Inorg. Chem. **1980**, *19*, 1091–1093

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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 16. Preparation, Acid-Catalyzed Aquation, and Base Hydrolysis of *trans*-Chloro(carbonato)bis(ethylenediamine)cobalt(III) Chloride Monohydrate[1]

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All monodentate (carbonato)cobalt(III) complexes so far prepared in the pure solid form are of the type $Co(N_5)OCO_2^+$, where N_5 designates various nitrogen-donor ligand groups ranging from $(NH_3)_5$ to the straight-chain entity tetraethylenepentamine (tetren). A previously reported general method of preparation[2] for complexes of this type makes use of the rapid uptake of molecular carbon dioxide by the corresponding hydroxoamine species under carefully controlled conditions. By an extension of this preparative method, we have now succeeded in isolating for the first time[3] the stable mixed-ligand compound *trans*-$[Co(en)_2(OCO_2)Cl]H_2O$ (en ≡ ethylenediamine). Studies have been made of the kinetics of its hydrolysis in acidic solution, which results in decarboxylation, and in mildly basic solution, which leads to chloride release. The mechanistic conclusions derived from the data are compared with the existing information concerning related systems.

Experimental Section

Preparation of Complexes. All chemicals were of reagent grade, and the distilled water was deionized and degassed before use. *trans*-$[Co(en)_2(OH)Cl]Cl{\cdot}H_2O$ was prepared as described previously.[4] A weighed sample of this compound is dissolved in ice-cooled CO_2-saturated aqueous $(NH_4)_2CO_3$ solution (pH ~8), and CO_2 is bubbled through the solution until the pH decreases to ~7. Addition of ice-cold 1:1 ethanol/ether mixture precipitates a blue-black solid. This is purified by redissolving in a minimum of water, reprecipitating with ethanol/ether mixture, filtering, and washing the precipitate with ether, while maintaining the system at 0 °C. The final dark blue precipitate after drying in vacuo yielded the following CHN analysis. Anal. Calcd for $[Co(en)_2(OCO_2)Cl]H_2O$: C, 20.52; H, 6.20; N, 19.15. Found: C, 20.63; H, 6.54; N, 19.28. The significant spectral features of the compound were determined on a Cary 118 spectrophotometer and are recorded in Figure 1, together with data for other related complexes of interest in this study. It is obvious from the spectral comparisons that no isomerization from the trans to the cis form occurs during CO_2 uptake, as expected for such a rapid reaction. A similar situation exists[5] in the CO_2 uptake by *trans*-$[Co(en)_2(OH_2)(OH)]$.

The pure compound *trans*-$[Co(en)_2OCO_2)Cl]H_2O$ is hygroscopic and somewhat unstable, so it was prepared in solution as needed for each rate experiment. In a typical experiment, the procedure was as follows: Sodium bicarbonate (84 mg) is dissolved in 7 mL of H_2O at 0 °C, to which is added 12 drops of ice-cold 1.2 N $HClO_4$. To this solution is added 71.2 mg of *trans*-$[Co(en)_2(OH)Cl]Cl{\cdot}H_2O$, and, after being shaken for 2 min, the mixture is poured into an ice-jacketed cation-exchange column (Dowex 50W-X8, Na form, 50–100 mesh). The column is eluted with ice water to obtain the desired uncharged chloro–carbonato species in aqueous solution, uncontaminated by the parent chloro–hydroxo complex ion.

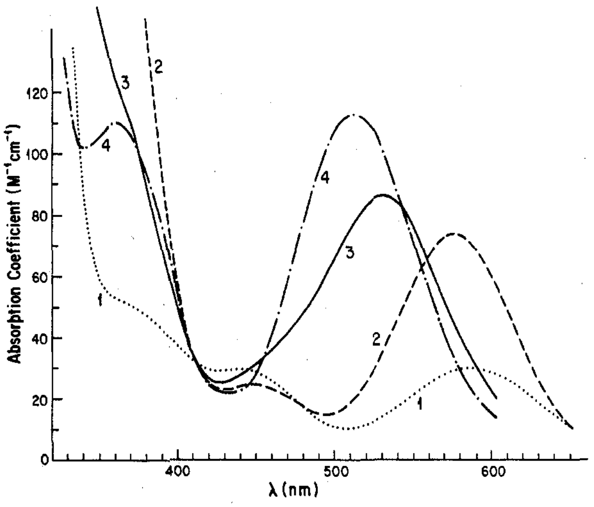

Figure 1. Spectra of complexes of significance to this study: (1) *trans*-$Co(en)_2(OH_2)Cl^{2+}$; (2) *trans*-$Co(en)_2(CO_3)Cl$; (3) *trans*-$Co(en)_2(CO_3)(OH)$; (4) *cis*-$Co(en)_2(CO_3)(OH)$.

