

Figure 1.—Geometrical isomers of *trans*-nitropyridinebis( $\beta$ -diketonato)cobalt(III); R = CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>OCH<sub>3</sub>.

forms<sup>6</sup> (in addition to their three optical antipodes). The isomers are displayed in Figure 2. The “*cis*” and “*trans*” isomers both have a set of equivalent methyls while the “*cis*” (t) isomer has nonequivalent methyl groups (and R groups). The chemical shifts of the methyl protons could be different in each case. The nmr spectrum could then show four methyl resonances for a mixture of the three isomers.<sup>28</sup> The nmr spectrum of [Co(macac)<sub>2</sub>en]<sup>+</sup> shows two clearly resolved resonances each for the ether methyl and methylene protons as well as for the methyl protons. Each pair of lines shows approximately a 3:2 intensity ratio. This latter point rules out the possibility of the material being the pure “*cis*” (t) isomer since the ratio in this case would be 1:1. The nmr spectrum of [Co(prac)<sub>2</sub>en]<sup>+</sup> shows a complex pattern of lines. There are at least two superimposed ethyl patterns and the methyl proton resonance shows three values. For both [Co(dik)<sub>2</sub>en]<sup>+</sup> ions the methine proton resonances are not split. The above data are consistent with the notion that the

(28) J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc.*, 1749 (1966).

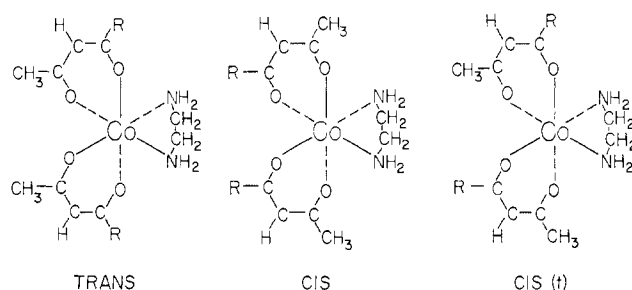


Figure 2.—Geometrical isomers for the ethylenediaminebis( $\beta$ -diketonato)cobalt(III) cation; R = CH<sub>2</sub>CH<sub>3</sub> or CH<sub>2</sub>OCH<sub>3</sub>.

materials examined are a mixture of the three possible isomers. The distribution should be close to statistical since there should be very little free energy difference between them.<sup>6</sup> It is interesting to note that there is apparently a substantial difference in chemical shifts for methyl protons exclusively *cis* to the ethylenediamine and for methyl protons *trans* to it. This is not observed for [Co(acac)<sub>2</sub>en]<sup>+</sup>. The reason for this may involve the differing steric interactions of the ethyl and methoxymethyl groups as opposed to a methyl group. Further comment on these very interesting isomers must await their separation and individual characterization. Work of this sort is in progress.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY OF ROME, ROME, ITALY

## The Stepwise Base Hydrolysis of *cis*- and *trans*-Diacetatobis(ethylenediamine)cobalt(III) Ions<sup>1</sup>

BY VINCENZO CARUNCHIO, GABRIELLO ILLUMINATI, AND GIANCARLO ORTAGGI

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Our previous knowledge on the stepwise hydrolysis of *cis*- and *trans*-diacetatobis(ethylenediamine)cobalt(III) ions is complemented by the determination of the kinetics of the reaction of the intermediate acetatohydroxo complexes and by a study of the stereochemical course. In both *cis* and *trans* configurations the second step is found to be slower than the first one. Also, a nearly complete *trans*  $\rightarrow$  *cis* change is observed in the second step, while *cis* or *trans* configurations are retained in the other cases. The results are compared with several other data of the same type of reactions and are found to be consistent with a dissociative mechanism.

### Introduction

Previous work<sup>2</sup> has dealt with the base hydrolysis of the first functional group of dicarboxylato complexes of the general type Co(en)<sub>2</sub>(OCOR)<sub>2</sub><sup>+</sup>, the R groups

(1) (a) Structure and Reactivity in Octahedral Complexes, Part IX; (b) Previous paper in this series: G. Illuminati and F. Monacelli, *J. Inorg. Nucl. Chem.*, in press.

