Dinuclear Complexes of Transition Metals containing Carbonate Ligands. Part 3.† Kinetics and Mechanism of Bridge Cleavage in the Di-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] Ion in Weakly Basic Aqueous Solution containing Carbonate Ions

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The kinetics of the reaction of the title dinuclear ion $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ with aqueous carbonate have been followed spectrophotometrically at 340 nm over the ranges $8.26 \leqslant pH \leqslant 9.4$, $35 \leqslant \theta_c \leqslant 45$ °C, and $0.05 \leqslant [CO_3^{2-}] \leqslant 0.2$ mol dm^{-3} at an ionic strength of 0.5 mol dm^{-3} ($LiClO_4$). During the reaction the complete cleavage of the hydroxo-bridges occurs and the sole reaction product is $[Co(en)_2(CO_3)]^+$. The rate of the bridge cleavage is completely independent of pH as well as total carbonate in solution. The rate data required a consecutive reaction treatment to resolve the $k_{obs.}$ values into the components k_1 and k_2 which have been assigned to the first and second bridge cleavages of the title complex. At 25 °C and $I = 0.5$ mol dm^{-3}, the values of k_1 and k_2 are $(1.7 \pm 0.3) \times 10^{-3}$ and $(0.46 \pm 0.05) \times 10^{-3}$ s^{-1} with the Eyring–Polyani parameters $\Delta H_1^{\ddagger} = 101 \pm 9$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = 28.5 \pm 28.0$ J K^{-1} mol^{-1} and $\Delta H_2^{\ddagger} = 90.8 \pm 5.4$ kJ mol^{-1}, $\Delta S_2^{\ddagger} = -13.0 \pm 18.4$ J K^{-1} mol^{-1} respectively. The reaction has also been studied without any added carbonate over the range $8.21 \leqslant pH \leqslant 9.25$ at 40 °C and $I = 0.5$ mol dm^{-3}. The rate constants are found to be independent of pH here also and have average values of $(1.05 \pm 0.06) \times 10^{-3}$ and $(2.98 \pm 0.03) \times 10^{-4}$ s^{-1} respectively. The higher values for the rate constants in carbonate-containing solutions indicate a mechanism involving some form of carbonate catalysis during the bridge cleavage.

Several studies[1-3] in the past have clearly demonstrated that mononuclear cobalt(III) amine complexes containing hydroxo-groups can effectively hydrate carbon dioxide in an irreversible manner to form stable carbonato-complexes. Although the mechanism of formation and decarboxylation of mononuclear carbonato-complexes has been well documented,[3] there has been few reports of dinuclear cobalt(III) complexes containing carbonate either as a bridging[4] or a terminal[5] ligand. Our attempts to synthesize μ-carbonato-complexes from other dinuclear complexes containing bridging hydroxo-groups have revealed[6] that the bridging hydroxide has little tendency to react with free CO_2 or carbonate ion. However, when one of the hydroxo-bridges cleaves in a multi-bridged system, generating an intermediate containing a terminal hydroxo-group, it will then be expected to react with CO_2 in much the same way as it does in mononuclear systems. Keeping these facts in mind we have selected the dinuclear complex ion $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4-}$ (**1**) (en = ethylenediamine) for our study on the possibility of μ-carbonato-complex formation. The hydroxo-bridge cleavage of (**1**) in acidic and basic solutions has been the subject of several publications in the past.[7-10] A variety of mechanisms have been proposed to interpret the experimental rate laws. One common feature of all such mechanisms is the proposal[9,10] of a singly bridged hydroxo-species as an intermediate. For example, the intermediates, $[(en)_2(H_2O)Co(\mu\text{-}OH)Co(OH)(en)_2]^{4+}$ and $[(en)_2(OH)Co(\mu\text{-}OH)Co(OH)(en)_2]^{3+}$ have been proposed to form in basic solution. Such intermediates could then be used, in our case, for CO_2 uptake followed by the formation of a carbonato-bridged complex. However, contrary to the expectation the complex ion (**1**) undergoes complete bridge cleavage in carbonate solution producing $[Co(en)_2(CO_3)]^+$ as a final reaction product. We report here a detailed kinetic study of the reactions of (**1**) in weakly basic carbonate solution.

