]
8.0	2.30×10^{-1}	5.27×10^{-4}	1.67×10^{-6}	1.32×10^{-4}[b]	...	1.60×10^{-4}
	3.30×10^{-1}	7.56×10^{-4}	2.39×10^{-6}	2.60×10^{-4}[b]	...	2.88×10^{-4}
9.0	1.30×10^{-1}	4.34×10^{-3}	1.34×10^{-4}	4.34×10^{-4}	6.68×10^{-4}	6.60×10^{-4}
	2.30×10^{-1}	7.68×10^{-3}	2.39×10^{-4}	7.68×10^{-4}	1.11×10^{-3}	1.20×10^{-3}
	3.30×10^{-1}	1.10×10^{-2}	3.24×10^{-4}	1.10×10^{-3}	1.54×10^{-3}	1.53×10^{-3}
9.5	1.30×10^{-1}	1.33×10^{-2}	1.25×10^{-3}	4.20×10^{-4}	2.67×10^{-3}	2.71×10^{-3}
	2.30×10^{-1}	2.35×10^{-2}	2.21×10^{-3}	7.41×10^{-4}	3.95×10^{-3}	3.80×10^{-3}
	3.30×10^{-1}	3.37×10^{-2}	3.17×10^{-3}	1.07×10^{-3}	5.24×10^{-3}	5.22×10^{-3}
10.0	1.30×10^{-1}	3.47×10^{-2}	9.16×10^{-3}	3.47×10^{-4}	1.33×10^{-2}	1.27×10^{-2}
	2.30×10^{-1}	6.13×10^{-2}	1.61×10^{-2}	6.13×10^{-4}	2.05×10^{-2}	2.21×10^{-2}
	3.30×10^{-1}	8.80×10^{-2}	2.32×10^{-2}	8.80×10^{-4}	2.79×10^{-2}	2.98×10^{-2}
10.5	1.30×10^{-1}	6.97×10^{-2}	4.22×10^{-2}	2.21×10^{-4}	4.62×10^{-2}	4.28×10^{-2}
	2.30×10^{-1}	1.23×10^{-1}	7.45×10^{-2}	3.93×10^{-4}	7.87×10^{-2}	7.44×10^{-2}
	3.30×10^{-1}	1.77×10^{-1}	1.09×10^{-1}	4.59×10^{-4}	1.13×10^{-1}	1.02×10^{-1}
11.0	1.30×10^{-1}	1.02×10^{-1}	1.05×10^{-1}	1.01×10^{-4}	1.09×10^{-1}	1.22×10^{-1}
	2.30×10^{-1}	1.81×10^{-1}	1.88×10^{-1}	1.82×10^{-4}	1.92×10^{-1}	1.89×10^{-1}
	3.30×10^{-1}	2.59×10^{-1}	2.69×10^{-1}	2.60×10^{-4}	2.73×10^{-1}	2.40×10^{-1}
11.5	2.30×10^{-1}	2.12×10^{-1}	3.04×10^{-1}	6.71×10^{-5}	3.08×10^{-1}	2.96×10^{-1}
	3.30×10^{-1}	3.04×10^{-1}	4.07×10^{-1}	9.61×10^{-5}	4.11×10^{-1}	4.59×10^{-1}

[a] The average per cent. difference in calculated and experimental values is 6% for the seventeen pertinent entries. All values are at least duplicate experimental results. In some cases as many as six repetitions were performed. [b] These values are essentially residues.

TABLE III

RATE CONSTANTS FOR THE REACTION OF $Co(PDTA)^-$ WITH ETHYLENEDIAMINE AT 44.3°

$\mu = 0.8$; $[Co(PDTA)^-] = 2.270 \times 10^{-3}$ *M* (time in min.).