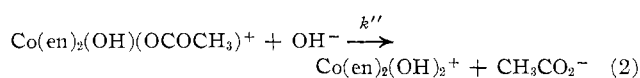
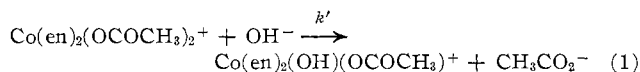
(2) V. Carunchio, G. Illuminati, and F. Maspero, *ibid.*, **28**, 2693 (1966).

being of widely different structure. It seemed of interest, at least in one typical case, to consider the reaction of the second functional group for a more complete picture of the reaction kinetics. In this paper we report some observations on the kinetics and stereochemical course of the consecutive base hydrolysis reactions of the *cis*- and *trans*-diacetato complexes as described by eq 1 and 2.

TABLE I  
 SPECTRAL DATA FOR SOME COMPLEX IONS OF THE TYPE  $\text{Co}(\text{en})_2\text{AB}^{n+}$ 

Complex ion	<i>cis</i> Isomers		<i>trans</i> Isomers		
	Band I	Band II	Band Ia	Band Ib	Band II
$\text{Co}(\text{en})_2(\text{OH}_2)\text{OCOCH}_3^{2+}$	2.00 (498)	1.89 (360)	1.71 (543)	1.51 (445)	1.82 (355)
$\text{Co}(\text{en})_2(\text{OH}_2)_2^{3+ a}$	1.85 (495)	1.82 (355)	1.52 (545)	1.57 (441)	1.73 (349)
$\text{Co}(\text{en})_2(\text{OH})_2^{+ a}$	1.97 (517)	2.01 (370)	1.72 (527)		1.73 (380)
$\text{Co}(\text{en})_2(\text{OH})\text{OCOCH}_3^+$	2.01 (512)	1.93 (365)	1.76 (527)		1.88 (365)
$\text{Co}(\text{en})_2(\text{OCOCH}_3)_2^+$	2.18 (505)	1.99 (360)	1.71 (540)		1.83 (360)

<sup>a</sup> Data from J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).



$k'$  and  $k''$  are observed second-order rate constants.

### Results and Discussion

Of the isomeric aquoacetato complexes, *trans*- $[\text{Co}(\text{en})_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$  was obtained by the time-controlled hydrolysis of the *trans*-diacetato complex in aqueous solution, and *cis*- $[\text{Co}(\text{en})_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$  by the isomerization of the *trans* complex in methanol solution. Spectral characterization of these compounds and of the corresponding hydroxo derivatives was made by comparison with related complexes as shown in Table I and Figure 1.

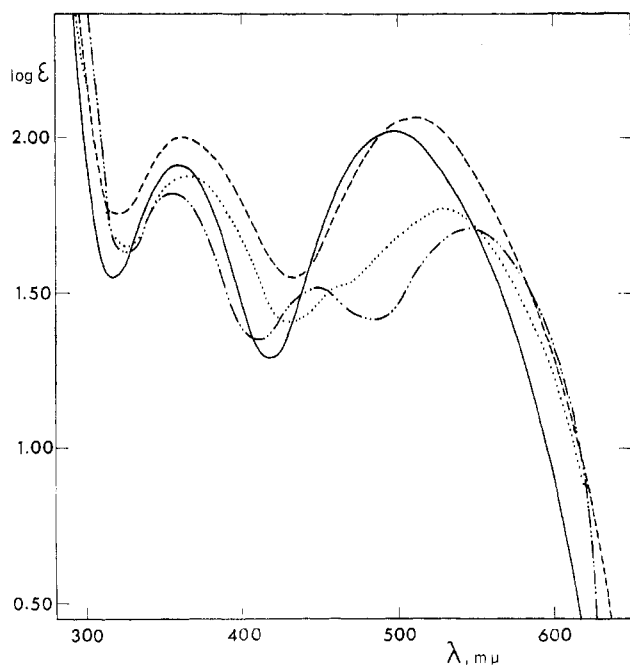


Figure 1.—Absorption spectra of the *cis* (—) and *trans* (---) isomers of  $[\text{Co}(\text{en})_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$  and of the *cis* (- · - ·) and *trans* (· · · ·) isomers of  $[\text{Co}(\text{en})_2(\text{OH})\text{OCOCH}_3]\text{ClO}_4$ .