Table I. Rate Data for Acid Hydrolysis of *trans*-$[Co(en)_2(OCO_2)Cl]$[a]

10 °C		15 °C		20 °C	
pH	k_{obsd},[b] s^{-1}	pH	k_{obsd},[b] s^{-1}	pH	k_{obsd},[b] s^{-1}
2.30	0.210	2.19	0.340	2.28	0.638
2.93	0.210	3.03	0.352	3.00	0.601
		6.03	0.269	4.09	0.633
		6.07	0.232	5.26	0.616
		6.26	0.211	6.27	0.448
		6.72	0.132	6.90	0.205
		7.35	0.046		

[a] [Complex] = 3×10^{-3} M; ionic strength = 0.5 M ($NaClO_4$). [b] Mean of five or six stopped-flow runs. Average error is approximately ±5% for each mean value.

Rate Measurements. For the *acid decomposition studies*, solutions of the complex made by the method just described are adjusted to pH 9 with NaOH and to an ionic strength of 0.5 M ($NaClO_4$), diluting with sufficient ice-cold water to set the complex concentration at 3×10^{-3} M. This solution is placed in one storage syringe of the previously described[6] stopped-flow kinetics apparatus. A citrate–phosphate buffer/$NaClO_4$ solution at the desired predetermined pH and at 0.5 M ionic strength is placed in the other storage syringe. Pseudo-first-order rate constants are determined in the conventional manner by use of the absorbance decrease at 570 nm, after allowing time for attainment of reaction temperature by the reactant samples. The *base hydrolysis rates* were obtained in two ways. In the first, the spectral change at 510 nm is followed on a Cary 15 or 118 spectrophotometer in thermostated reactant solution samples. These made use of purified complex from the cation-exchange column, with the pH, ionic strength, and free carbonate concentration adjusted to the desired values by additions of buffer (Tris–$HClO_4$, borate, or diethylamine–$HClO_4$), $NaClO_4$, and Na_2CO_3, respectively. In the second method, the rate of appearance of free Cl^- ion is determined by use of an Orion Model 94-17 chloride ion electrode coupled with the necessary voltage-measuring devices. A calibration curve was obtained previously by using known chloride solutions under the same conditions (basicity, ionic strength, and carbonate concentration) as in the kinetic runs.

Results and Discussion

A. Decarboxylation Reactions. Preliminary experiments showed that acidification of solutions of *trans*-$[Co(en)_2(OCO_2)Cl]$ resulted in immediate loss of CO_2 and change in

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(1) Part 15: Krishnamoorthy, C. R.; Palmer, D. A.; van Eldik, R.; Harris, G. M. *Inorg. Chim. Acta* **1979**, *35*, L361.

(2) Ficner, S.; Palmer, D. A.; Dasgupta, T. P.; Harris, G. M. *Inorg. Synth.* **1977**, *17*, 152.

(3) After the completion of our study, a report appeared concerning the spectral properties of a complex identified as *trans*-$[Co(en)_2Cl(HCO_3)]^+$, which was prepared in solution only. Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

(4) Baldwin, M. E.; Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1961**, 4637.

(5) Wan, W. K. Ph.D. thesis, State University of New York at Buffalo, Feb 1978, Chapter 2.

(6) Harris, G. M.; Ficner, S. "Abstracts of Papers", 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975; American Chemical Society: Washington, D.C., 1975; No. COMP. 7.

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the spectrum to that of *trans*-$[Co(en)_2(OH_2)Cl]^{2+}$ (see Figure 1). The stopped-flow rate data (Table I) are very similar to those obtained for other monodentate (carbonato)cobalt(III) species. One can therefore adopt the conventional proton preequilibration/CO_2 elimination mechanism previously utilized,[7] which for the present system involves reactions 1–3 (RD = rate determining).

$$[Co(en)_2(OCO_2)Cl] + H^+ \overset{\text{fast}}{\rightleftharpoons} [Co(en)_2(OCO_2H)Cl]^+ \quad 1/K \quad (1)$$

$$[Co(en)_2(OCO_2H)Cl]^+ \xrightarrow{\text{RD}} [Co(en)_2(OH)Cl]^+ + CO_2 \quad k \quad (2)$$

$$[Co(en)_2(OH)Cl]^+ + H^+ \overset{\text{fast}}{\rightleftharpoons} [Co(en)_2(OH_2)Cl]^{2+} \quad (3)$$