*p*H	Total (en), *M*	Free (en), *M*	$k_{en}(en)$	$k_{enH^+}(enH^+)$	k_{calcd}[a]	k_{obsd}[a]
8.0	1.30×10^{-1}	2.70×10^{-4}	1.83×10^{-5}	1.61×10^{-4}[b]	...	2.09×10^{-4}
	2.30×10^{-1}	4.77×10^{-4}	3.23×10^{-5}	1.86×10^{-4}[b]	...	2.48×10^{-4}
	3.30×10^{-1}	6.85×10^{-4}	4.64×10^{-5}	1.93×10^{-4}[b]	...	2.69×10^{-4}
9.0	1.30×10^{-1}	4.09×10^{-3}	2.67×10^{-4}	5.88×10^{-4}	1.18×10^{-3}	1.07×10^{-3}
	2.30×10^{-1}	7.24×10^{-3}	4.73×10^{-4}	1.04×10^{-3}	1.81×10^{-3}	1.68×10^{-3}
	3.30×10^{-1}	1.04×10^{-3}	6.27×10^{-4}	1.50×10^{-3}	2.43×10^{-3}	2.27×10^{-3}
9.5	1.30×10^{-1}	1.26×10^{-2}	2.38×10^{-3}	5.75×10^{-4}	4.70×10^{-3}	4.71×10^{-3}
	2.30×10^{-1}	2.23×10^{-2}	4.21×10^{-3}	1.02×10^{-3}	6.97×10^{-3}	7.24×10^{-3}
	3.30×10^{-1}	3.20×10^{-2}	6.05×10^{-3}	1.46×10^{-3}	9.25×10^{-3}	9.43×10^{-3}
10.0	1.30×10^{-1}	3.33×10^{-2}	1.59×10^{-2}	4.80×10^{-4}	2.34×10^{-2}	2.27×10^{-4}
	2.30×10^{-1}	5.89×10^{-2}	2.81×10^{-2}	8.47×10^{-4}	3.60×10^{-2}	3.66×10^{-2}
	3.30×10^{-1}	8.45×10^{-2}	4.03×10^{-2}	1.22×10^{-3}	4.85×10^{-2}	4.60×10^{-2}
10.5	1.30×10^{-1}	6.79×10^{-2}	6.22×10^{-2}	3.09×10^{-4}	6.95×10^{-2}	6.18×10^{-2}
	2.30×10^{-1}	1.20×10^{-1}	1.10×10^{-1}	5.46×10^{-4}	$1.17 + 10^{-1}$	9.98×10^{-2}
	3.30×10^{-1}	1.72×10^{-1}	1.58×10^{-1}	7.84×10^{-4}	1.66×10^{-1}	1.33×10^{-1}
11.0	1.30×10^{-1}	1.01×10^{-1}	1.31×10^{-1}	1.46×10^{-4}	1.38×10^{-1}	1.59×10^{-1}
	2.30×10^{-1}	1.78×10^{-1}	2.31×10^{-1}	2.57×10^{-4}	2.38×10^{-1}	2.47×10^{-1}
	3.30×10^{-1}	2.56×10^{-1}	3.33×10^{-1}	3.68×10^{-4}	3.40×10^{-1}	3.58×10^{-1}

[a] The average per cent. difference in experimental and measured values for the fifteen pertinent entries is 8%. All experiments were performed in duplicate or triplicate. [b] These values are essentially residues.

diamine to form that product. The obvious absence of measurable concentrations of intermediates requires that the reactions be treated as involving no consecutive rate-determining processes.

Other investigations in these Laboratories[10,11] have shown that $Co(EDTA)^-$ and $Co(PDTA)^-$ react with hydroxide ion at rates comparable to

[10] D. W. Cooke and D. H. Busch, paper presented before the 137th National Meeting of the American Chemical Society, Cleveland, 1960.

[11] D. H. Busch, Y. A. Im, D. W. Cooke, and K. Swaminathan, paper presented at the Sixth International Conference on Coordination Chemistry, Detroit, 1961.