It is of interest to note that the split band I known for the *trans* isomers of this type is better resolved in the case of the aquo complexes (well-defined peak for band Ib) than in the case of the hydroxo and the diacetato complexes.

As established in previous papers,<sup>2,3</sup> the base hydrolysis of both the diacetato and the hydroxoacetato complexes is first order in complex and first order in hydroxide ion. The kinetics were studied by a potentiometric method in the concentration range of  $4.5\text{--}9 \times 10^{-3} M$  in both substrate and hydroxide ion. The second-order rate constants at diverse temperatures and the activation parameters are reported in Table II.

TABLE II  
KINETIC DATA FOR THE BASE HYDROLYSIS OF SOME COMPLEX IONS OF THE TYPE  $\text{Co}(\text{en})_2\text{A}(\text{OCOCH}_3)^+ a$

A	$10^3k, M^{-1} \text{sec}^{-1}$			$E_a,$ kcal/mole	$\Delta S^\ddagger,$ eu
	25°	35°	45°		
<i>cis</i> - $\text{CH}_3\text{CO}_2$	2.41 <sup>b</sup>	10.3	38.0	26.2	18.4
<i>cis</i> -OH	0.815 <sup>c</sup>	3.05	13.1	26.4	15.8
<i>trans</i> - $\text{CH}_3\text{CO}_2$	5.06 <sup>b</sup>	23.5	81.8	26.9	22.4
<i>trans</i> -OH	0.126 <sup>c</sup>	0.588	2.41	28.4	21.4

<sup>a</sup> The kinetic experiments were run in duplicate except when otherwise indicated. The tabulated rate constants correspond to experiments run at the same concentrations in all cases ( $4.5 \times 10^{-3} M$  in complex and  $9 \times 10^{-3} M$  in hydroxide ion) for a straightforward structural comparison at the same ionic strength, which was derived from the presence of the two reactants only. The probable errors in  $k$ ,  $E_a$ , and  $\Delta S^\ddagger$  were found to be 2.1%, 0.6 kcal/mole, and 2 eu, respectively. <sup>b</sup> See ref 2. <sup>c</sup> Run in triplicate.

A first inspection of these data shows that whatever is the stereochemical course of the hydrolysis of the diacetato complexes, the second step (eq 2) is slower than the first one (eq 1). The rate difference is such as to confirm the validity of the reported determination of the rate constant for reaction 1 as based on the early part of the over-all process.<sup>2</sup>

When the *trans*-diacetato complex undergoes base hydrolysis, its configuration remains essentially unchanged, and since in this case the value of the  $k'/k''$  ratio is sufficiently large ( $5.06/0.126 = 40.2$ , see Table II), the *trans*-acetatohydroxo complex can be isolated from the reaction mixture.

Starting from the *cis*-diacetato complex the isolation of the intermediate product was attempted without any success and the reaction mixtures at diverse reaction times were accordingly found to consist of all three possible species, *i.e.*, the intermediate in the presence of both the initial and final complexes, by chromatographic techniques. These results indicate that the  $k'/k''$  ratio is close to the lowest value of the possible

(3) F. Aprile, V. Caglioti, and G. Illuminati, *J. Inorg. Nucl. Chem.*, **21**, 325 (1961).

TABLE III  
 SECOND-ORDER RATE CONSTANTS ( $M^{-1} \text{ SEC}^{-1}$ ) FOR THE BASIC HYDROLYSIS OF  $\text{Co}(\text{en})_2\text{AX}^{n+}$  IONS<sup>a</sup>