Table 1. Effect of pH on the rate constants for the reaction of (**1**) in aqueous carbonate solution. $[(\mathbf{1})] = 2 \times 10^{-3}$, $[CO_3^{2-}]_T = 0.05$, $I = 0.5$ mol dm^{-3}

pH	10^3k_1/s^{-1}	10^3k_2/s^{-1}	θ_c/°C
8.28	1.79 ± 0.04	0.54 ± 0.02	35
8.38	1.79 ± 0.05	0.54 ± 0.01	35
8.57	1.81 ± 0.05	0.55 ± 0.01	35
8.82	1.77 ± 0.05	0.55 ± 0.02	35
9.03	1.75 ± 0.01	0.55 ± 0.01	35
9.23	1.85 ± 0.04	0.54 ± 0.01	35
9.37	1.75 ± 0.03	0.54 ± 0.02	35
8.29	3.02 ± 0.15	1.02 ± 0.04	40
8.43	3.87 ± 0.07	0.94 ± 0.02	40
8.65	3.50 ± 0.05	0.97 ± 0.01	40
8.80	3.54 ± 0.04	1.10 ± 0.05	40
9.00	3.49 ± 0.05	0.91 ± 0.08	40
9.18	3.57 ± 0.04	1.04 ± 0.05	40
9.40	3.50 ± 0.04	0.98 ± 0.04	40
8.18	5.59 ± 0.05	1.33 ± 0.02	42
8.57	5.43 ± 0.05	1.29 ± 0.03	42
8.79	5.00 ± 0.22	1.37 ± 0.01	42
8.97	5.25 ± 0.24	1.41 ± 0.01	42
9.14	5.64 ± 0.01	1.43 ± 0.02	42
9.35	5.54 ± 0.03	1.36 ± 0.05	42
8.26	6.10 ± 0.02	1.64 ± 0.04	45
8.58	5.99 ± 0.07	1.62 ± 0.02	45
8.83	6.36 ± 0.08	1.72 ± 0.02	45
8.96	6.09 ± 0.26	1.67 ± 0.03	45
9.18	6.44 ± 0.15	1.73 ± 0.07	45
9.35	6.46 ± 0.09	1.67 ± 0.01	45

Results and Discussion

The data for the reaction of (**1**) with aqueous carbonate as a function of pH at a constant $[CO_3^{2-}]_T$ are presented in Table 1. It is clear from Table 1 that the rates are remarkably constant

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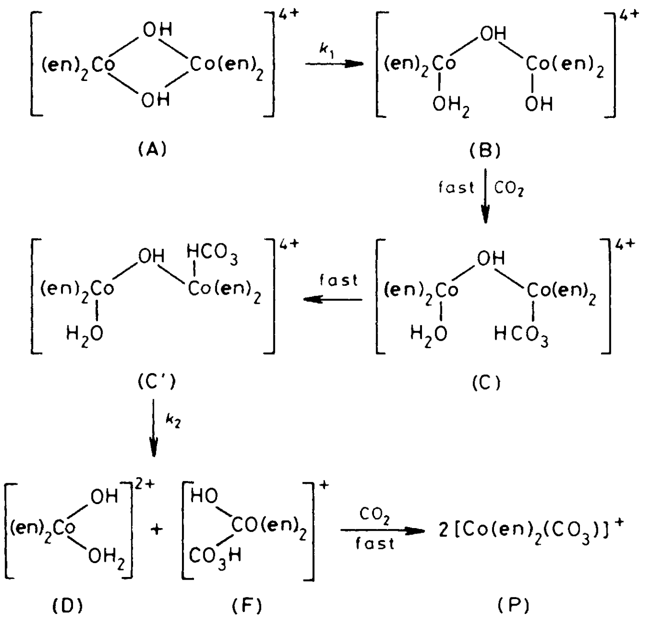
† Part 2, K. Koshy and T. P. Dasgupta, *Inorg. Chim. Acta*, 1982, **61**, 207.