TABLE IV

RATE CONSTANTS FOR THE REACTION OF $Co(EDTA)^-$ WITH ETHYLENEDIAMINE AT 44.0°

$\mu = 0.8$; $[Co(EDTA)^-] = 2.00 \times 10^{-3}$ M (time in min.).

pH	Total (en), M	Free (en), M	k_{en}(en)	k_h	k_{calcd}	k_{exptl}
10	1.30×10^{-1}	3.33×10^{-2}	5.40×10^{-3}	3.60×10^{-3}	9.00×10^{-3}	9.39×10^{-3}
	2.30×10^{-1}	5.89×10^{-2}	9.83×10^{-3}		1.34×10^{-2}	1.45×10^{-2}
	3.30×10^{-1}	8.45×10^{-2}	1.41×10^{-2}		1.77×10^{-2}	1.98×10^{-2}
10.5	1.30×10^{-1}	6.79×10^{-2}	2.34×10^{-2}	1.14×10^{-2}	3.48×10^{-2}	3.42×10^{-2}
	2.30×10^{-1}	1.20×10^{-1}	4.19×10^{-2}		5.33×10^{-2}	5.07×10^{-2}
	3.30×10^{-1}	1.72×10^{-1}	5.94×10^{-2}		7.08×10^{-2}	5.95×10^{-2}
11.0	1.30×10^{-1}	1.01×10^{-1}	5.32×10^{-2}	3.60×10^{-2}	8.92×10^{-2}	7.49×10^{-2}
	2.30×10^{-1}	1.78×10^{-1}	9.37×10^{-2}		1.30×10^{-1}	1.17×10^{-1}
	3.30×10^{-1}	2.56×10^{-1}	1.35×10^{-1}		1.71×10^{-1}	1.54×10^{-1}
11.5	1.30×10^{-1}	1.19×10^{-1}	7.44×10^{-2}	1.14×10^{-1}	1.88×10^{-1}	1.64×10^{-1}
	2.30×10^{-1}	2.11×10^{-1}	1.32×10^{-1}		2.46×10^{-1}	3.02×10^{-1}
	3.30×10^{-1}	3.02×10^{-1}	1.89×10^{-1}		3.03×10^{-1}	4.68×10^{-1}

TABLE V

CONSTANTS FOR THE KINETICS OF THE REACTIONS OF $Co(Y)^-$ WITH ETHYLENEDIAMINE

Y	T, °C.	k_1, M^{-1} min.$^{-1}$	k_2'/k_{-1}	k_h, M^{-1} min.$^{-1}$	k_{enH^+} M^{-1} min.$^{-1}$
PDTA	34.7	1.55	2.045×10^3	3.83×10^{-3}[a]	1.31×10^{-2}
PDTA	44.3	1.61	4.23×10^3	7.00×10^{-3}[a]	3.5×10^{-2}
EDTA	44.0	6.90×10^{-1}	2.20×10^3	36.0	...

[a] This value applies at pH > 9.5. Other values are given in Table VI.

the velocities of the processes of interest here. It is not surprising that $Co(Y)OH^{2-}$ reacts to form $Co(en)_3{}^{3+}$, since the corresponding pentadentate complexes containing bromide or chloride as the monodenatate group previously have been shown to react in this manner.[1,2]

The pseudo first order rate constants are of the form

$$k_{obsd} = k_{en}(en) + k_h(OH^-)^n + k_{enH^+}(enH^+) \quad (2)$$

The first term also is dependent on hydroxide concentration, as shown in eq. 3. This expression is related to the series of reactions represented by eq. 4 and 5. The steady state assumption

$$k_{en} = k_1(k_2'/k_{-1})(OH^-)/[1 + (k_2'/k_{-1})(OH^-)] \quad (3)$$

$$Co(Y)^- + en \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(Y)en^- \quad (4)$$

$$Co(Y)en^- + OH^- \xrightarrow{k_2'} \text{products} \quad (5)$$

must be applied to the concentration of the intermediate $Co(Y)en^-$. Values of the rate constants characterizing this rate law are given in Table V.