X	A	$k'$		A	$k''$		$k'/k''$ ratio	
		<i>trans</i>	<i>cis</i>		<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
F	F	64 <sup>b</sup>	...	OH	0.0092 <sup>c</sup>	0.072 <sup>d</sup>	6960	...
Cl	Cl	3,160 <sup>e</sup>	710 <sup>e</sup>	OH	0.56 <sup>f</sup>	11.9 <sup>e</sup>	5650	60
Cl	Br	5,300 <sup>e</sup>	840 <sup>e</sup>	OH	0.56 <sup>f</sup>	11.9 <sup>e</sup>	9450	71
Br	Cl	12,100 <sup>e</sup>	2640 <sup>e</sup>	OH	7 <sup>e</sup>	86 <sup>e</sup>	1730	31
Br	Br	12,000 <sup>b</sup>	...	OH	7 <sup>e</sup>	86 <sup>e</sup>	1710	...
CH <sub>3</sub> CO <sub>2</sub>	CH <sub>3</sub> CO <sub>2</sub>	0.0506 <sup>g</sup>	0.0241 <sup>g</sup>	OH	0.00126	0.00815	40	3
NO <sub>2</sub>	NO <sub>2</sub>	0.763 <sup>h</sup>	0.208 <sup>h</sup>	OH	0.0346 <sup>h</sup>	0.245 <sup>h</sup>	24	0.9

<sup>a</sup> Data at 25.4° except as indicated. <sup>b</sup> Data from R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956), at 25°. <sup>c</sup> Data from ref 7 at 25.2°. <sup>d</sup> Data from ref 7 at 20.8°. <sup>e</sup> See ref 8b. <sup>f</sup> Data from ref 8b at 25°. <sup>g</sup> Data from ref 2 at 25°. <sup>h</sup> Data from J. B. Clarke, K. A. Pilkington, and P. J. Staples, *J. Chem. Soc., Sect. A*, 153 (1966), at 34.6°.

ones derived from the rate constants listed in Table II at any given temperature (for example,  $2.41/0.815 = 9.26$  at 25°) and, therefore, that the *cis*-diacetato complex yields a *cis*-acetatohydroxo product. The visible spectra would also seem to confirm this conclusion since no apparent split bands typical of *trans* complexes were observed from the reaction mixtures.

As to the subsequent step of the hydrolysis, we allowed the reaction of the *cis* and *trans* complexes to occur rapidly to 10 half-lives in an excess of sodium hydroxide in order to avoid the establishment of isomerization equilibria in the hydrolysis products. The solution was then made acid and the *cis/trans* ratio of diaquo complexes was calculated from spectrophotometric data by the method of Ingold, *et al.*<sup>4</sup> Separate experiments showed that the acidification takes place without isomerization, so the analysis of the diaquo complexes could be related directly to the *cis/trans* composition of the primary dihydroxo product. The results obtained showed that both *cis*- and *trans*- $\text{Co}(\text{en})_2(\text{OH})\text{OCOCH}_3^+$  yield the *cis*-dihydroxo complex in about 95%.

In view of the tendency of the *trans* complexes to isomerize under certain conditions, it seemed worthwhile to check that no isomerization occurred prior to the base hydrolysis of *trans*- $\text{Co}(\text{en})_2(\text{OH})\text{OCOCH}_3^+$ . To this end the reaction was also followed by the spectral change at 410  $m\mu$ . Since the extinction coefficient for the *cis*-acetatohydroxo complex is greater than that of the starting *trans* isomer and that of the *cis*-dihydroxo product is smaller, any preliminary isomerization would alter the optical density *vs.* time curve, which was in fact smooth according to its regular second-order course. Furthermore, the rate constant for the hydrolysis of the *trans*-acetatohydroxo to the *cis*-dihydroxo complex, as determined by the spectral method, was found to be  $0.137 \times 10^{-2} M^{-1} \text{ sec}^{-1}$ , *i.e.*, equal to that obtained by the potentiometric method within experimental error. Thus, we can say that isomerization accompanies, but does not precede, hydrolysis.

Previous studies<sup>1b,2,8</sup> on the base hydrolysis of carboxylato ligands of amino complexes of  $\text{Co}(\text{III})$  have indicated the ionization *via* conjugate base ( $\text{SN1cb}$ )<sup>5</sup>

(4) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

as the most likely mechanism for this reaction. However, much of the reactivity behavior of complex ions of the series  $\text{Co}(\text{en})_2\text{AX}^{n+}$  ( $\text{X} =$  leaving ligand) has found reasonably satisfactory interpretations with this mechanism as well as the alternative one based on a bimolecular attack of some kind by the hydroxide reagent.<sup>6</sup>