Scheme.

over more than a ten-fold change in $[H^+]$. The rate data presented in Table 2 show the effect of variation of $[CO_3^{2-}]_T$ at a fixed pH. Again the rates are clearly insensitive to any change in carbonate concentration. A third set of data, which were obtained by variation of pH without adding any carbonate, are displayed in Table 3. It is interesting to note that the data for base hydrolysis displayed in Table 3 are quite comparable to those for carbonate-assisted bridge cleavage. These observations and the kinetic data can be interpreted by a mechanism involving the formation and subsequent decomposition of a monobridged hydroxo-intermediate as shown in the Scheme. This mechanism is very similar to the one proposed for base hydrolysis of (**1**) by El-Awady and Huges.[9,*] Since k_1 and k_2 are both independent of hydrogen ion concentration and total carbonate concentration, bridge cleavages must therefore occur spontaneously. The first bridge cleavage (A ⟶ B) can occur either by a concerted mode (S_N2) or *via* a five-co-ordinate intermediate (S_N1) as shown below.

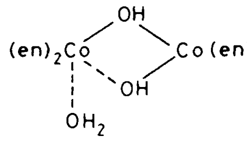
Table 2. Effect of total carbonate concentration on the rate constants for the reaction of (**1**) in aqueous carbonate solution. $[(\mathbf{1})] = 2 \times 10^{-3}$, $I = 0.5$ mol dm^{-3}, pH 8.30

$[CO_3^{2-}]_T$/ mol dm^{-3}	10^3k_1/s^{-1}	10^3k_2/s^{-1}	θ_c/°C
0.050	1.69 ± 0.05	0.51 ± 0.01	35
0.075	1.64 ± 0.06	0.54 ± 0.02	35
0.100	1.76 ± 0.07	0.54 ± 0.04	35
0.125	1.70 ± 0.08	0.59 ± 0.06	35
0.150	1.60 ± 0.06	0.56 ± 0.04	35
0.200	1.65 ± 0.04	0.55 ± 0.04	35
0.050	3.03 ± 0.20	1.00 ± 0.03	40
0.075	3.61 ± 0.06	0.97 ± 0.05	40
0.100	3.71 ± 0.17	0.98 ± 0.04	40
0.130	3.46 ± 0.05	0.94 ± 0.05	40
0.150	3.42 ± 0.02	0.95 ± 0.05	40
0.200	3.50 ± 0.04	1.00 ± 0.01	40
0.050	4.33 ± 0.01	1.15 ± 0.05	42
0.080	4.38 ± 0.05	1.23 ± 0.01	42
0.100	4.62 ± 0.09	1.24 ± 0.02	42
0.130	4.60 ± 0.07	1.17 ± 0.08	42
0.150	4.44 ± 0.06	1.16 ± 0.10	42
0.200	4.43 ± 0.03	1.16 ± 0.07	42
0.050	5.88 ± 0.10	1.65 ± 0.05	45
0.080	5.81 ± 0.07	1.64 ± 0.08	45
0.100	5.66 ± 0.06	1.73 ± 0.11	45
0.130	5.79 ± 0.05	1.65 ± 0.05	45
0.150	5.71 ± 0.03	1.74 ± 0.08	45
0.200	5.78 ± 0.08	1.73 ± 0.04	45

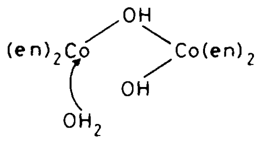
$\Delta H_1^{\ddagger} = 101 \pm 9$ kJ mol^{-1}, $\Delta H_2^{\ddagger} = 90.8 \pm 5.4$ kJ mol^{-1}, $\Delta S_1^{\ddagger} = 28.5 \pm 28.0$ J K^{-1} mol^{-1}, $\Delta S_2^{\ddagger} = -13.0 \pm 18.4$ J K^{-1} mol^{-1}