The exponent n is retained in the second term of eq. 2 in order to include all systems in this single formulation. In the case of $Co(EDTA)^-$, the base hydrolysis rate is first order in (OH^-); however, at pH values greater than 10, the corresponding reaction of $Co(PDTA)^-$ is zero order in (OH^-). The validity of this term may be judged from Table VI, where hydrolysis constants determined during the course of this work are compared with those resulting from direct measurement.[10,11]

As Tables II, III, and IV reveal, the third term of eq. 2 dominates the rate at low pH values,

TABLE VI

BASE HYDROLYSIS CONSTANTS FOR $Co(Y)^-$—FIRST CONSECUTIVE STEP

T, °C.	pH	k_h a	 b
		$Co(PDTA)^-$	
34.7	9.0	1.0×10^{-4}	$\sim 10^{-4}$
	9.5	1.0×10^{-3}	$\sim 10^{-3}$
	10.0	3.7×10^{-3}	$3.8_3 \times 10^{-3}$
	10.5	$\sim 5.0 \times 10^{-3}$	$3.8_3 \times 10^{-3}$
44.3	9.0	3.0×10^{-4}	...
	9.5	$1.7_4 \times 10^{-3}$	...
	10.0	9.0×10^{-3}	7.0×10^{-3}
	10.5	$\sim 1.0 \times 10^{-3}$	7.0×10^{-3}
		$Co(EDTA)^-$	
44.0	10.0	25	36 (av.)[a,c]
	10.5	47	
	11.0	25	
	11.5	47	

[a] Determined as described in this work. [b] Measured directly and to be reported elsewhere.[10,11] [c] Direct measurement gives 34 M^{-1} min.$^{-1}$ for this constant.

while the first term is most significant at high *p*H. It is this first term which is most deserving of detailed study since it represents the path which leads to the remarkable stereospecific formation of $Co(en)_3^{3+}$ from active $Co(Y)^-$ (for the formation of $Co(EDTA)OH^{2-}$ is heralded by racemization[7]).

The agreement of the data with the experimental rate law is shown in Tables II, III, and IV, where values are given for the contributing constants and the calculated and observed total rate constants are compared. The measurements involving $Co(PDTA)^-$ (particularly at 34.7°) are most extensive and are considered the more reliable. The relative inconvenience caused by the competing reaction with hydroxide ion is at a minimum for the reaction of $Co(PDTA)^-$ at high *p*H because of the zero order dependence of that process on (OH^-).

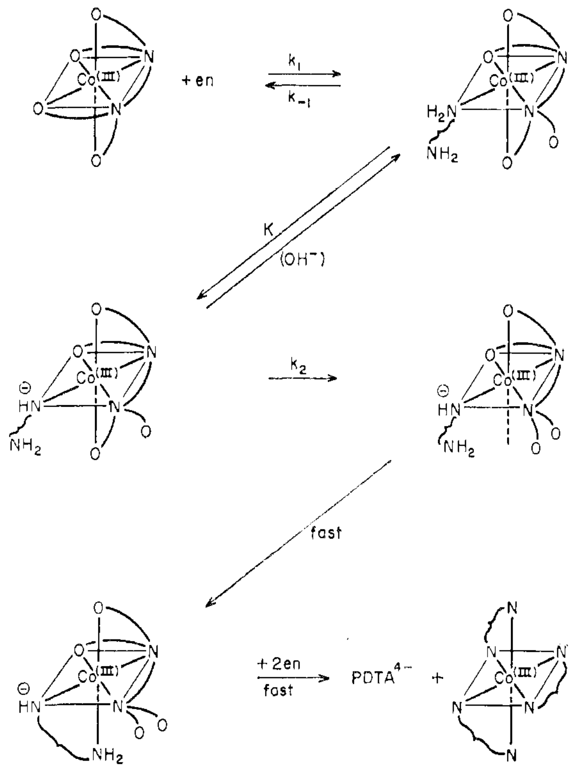

Fig. 1.—Mechanism for the displacement of $EDTA^{4-}$ or $PDTA^{4-}$ from the hexadentate cobalt(III) complex by ethylenediamine.