The present results have a bearing on both the problem of structure-reactivity correlations and that of the stereochemical course of the reactions. As to the former problem, change from the acetato to the hydroxo group in the ligand A has a rate-depressing effect with either *cis* or *trans* configuration. It is of interest to note from the rate data of Table II that the reactivities are *more* broadly spaced in the *trans* than in the *cis* series. This phenomenon is common to a number of available cases as reported in Table III and is probably due to the fact that the hydroxo group is being compared to an essentially uniform category of electron-attracting ligands (F, Cl, Br, RCO<sub>2</sub>, NO<sub>2</sub>). We believe that this general picture is not in contrast with an  $\text{SN1cb}$  mechanism. It may be argued<sup>7</sup> that  $\pi$  bonding of the hydroxo group is expected to play a role in the dissociation step of such a mechanism and, if so, to be rate enhancing. However, the  $\pi$ -bonding effect of the nitrogen atoms of the chelating en ligands in their conjugate base form is markedly stronger than that of the hydroxo group, so the insertion of the latter into the complex should not bring any important effect of this kind. Then, there may remain a predominant influence of the polar effect of the ligand A on the first stage of the reaction (acid-base preequilibrium) which would be a major factor for the observed reactivity order.

As to the stereochemical results, again reasonable explanations have been proposed with both mechanisms.<sup>8,9</sup> A detailed analysis in favor of the  $\text{SN1cb}$  mechanism has recently been offered by Pearson and Basolo.<sup>10</sup> Jordan and Sargeson<sup>11</sup> have compared the stereochemical course for a number of cases of complexes of the type  $\text{Co}(\text{en})_2\text{AX}^{n+}$  and found essentially constant isomeric proportions for those complexes ex-

(6) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **194**, 344 (1962).

(7) S. C. Chan and O. W. Lau, *J. Chem. Soc., Sect. A*, 1800 (1966).

(8) (a) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962); (b) S. C. Chan and J. Miller, *Rev. Pure Appl. Chem.*, **15**, 11 (1965); see, also, ref 6.

(9) R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

(10) R. G. Pearson and F. Basolo, *Inorg. Chem.*, **4**, 1522 (1965).

(11) R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

pected to hydrolyze *via* a common dissociation intermediate. Our data for  $\text{Co(en)}_2(\text{OH})\text{OCOCH}_3^+$  also fit in this picture, since about 95% *cis*-hydroxo product was obtained from both isomers in accord with the behavior of other complexes of the type  $\text{Co(en)}_2(\text{OH})\text{X}^+$ . Such observations are consistent with an  $\text{S}_{\text{N}}1\text{cb}$  mechanism, and they will be further discussed in a subsequent paper in connection with the reactivity of bis-dipyridyl complexes.

### Experimental Section

**Materials.**—*cis*- and *trans*- $[\text{Co(en)}_2(\text{OCOCH}_3)_2]\text{ClO}_4$  were prepared as described by Linhard and Stirn.<sup>12</sup> The other chemicals were reagent grade.

***trans*-Aquoacetatobis(ethylenediamine)cobalt(III) Perchlorate.**—A solution of 0.25 g of NaOH in 1 ml of water was slowly poured dropwise, with continuous stirring, into a solution of 2 g of *trans*- $[\text{Co(en)}_2(\text{OCOCH}_3)_2]\text{ClO}_4$  in *ca.* 4 ml of water. The reaction was carried out at 55° for 20 min. After cooling at 0°, the solution was treated with 0.84 ml of 70%  $\text{HClO}_4$  and 0.5 g of  $\text{NaClO}_4$ , and then kept in a refrigerator at about 0°. After 2 hr, a first crop of crystals was removed by filtration and discarded, the resulting mother liquor was kept again in the refrigerator for about 3 days, and the needles thus precipitated were collected on filtration, washed with absolute ethanol and ether, and finally air dried at room temperature; yield, 0.46 g (20%).

*Anal.* Calcd for  $[\text{Co(en)}_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$ : Co, 12.93; C, 15.80; N, 12.31; H, 4.62;  $\text{ClO}_4$ , 43.71;  $\text{H}_2\text{O}$  coordinated, 3.96. Found: Co, 12.91; C, 15.70; N, 12.17; H, 5.25;  $\text{ClO}_4$ , 43.61;  $\text{H}_2\text{O}$  coordinated, 4.0.