The corresponding rate law is

$$k_{\text{obsd}} = k[H^+]/K + [H^+] \quad (4)$$

At low pH's, k_{obsd} attains the limiting value of k, as seen in Table I for runs with pH ≤5. There is not sufficient data to enable good double reciprocal plots from which to evaluate both k and K, but reasonable estimates of the latter constant are obtainable at 15 and 20 °C, since $K = [H^+]$ at the point where $k_{\text{obsd}} = {}^1/_2k$. These interpolated values of K along with the average limiting values of k obtained from the low pH runs are as follows:

	10 °C	15 °C	20 °C
k, s^{-1}	0.21 ± 0.01	0.35 ± 0.01	0.62 ± 0.02
K, M		~6.5	~6.6

The corresponding temperature parameters for the rate constant are $\Delta H^{\ddagger} = 17.4 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 4$ cal deg^{-1} mol^{-1}. The extrapolated value for k at 25 °C is 1.02 s^{-1}, and it is seen that the decarboxylation rate parameters for this species are very similar to those recently tabulated for a number of other monodentate (carbonato)cobalt(III) complexes,[7] particularly the cis and trans forms of $[Co(en)_2(NH_3)(CO_3)]^+$. From this tabulation, it is clear that, whether the ligand trans to the CO_3 group in complexes of the type *trans*-$[Co(N)_4LCO_3]^{n+}$ is NH_3, H_2O, or Cl^-, there is little effect on the kinetic parameters of the acid-catalyzed CO_2 elimination reaction. However, the species[1] *trans*-$[Co(NH_3)_4(CN)(CO_3)]$, with a rate constant at 25 °C bracketed within the same range as all the others, deviates somewhat in terms of the typical temperature variation parameters which are bracketed within the range $\Delta H^{\ddagger} = 15.5 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5 \pm 5$ cal deg^{-1} mol^{-1}. For the cyano complex, these parameters have the significantly higher values of 21.5 ± 1.0 kcal mol^{-1} and 11 ± 4 cal deg^{-1} mol^{-1}, which has been explained in terms of the unusually large trans effect of this ligand as compared to NH_3, H_2O, or Cl^-.

B. Base Hydrolysis Reaction. Preliminary spectral change observations made in the range 7 < pH < 9 and in the absence of added carbonate indicated that a mixture of reactions occurred, probably involving both CO_2 elimination and Cl^- release. However, a number of runs were made within this pH range in the presence of increasing concentrations of added bicarbonate. These showed that above [free carbonate] = 0.15 M, the kinetics of the hydrolysis attain simple first-order characteristics, and the rate constants are independent of the pH values. Several such runs made over a range of pH values ([free carbonate] = 0.20 M, t = 30 °C) yielded the following data:

pH	7.35	7.49	7.96	8.32
10^5k_{obsd}, s^{-1}	21	24	22	25

with an average value of $k_{\text{obsd}} = (23 \pm 2) \times 10^{-5}$ s^{-1}. The complete spectral data for another run of this type of pH 9.2 and t = 20 °C (see Figure 2) illustrate the clean-cut first-order kinetics, with persistent isosbestic points at 444 and 556 nm. It is seen that the spectrum of the final product is very close to that previously reported[9] (see Figure 1) for *cis*-$[Co(en)_2(OCO_2)(OH)]$. When this product is acidified, the spectrum of the diaquo species obtained is identical with that of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, confirming the complete geometrical transformation. Analysis of the data derived from Figure 2 and a duplicate run yielded an average value for k_{obsd} of (3.2 ± 0.1) × 10^{-5} s^{-1}.

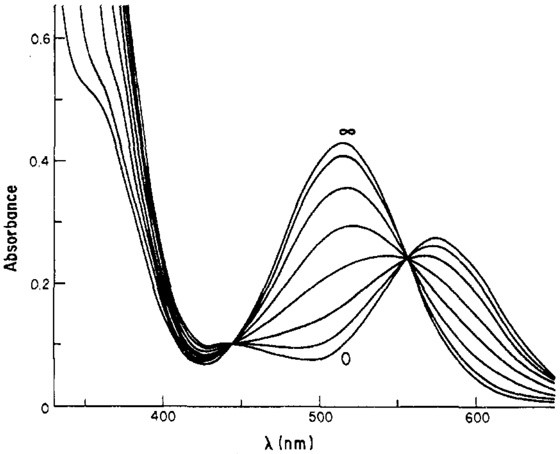

Figure 2. Spectral data for hydrolytic chloride ion release from *trans*-$Co(en)_2(CO_3)Cl$ at pH 9.2 and 20 °C.