Discussion

The experimental rate law (eq. 2 and 3) provides gratifying insight into one of the most dramatic stereospecific processes known, the consecutive peeling away of the doubly branched, hexadentate ligand and its replacement by three moles of bidentate ligand.

The form of the first term of that rate law certainly has not been anticipated; however, it may immediately be explained and applied. Implicit in this function is the close coöperation of a molecule of ethylenediamine and a hydroxide ion in substitution of the sequestered metal ion. Also, the treatment presented above suggests that it is the ethylenediamine which first attacks the complex. The scheme presented in Fig. 1 offers a complete explanation of the rate process and accords with existing knowledge on the kinetics of similar reactions and on the nature of the stereospecific reaction. It only is necessary to replace k'_2 in eq. 2 by k_2K to obtain the forms derived under the steady state assumption from the scheme given in Fig. 1 (eq. 6).

$$k_{en} = k_1(k_2K/k_{-1})(OH^-)/[1 + (k_2K/k_{-1})(OH^-)] \quad (6)$$

It is assumed that, in its initial attack on $Co(Y)^-$, en becomes attached to the cobalt atom through only one of its nitrogen atoms; *i.e.*, it is monodentate. The attaching of a single NH_2 group to the cobalt(III) ion opens the way for an SN1cb mechanism,[12,13] and the role of the OH^- is to install the equilibrium shown as the second sequential step in Fig. 1. The conjugate base produced by that equilibrium then is capable of undergoing a rapid SN1 process which involves dissociation of a carboxyl group to form the five-coördinate intermediate. The second NH_2 group of the monodentate en molecule is bonded rapidly to complete the rate-determining process. The presence of that first en molecule then facilitates sequential SN1cb stages which involve dissociation of the most weakly bound group and its replacement by NH_2 functions of the second and third molecules of en. In this fashion, the intervention of an SN1cb mechanism after coördination of the first amino group immediately clarifies the relatively great rates at which the second and third ethylenediamine molecules are added.

Depending on the symmetry of the polydentate ligand, there may be two or more groups which are at once equivalent and most likely to dissociate. In the case of hexadentate EDTA, Weakliem and Hoard[14] have shown that the carboxyl groups which are coplanar with the N–C–C–N chelate ring are more highly strained than those occupying "apical" positions. Con-

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[12] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

[13] R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4434 (1960).

[14] H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 550 (1959).

sequently, the pentadentate intermediate should form with the NH_2 group at one of these planar points. Indeed, Smith and Hoard[15] have shown this to be the structure of $Ni(H_2EDTA)H_2O$. We have reported the mechanistic and stereochemical consequences of this restriction in an earlier communication.[6] However, the full significance can be realized better in terms of the kinetic information now at hand.

It also is useful to recall the results of studies on the conversion of complexes of the form $Co(Y)X^-$ (X^- is a monodentate anion) into the hexadentate complex.[16–19] These reactions are explained best in terms of mechanisms of SN1 type, for all available data point to the breaking of the Co–X bond as the rate-determining process. It has been shown that these reactions all proceed with complete retention of enantiomorphic configuration when optically active complexes are used. Consequently, it is to be expected that processes occurring among EDTA and PDTA complexes of cobalt(III) by way of unimolecular nucleophilic paths will proceed with retention of configuration. In this regard, the postulated mechanism for the reaction of en with $Co(Y)^-$ obviously is appropriate.

The results of studies on the kinetics of racemization of $Co(EDTA)^-$ under a variety of conditions also support the probability that the mechanism postulated here would involve retention of configuration, for all racemization paths differ sharply in their kinetic aspects from the processes to which SN1 mechanisms have been assigned.[20,21]