***cis*-Aquoacetatobis(ethylenediamine)cobalt(III) Perchlorate.**—A solution of 0.5 g of *trans*- $[\text{Co(en)}_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$  in 30 ml of absolute methanol was kept in a thermostat at 25° and *trans* to *cis* isomerization was allowed to occur. The reaction was followed by means of spectrophotometric measurements and was completed after 3 days. The solution was evaporated to dryness at room temperature, and the crystalline residue (needles) was washed with absolute ethanol; yield, 0.4 g (80%).

*Anal.* Calcd for  $[\text{Co(en)}_2(\text{OH}_2)\text{OCOCH}_3](\text{ClO}_4)_2$ :  $\text{H}_2\text{O}$  coordinated, 3.96. Found:  $\text{H}_2\text{O}$  coordinated, 3.93.

**Chromatographic Characterization.**—The complexes were analyzed by an ion-exchange chromatographic method, as described elsewhere,<sup>13</sup> on Amberlite SA-2 paper (Rohm and Haas). A solution of 2.5 M  $\text{NaClO}_4$  was employed for the elution of the *cis* isomer at pH 4.0 and of the *trans* isomer at pH 1.5. The charge of the complexes present in the solution was deduced from the position of the spots.

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

(13) V. Carunchio, G. G. Strazza, G. Ortaggi, and C. Padiglione, *J. Inorg. Nucl. Chem.*, **27**, 841 (1965).

**Spectrophotometric Measurements.**—Absorption spectra in the ultraviolet and visible regions were obtained with a Beckman Model DU spectrophotometer. Solutions of the complexes were about  $3.5 \times 10^{-3}$  M. The absorbances of such solutions were measured in 10-mm silica cells, inserted in a constant-temperature cell regulated at 0°.

**Rate Measurements.**—In the case of the basic hydrolysis reactions, a solution of a calculated amount of complex in  $\text{CO}_2$ -free water was prepared in a ground-glass stoppered container. After thermal equilibration at a given temperature, a solution of 0.1 N sodium hydroxide was added, and the final concentrations were *ca.*  $4.5 \times 10^{-3}$  M in the complex and *ca.*  $9 \times 10^{-3}$  M in NaOH. At convenient time intervals a number of samples were withdrawn and the reaction was quenched in an excess of perchloric acid. The resulting solution was back-titrated with a  $\text{CO}_2$ -free 0.01 N sodium hydroxide solution, by a potentiometric method using a Beckman Model G pH meter with conventional external glass and saturated calomel electrodes.

**Isolation Experiments in the Hydrolysis of the *cis*-Diacetato Complex.**—In order to isolate *cis*- $\text{Co(en)}_2(\text{OH})\text{OCOCH}_3^+$  as an intermediate of the gradual base hydrolysis of *cis*- $\text{Co(en)}_2(\text{OCOCH}_3)_2^+$ , a 0.5 M solution of the latter complex was treated with the equivalent amount of NaOH solution at 25°. Time intervals (5–15 min) were selected on the basis of the known value of the first reaction rate constant.<sup>2</sup> Some attempts to precipitate the intermediate were carried out from the basic solutions both directly and after acidification with  $\text{HClO}_4$ . No precipitate appeared from these fractions when treated with  $\text{NaClO}_4$  and kept in a refrigerator for some days. Moreover, ion-exchange chromatographic experiments showed that the starting complex and the mono- and dihydroxo complexes are all present in the examined fractions. Absorption spectra of the same samples exhibit the behavior of the *cis* compounds of this series,  $\lambda_{\text{max}}$  values being 510 and 365 m $\mu$ . The spectra of the acidified solutions are similar.

Other attempts were carried out from the acid hydrolysis solutions of *cis*- $\text{Co(en)}_2(\text{OCOCH}_3)_2^+$ . A sample withdrawn after about 30 min from a reaction mixture at pH 4.0 and 25° shows the same absorption spectrum as an authentic specimen of the aquoacetato complex. Accordingly, by ion-exchange chromatography the solution was found to consist of +2 charged species only. Attempts to isolate the complex by precipitation were unsuccessful. However, when the calculated amount of an NaOH solution was added to the solution and a base hydrolysis reaction was followed, the value of the observed second-order rate constant turned out to be the same as that determined from experiments starting with an authentic specimen of the intermediate complex.

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