Table 3. Effect of pH on the rate constants for the hydrolysis of (**1**). At 40 °C, $[(\mathbf{1})] = 2 \times 10^{-3}$, $I = 0.5$ mol dm^{-3}

pH	10^3k_1/s^{-1}	10^4k_2/s^{-1}
8.21	1.08 ± 0.05	2.96 ± 0.03
8.40	1.00 ± 0.07	2.99 ± 0.02
8.63	0.97 ± 0.06	3.05 ± 0.04
8.75	1.10 ± 0.10	2.94 ± 0.01
9.03	1.13 ± 0.08	3.01 ± 0.03
9.25	1.02 ± 0.04	2.97 ± 0.02



(I)



(II)

At this stage CO_3^{2-} could also be a good contender for the nucleophilic attack at the cobalt centre in the intermediate (II). However, the possibility of CO_3^{2-} attack in a concerted manner at the metal centre of intermediate (I) can be ruled out since the rate of the reaction is completely independent of $[CO_3^{2-}]$. There are two possibilities now. First, CO_2 uptake by intermediate (B) and secondly, CO_3^{2-} attack at the five-co-ordinate intermediate (II). Both lead to the same product (C). Since it is known[11] that the rates of CO_2 uptake by hydroxo-complexes are fast, it is impossible to distinguish between the two processes. Once the intermediate (C) is formed it can either undergo second bridge cleavage or form a carbonate bridge by the elimination of water. Since the product of our reaction is the mononuclear carbonatobis(ethylenediamine)cobalt(III) ion, obviously complete bridge cleavage had occurred. It is not clear why the bridge formation did not occur although it has been established[†] that the bridge formation is facilitated if carbonate and aquo groups are adjacent (*Z* isomer) to each other in a complex binuclear molecule. Hence the possibility of isomerization of the intermediate (C) to an intermediate (C′), where HCO_3 and H_2O are apart (*E* isomer) from each other, could be envisaged as

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[*] El-Awady's mechanism involves deprotonation equilibrium prior to bridge cleavage. That might be so at very high pH values. We prefer solvent-assisted bridge cleavage at the pH we have been working.

[†] The complex ions tri-μ-hydroxo-bis[triamminecobalt(III)] and μ-amido-μ-hydroxo-bis[bis(ethylenediamine)cobalt(III)] can be converted easily to the μ-carbonato-complexes by the reaction of CO_2 or HCO_3^- ion. The mechanism involves bridge cleavage and then CO_2 uptake by the hydroxo-group attached to one Co^{III} centre, followed by carbonate bridge formation (G. Sadler and T. P. Dasgupta, Proceedings of the 3rd International Conference on the Mechanisms of Reactions in Solution, Canterbury, 1982, p. C5).

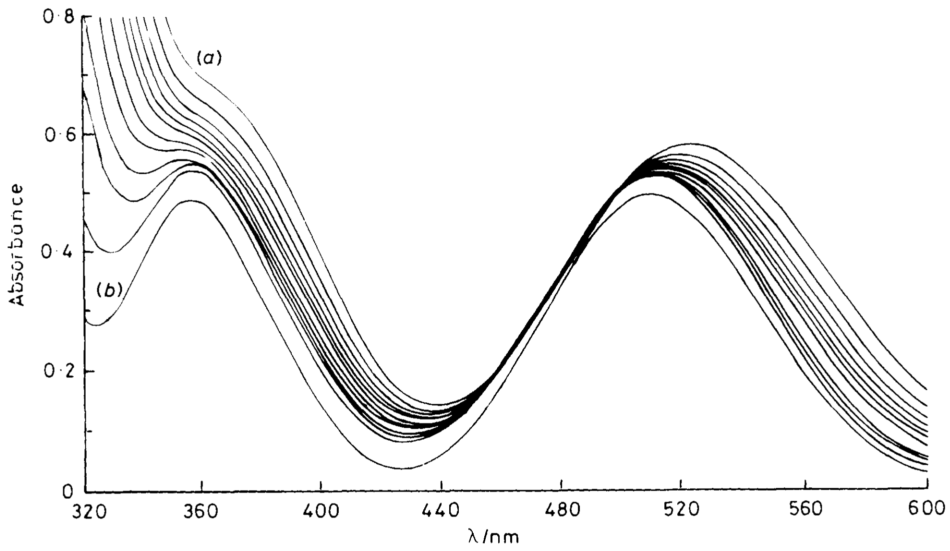

Figure. Spectral changes during the reaction of the cation (**1**) in bicarbonate solution. [(**1**)] = 2 × 10^{-3}, [$NaHCO_3$] = 0.05 mol dm^{-3}, 1-cm cell, at 35 °C, scanning interval 10 min: (*a*) the first spectrum; (*b*) [$Co(en)_2(CO_3)^+$] = 4 × 10^{-3} mol dm^{-3}