It appears beyond doubt that a species of the form $Co(Y)en^-$, containing pentadentate EDTA and monodentate en, is the critical intermediate in this reaction. Yet this species is very fleeting, for shortly after its formation, the hydroxide ion catalyzes the bonding of the second NH_2 group of the en to form a new chelate ring. If the monodentate bonding of en represents the formation of the *critical kinetic intermediate*, the formation of that *first en chelate ring* represents the *critical stereochemical step*. This is sharply delineated in Fig. 2, which summarizes the consequences of the three permissible points of attachment of the second extremity of the first en molecule to enter the complex.[6] It will be noted that if both apical positions are attacked in equal probability (paths 1 and 3), a racemate results, while attack solely at the second planar position (path 2) would give complete retention of configuration (retention because the absolute rotation of the natural chelate helix is the same in reactant and product). Equal participation by all three paths would produce 67% retention and 33% inversion of configuration. (The unlisted assumptions are spelled out and justified in an earlier communication.[6])

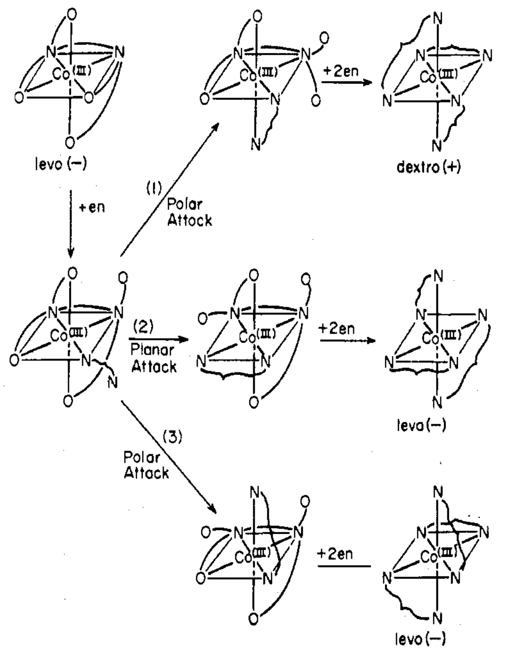

Fig. 2.—Stereochemical paths for the displacement of $EDTA^{4-}$ from the cobalt(III) complex by ethylenediamine.

It was recalled above that reactions involving the hexadentate and pentadentate EDTA complexes of cobalt(III) and ethylenediamine have been reported to produce as much as 63% of the more abundant isomer (anhydrous en). Further, the stereochemical path presented in the preceding paragraph has been used as a basis for assigning the absolute configurations of $Co(EDTA)^-$, $Co(EDTA)Br^-$, and $Co(EDTA)Cl^-$.[6] The inevitability of the assigned configurations resides in the fact that the contrary set of relationships could be derived only from arbitrary, complex, and unjustifiable assumptions. The

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(15) G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.* **81**, 556 (1959).

(16) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

(17) M. L. Morris and D. H. Busch, *J. Phys. Chem.*, **63**, 340 (1959).

(18) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).

(19) K. Swaminathan and D. H. Busch, *Inorg. Chem.*, **1**, 256(1962).

(20) Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).

(21) D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962).

reaction of $Co(EDTA)^-$ with OH^- has been found[10,21] to produce racemization, so that the reaction in water (eq. 2) will always lead to diminished yields of the excess isomer. Assuming that 50% aqueous en is 7.9 M with respect to en and 2.6×10^{-2} M with respect to OH^-, the data of Table IV and eq. 2 lead to the prediction that the yield of excess isomer will be reduced (44°) to 57% (reported, 56.6%).

From these several considerations it may be concluded that the reaction of $Co(EDTA)^-$ with ethylenediamine proceeds by the mechanism of Fig. 1, but that all three of the remaining carboxyl groups of EDTA are replaced with essentially equal probability as the second terminus of the first en molecule enters the coördination sphere (Fig. 2). The optical isomer in excess in the product $Co(en)_3^{3+}$ has the same absolute configuration as the starting material.