Table II. Rate Constants and Activation Parameters for Base Hydrolysis of *trans*-$[Co(en)_2(OCO_2)Cl]$ [a]

t, °C	10^5k_0, s^{-1}	k_1, M^{-1} s^{-1}
20	3.6 ± 0.7	0.27 ± 0.03
25	9.9 ± 0.5	0.60 ± 0.01
30	21.8 ± 1.0	1.17 ± 0.03
$\Delta H^{\ddagger}$, kcal mol^{-1}	31.1 ± 2.1	25.2 ± 1.3
$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	27.3 ± 2.6	25.0 ± 1.6

[a] [Free carbonate] = 0.20 M; ionic strength = 0.7 M ($NaClO_4$).

For runs at pH >10, dependence of the rate of reaction on $[OH^-]$ becomes evident. Several sets of runs were carried out, in the range 10 < pH < 11 and 20 °C < t < 30 °C, with [free carbonate] constant at 0.2 M. All runs were performed spectrophotometrically as illustrated in Figure 2 with similar observations with respect to the trans to cis conversion during the hydrolysis. The results are presented in Figure 3, together with data points obtained in two runs made by means of the chloride determination technique. These points confirm that the observed reaction is solely release of chloride, as already shown by the spectrophotometric runs. Release of carbonate under our mildly basic conditions is not to be expected in any case, since it has been found previously[8] that various closely related complexes lose carbonate at rates as little as 10^{-5} as great as for the chloride elimination.

It is obvious from Figure 3 that the base hydrolysis data are consistent with a rate law of the form

$$k_{\text{obsd}} = k_0 + k_1[H^+] \quad (5)$$

Least-squares analyses of the results yield the values of the rate parameters set forth in Table II. It is noteworthy that the magnitudes of the derived values of k_0 at 20 and 30 °C

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(7) Dasgupta, T. P.; Harris, G. M. *Inorg. Chem.* **1978**, *7*, 3123.

(8) Reference 7, p 3126 and references quoted therein.

(9) Scheidegger, H. A. Ph.D. thesis, Eigenössichen Technischen Hochschule, Zürich, 1966, p 40.

Table III. Rate Parameters and Steric Course of Hydrolysis Reactions[a] of Complexes of the Type [*trans*-Co(en)$_2$LCl]$^{n+}$

	aquatn				base hydrolysis			
L	$10^5 k_0$, s^{-1}	retention, %	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	k_1, M^{-1} s^{-1}	retention, %	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}
Cl	3.1	65	27.5	13.1	3200	95	22.6	33.3
Br	4.5	50	24.6	4.1	5300	100	24.3	40.0
OH	160	25[b]	25.6	14.6	0.56	6	22.2	14.8
CN	7.8	100	22.0	−3.4	4.9	100	22.6	20.6
NO_2	98	100	20.9	−2.2	3.7	94	23.8	23.9
NCS	0.005	~40[b]	29.8	7.8	13	26	22.6	22.3
CH_3COO	31	80	26.8	6.7	11	80	22.6	22
N_3	22	80[b]	23.1	2.2				
NH_3	0.037	~90	23.0	−10.8				
CO_3[c]	10	~0	31.1	27.3	0.60	~0	25.2	25.0

[a] Data at 25 °C as given in review by: Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* 1974, *11*, 47. [b] Data from Table I, ref 9. [c] This work.

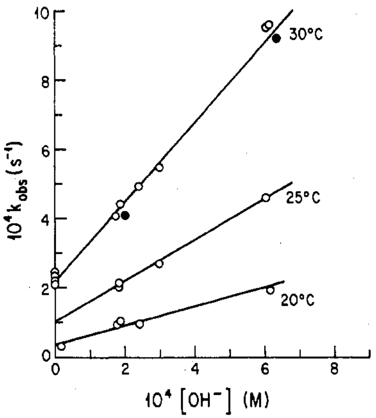
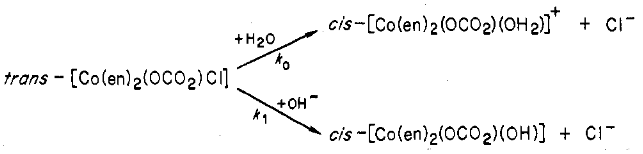