shown in the Scheme. This kind of isomerization has been known[12,13] to occur in the case of the tri-μ-hydroxo-bis-[triamminecobalt(III)] ion which undergoes bridge cleavage followed by rapid isomerization to the *E* isomer.[14] It is quite probable that the same type of isomeric transformation occurs in our monobridged intermediate species (C). This kind of isomerization would prevent carbonate bridge formation in (**1**). The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both bridge-cleavage processes, k_1 and k_2, were derived in the conventional manner by a least-squares analysis of the linear Eyring–Polanyi plots of the tabulated data and are presented at the foot of Table 2. It is noteworthy that the values of enthalpies of activation for both bridge-cleavage processes are nearly the same, indicating further that the mechanistic details for these processes are similar. The final product, [$Co(en)_2(CO_3)$]$^+$, forms quite rapidly from (D) and (F) as soon as second bridge cleavage occurs, since the CO_2 uptake by (D) and subsequent ring closure of (D) and (F) are both rapid.*

Finally, it is interesting to note that the rate constants for the bridge cleavage processes in the absence of carbonate (Table 3) are nearly three times slower than the values in the presence of carbonate. This clearly indicates that carbonate ion somehow speeds up the bridge cleavage. It is possible that CO_2 or CO_3^{2-} forms weak bonding with bridging hydroxide in (**1**) and promotes the bridge cleavage. Second bridge cleavage is facilitated by the adjacent carbonate at one of the cobalt centres. It is unfortunate that the intermediate (C) could not be isolated and characterized, in spite of several attempts, probably due to the similarity in the values of k_1 and k_2.

The ion-pair formation in the presence of excess carbonate in solution has also been considered. Some differences in absorbtion coefficients are expected, expecially in the u.v. region, between the species [$(en)_2Co(\mu\text{-}OH)_2Co(en)_2$]$^{4+}$ ··· CO_3^{2-} and [$(en)_2Co(\mu\text{-}OH)_2Co(en)_2$]$^{4+}$. However, we did not observe any measurable difference in absorbtion coefficients between the above two species in spite of changing the carbonate concentration systematically during the spectroscopic measurements. It is worth mentioning here that during our work on the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] ion in aqueous carbonate we have, however, identified spectroscopically the existence of ion-pair complexes which have a marked effect on on the rate of reaction with carbonate.[6]

Experimental

Preparation of Di-μ-hydroxo-bis[bis(ethylenediamine)cobalt-(III)] Perchlorate.—Carbonatobis(ethylenediamine)cobalt(III) chloride[15] was converted into the complex [$(en)_2Co(\mu\text{-}OH)_2Co(en)_2$][$ClO_4$]$_4$ by the method of deMaine and Hunt.[8] The purity of the complex was checked by microanalysis† (Found: C, 12.1; H, 4.40; N, 13.95. Calc. for $C_8H_{34}Cl_4Co_2N_8O_{18}$: C, 12.15; H, 4.35; N, 14.20%). The visible spectrum of the complex compares very well with that reported in the literature.‡