Since $Co(EDTA)Cl^{2-}$ and $Co(EDTA)Br^{2-}$ are converted into $Co(EDTA)^-$ with complete retention of configuration, the configurational relationships may be delineated

$$\begin{tikzcd} \text{L-}(-)\text{-Co(EDTA)}^- \arrow[dd] & \text{L-}(+)\text{-Co(EDTA)Cl}^{2-} \arrow[l] \\ & \text{L-}(+)\text{-Co(EDTA)Br}^{2-} \arrow[dl] \\ \text{L-}(-)\text{-Co(en)}_3^{3+} & \end{tikzcd}$$

where L represents the absolute configuration of the chelate helix, based on the traditional naming of the isomer of $Co(en)_3^{3+}$, which is negatively rotating at the mercury green line. All other signs represent rotations at the same wave length. The absolute configuration of $Co(en)_3^{3+}$ was determined by a refined X-ray method.[22]

As shown independently by Irving and Gillard[4] and in our Laboratories,[5] en also exhibits a stereospecific displacement reaction with active $Co(PDTA)^-$. We have pointed out that the rotatory dispersion curves[6,10] of $(-)$-$Co(EDTA)^-$ and $(-)$-$Co((+)\text{-}PDTA)^-$ are essentially identical, establishing identity in absolute configuration. However, the most abundant isomer (almost 100%) from the reaction of $(-)$-$Co((+)\text{-}PDTA)^-$ with en has the opposite configuration to that obtained from $(-)$-$Co(EDTA)^-$ (eq. 7 and 8). Thus, the latter is an inversion in a very real sense for the absolute nature of the helix is reversed.

$$(-)\text{-Co(EDTA)}^- + 3\text{en} \longrightarrow (-)\text{-Co(en)}_3^{3+} + \text{EDTA}^{4-} \quad (7)$$

$$(-)\text{-Co((+)PDTA)}^- + 3\text{en} \longrightarrow (+)\text{-Co(en)}_3^{3+} + (+)\text{-PDTA}^{4-} \quad (8)$$

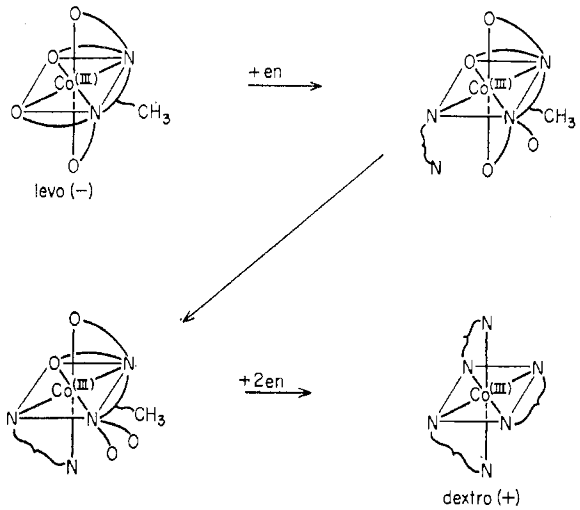

Fig. 3.—Stereochemical path for the displacement of $PDTA^{4-}$ from the cobalt(III) complex by ethylenediamine.

The fact that the model presented here may be applied to provide an explanation for this still more unusual stereochemical result provides very strong support for its validity. Figure 1 was, in fact, constructed in terms of this particular case. We previously have established the equatorial orientation (with respect to the chelate ring) of the CH_3 group, in conjunction with discussions on absolute configuration[6] and isomer distribution.[23] The interactions which militate against the stability of the diastereoisomer having an axial CH_3 group also will serve to individualize each of the carboxyl groups of the hexadentate PDTA ligand. One immediately expects the planar carboxyl group nearest the CH_3 group to be displaced first. Thereafter, one must conclude with regard to the second point of attack. This also may be resolved easily for, if the other planar group were replaced second (exclusively), 100% retention (Fig. 2), not inversion, of configuration would follow. Recalling that the EDTA case was handled at this point by assuming all three remaining carboxylates to be identical, and then reflecting on the steric source of the distinction among the carboxyl groups in the PDTA case, one is driven to consider the removal of the axially oriented carboxyl group nearest the CH_3 group. Figure 3 reveals how this order of displacement will lead to inversion of configuration. Figure 3 implies the additional assumption that the structure of the intermediate of the composition $Co(PDTA)(en)_2^-$ is such that the bidentate PDTA is linked through the two

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[22] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957); *Acta Cryst.*, **8**, 729 (1955).