Figure 3. Dependence of k_{obsd} for base hydrolysis of *trans*-Co(en)$_2$CO$_3$Cl on hydroxide ion concentration.

are the same within experimental error as the k_{obsd} values obtained at lower pH's at these temperatures as reported above. This is entirely as it should be, since in these "low pH" preliminary experiments, only k_0 is operative. The most reasonable mechanism for the combined hydrolysis process takes the conventional form



$$\begin{tikzcd} & cis\text{-}[Co(en)_2(OCO_2)(OH_2)]^+ + Cl^- \\ trans\text{-}[Co(en)_2(OCO_2)Cl] \arrow[ur, "+H_2O", "k_0"'] \arrow[dr, "+OH^-", "k_1"'] & \\ & cis\text{-}[Co(en)_2(OCO_2)(OH)] + Cl^- \end{tikzcd} \qquad (6)$$

This mechanism accounts for the two-term rate law (eq 5) and also explains the constant limiting rate of reaction within the 7 < pH < 10 range, provided that proton-promoted CO_2 elimination is suppressed by the presence of excess free carbonate.

Most of the previous studies of the base hydrolysis of cobalt(III) complexes of the type *trans*-[Co(en)$_2$LCl]$^{n+}$ where Cl$^-$ is the released group have yielded kinetics of the form $k_{obsd} = k_1[OH^-]$. However, in these instances the experiments were carried out at pH values exceeding 12, so that the second term of eq 5 swamps out any contribution from the aquation rate k_0. The latter, however, are in many cases available from separate studies at low pH, at least for complexes where L is retained as a ligand even in very acidic solutions. There are also much data relative to the steric course of such reactions, and a selection of the relevant data is given in Table III along with our present findings. For both types of hydrolysis, there is a very large range of rate constants, to a considerable extent determined by variations in the entropies of activation, particularly for base hydrolysis. Retention of geometry is the dominant factor in both aquation and base hydrolysis, and in the former a high degree of retention is in general correlated with lower values of $\Delta S^\ddagger$, as has been previously discussed.[10] The two exceptional species in both types of hydrolysis are the trans OH and trans CO_3 complexes. In aquation, these have low percentages of retention and rather high $\Delta S^\ddagger$ values, although the rate constants at 25 °C are not particularly unusual. In base hydrolysis, they show rather low rate constants and very low percentages of retention, although the temperature variation parameters are not outside the limits exhibited by the other species. The parallelism in the effects of hydroxo and carbonato ligands on the kinetic properties of cobalt(III)–amine complexes has been noted elsewhere. Thus, for example, the rate at 25 °C of trans to cis isomerization of *trans*-[Co(en)$_2$(OCO$_2$)(OH)] ($\sim 1 \times 10^{-6}$ s^{-1})[11] is very similar to that reported for *trans*-[Co(en)$_2$(OH)$_2$]$^+$ ($\sim 3 \times 10^{-6}$ s^{-1}).[12]

Acknowledgment. The authors gratefully acknowledge financial support from the John D. and Frances H. Larkin Foundation of the State University of New York at Buffalo.

Registry No. *trans*-Co(en)$_2$(OCO$_2$)Cl, 72827-35-1; *trans*-Co(en)$_2$(OH$_2$)Cl^{2+}, 14403-92-0; *trans*-Co(en)$_2$(CO$_3$)(OH), 55658-81-6; *cis*-Co(en)$_2$(CO$_3$)(OH), 26368-79-6; *trans*-[Co(en)$_2$(OH)Cl]Cl, 20941-80-4.

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(10) Tobe, M. L. *Inorg. Chem.* **1968**, *7*, 1261.

(11) Reference 9, p 43.

(12) Kruse, W.; Taube, H. *Inorg. Chem.* **1961**, *83*, 1280. Farago, M. E.; Page, B. A.; Mason, C. F. V. *Ibid.* **1969**, *8*, 2270.

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Significance of Nephelauxetic Effect in the Interpretation of Cobalt-59 Nuclear Magnetic Resonance Frequencies of Cobalt(III) Complex Compounds

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Due to second-order paramagnetism, which arises from the orbital angular momentum induced by mixing of low-lying paramagnetic states of the cobalt(III) ion under the influence of a magnetic field, one can expect a linear relationship between ^{59}Co resonant frequencies and the longest wavelength d–d transition in octahedral cobalt(III) complexes.[1,2]

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(1) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

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