Materials.—All the chemicals used were of reagent grade. Distilled water made from a Corning distillation unit was used for preparative work. Ultra-pure water obtained by deionizing ordinary distilled water using the Milli Q Reagent Grade Water System was used to make up solutions for physical measurements. The visible and u.v. spectra were obtained with a Pye-Unicam SP8-100 recording spectrophotometer. The i.r. spectra of the starting material (**1**) and the product [$Co(en)_2(CO_3)$]$^+$ were measured with a Perkin-Elmer model 735B spectrophotometer using the KBr-disc technique. The bridging hydroxo-group has a strong band at 1 050—1 120 cm^{-1} which can be assigned to the Co–O–H bonding mode.[16] The medium-strong peak at 540 cm^{-1} is presumed to be due to the presence of the four-membered cobalt–oxygen ring.[17] The peaks for the terminal ethylenediamine ligands are identical to those reported earlier.[18,19] The spectrum of [$Co(en)_2(CO_3)$]$^+$ shows two strong peaks at 1 590 and 1 270 cm^{-1}. These peaks are comparable to the strong peaks at 1 593 cm^{-1} [$\nu(CO_{II})$] and 1 265 cm^{-1} [$\nu(CO_I + O_I + CO_{II})$] obtained for bidentate carbonate.[16]

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* The ring-closure process for [$CoL_4(H_2O)(CO_3)$]$^+$ (L = NH_3 or other amine ligand) is comparatively faster than the rate of bridge cleavage in our system. The rate constant for ring closure ranges from 0.02 to 0.05 s^{-1} depending on L (see ref. 3).

† Microanalysis was done by Dr. Ellen Pascher, Mikroanalytisches Laboratory, Buschstrasse 54, Bonn, West Germany.

‡ The absorption coefficient of complex (**1**) is 292 dm^3 mol^{-1} cm^{-1} at 525 nm (lit.,[8] ε = 298 dm^3 mol^{-1} cm^{-1} at 525 nm).

Qualitative Observations.—A family of spectra (Figure) collected during the course of the reaction of (**1**) with aqueous carbonate reveals the overall sequence of the reaction. The peak at 525 nm corresponding to (**1**) slowly shifts to 511 nm with the development of a new peak at 358 nm. The final spectrum corresponds to that of the mononuclear complex ion $[\mathrm{Co(en)_2(CO_3)}]^+$. Also, it is evident that there is no clear-cut isosbestic point suggesting the formation of at least one intermediate in appreciable concentration during the reaction.

Rate Measurements.—All rate measurements were made at an ionic strength of 0.5 mol dm^{-3} ($\mathrm{LiClO_4}$) and over acidity and temperature ranges of $8.26 \leqslant \mathrm{pH} \leqslant 9.40$ and $35 \leqslant \theta_c \leqslant 45$ °C respectively. The total carbonate concentration varied within the range $0.05 \leqslant [\mathrm{CO_3}^{2-}]_T \leqslant 0.20$ mol dm^{-3}. A different set of experiments was also carried out at 0.5 mol dm^{-3} ionic strength without adding any carbonate but varying the acidity over the range mentioned above, to investigate the extent of base hydrolysis during carbonate addition. The final spectrum of the reactions carried out without any carbonate corresponds to the spectrum of $[\mathrm{Co(en)_2(OH)_2}]^+$. The progress of the reaction was followed spectrophotometrically at 340 nm where there is a maximum difference in molar absorptivities between (**1**) and the mononuclear complex species. The reactions were slow enough for conventional kinetics and the observed pseudo-first-order rate constants were calculated from ln $(A_t - A_\infty)$ *vs.* t plots where A_t and A_∞ are the absorbances at times t and ∞ respectively. An initial curvature is a gross feature of all such plots. Such a behaviour has been shown to be quite characteristic of systems undergoing an irreversible consecutive reaction[20-22] of the type shown below where R, I, and P

$$\mathrm{R} \xrightarrow{k_1} \mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

represent the starting reagent, the intermediate, and the product respectively. For the present case separation of the biphasic plots into their components was done by extrapolating the ln $(A_t - A_\infty)$ *vs.* time plots to zero time to obtain a value for ln $(A_{\mathrm{max.}} - A_t)$ where $A_{\mathrm{max.}}$ is the absorbance the working solution would have shown at the completion of the first reaction had the second reaction not occurred.[21] The rate constants k_1 and k_2 were then obtained from the slopes of the plots ln $(A_{\mathrm{max.}} - A_t)$ *vs.* time and ln $(A_t - A_\infty)$ *vs.* time respectively.

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