[23] Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3362 (1961).

tertiary nitrogen atoms. A precedent for such structures is found in the compounds of platinum(II) and palladium(II).[24] There appear to be no known bidentate derivatives of PDTA or EDTA for which other structures have so much as been proposed. It is not unlikely that all four carboxyl groups invariably are replaced before the nitrogen atoms for both PDTA and EDTA.

A point of difference in the reactions of Co(PDTA)$^-$ and of Co(EDTA)$^-$ requires emphasis. The former (Co(PDTA)$^-$) exhibits stereospecificity of the sort usually expected, that derived from steric repulsion. In contrast, the stereospecificity of the reaction of Co(EDTA)$^-$ with en derives from the low symmetry of the complex and the odd number of kinetically equivalent paths. In a sense, the latter is derived statistically. The contention that the PDTA case truly involves steric effects is supported further by the fact that reaction (k_{en}) is 2 to 3 times faster than the corresponding process for the EDTA complex, although the latter involves more kinetically equivalent paths. It is concluded that the crowding associated with the peripheral methyl group stabilizes the five-coördinate intermediate.

Acknowledgment.—The financial support of the National Science Foundation is gratefully acknowledged.

[24] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.* **78**, 716 (1956).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

Infrared Investigation of Certain Imidazole Derivatives and their Metal Chelates[1]

BY T. J. LANE, C.S.C., I. NAKAGAWA,[2] J. L. WALTER, C.S.C., AND A. J. KANDATHIL

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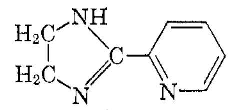
The infrared spectra of 2-(2-pyridyl)-imidazoline, 2-(2-pyridyl)-benzimidazole, 2-(*o*-hydroxyphenyl)-imidazoline, 2-(*o*-hydroxyphenyl)-benzimidazole, and their metal chelates have been measured in the region between 5000 and 300 cm.$^{-1}$. The observed bands are assigned by comparison with the frequencies of imidazole, of 1,2-dichloroethane, and of *ortho*-disubstituted benzene and pyridine for which normal coördinate analysis has been done. The spectra of metal chelates are interpreted by correlation with those of the ligands. The infrared spectra can be reasonably explained on the basis of the usually accepted structure in which chelation takes place through the unsaturated nitrogen atom and through the nitrogen atom of the pyridine ring or the phenolic oxygen atom. Assignments of metal–oxygen and metal–nitrogen stretching frequencies are made by comparing the spectra of the ligands with those of their metal chelates.

Introduction

Previous work on the infrared spectra of imidazole derivatives and their metal chelates dealt primarily with assignments of the bands in the 3-μ region in order to observe the effect of coördination on the N–H stretching frequency.[3] A further study was desirable because these compounds are becoming increasingly more important as analytical, biochemical, and anticancer reagents. In the present investigation the infrared spectroscopic measurements of 2-(2-pyridyl)-imidazoline (I), 2-(2-pyridyl)-benzimidazole (II), 2-(*o*-hydroxyphenyl)-imidazoline (III), and 2-(*o*-hydroxyphenyl)-benzimidazole (IV) and their Cu(II), Ni(II), Co(II), and Zn(II) chelates was undertaken in the 2–35-μ region in order to make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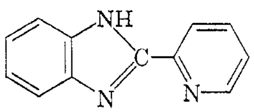
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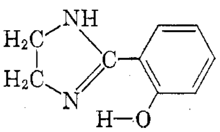
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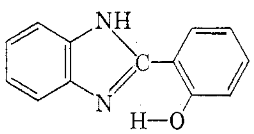
IV

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[1] Presented in part at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1961.

[2] Faculty of Science, University of Tokyo, Tokyo, Japan. Research Associate at the University of Notre Dame, summer of 1960.

[3] T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956).