Dinuclear Complexes of Transition Metals Containing Carbonate Ligands Part IX*. Kinetics and Mechanism of Decarboxylation and Formation of the μ-Amido-μ-carbonato-bis(bis(ethylenediamine)cobalt(III)) Ion in Aqueous Solution

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Abstract

The title compound has been prepared and characterized for the first time. The kinetics of acid hydrolysis of this compound leading to the μ-amido-μ-hydroxo-bis(bis(ethylenediamine)cobalt(III)) ion have been studied spectrophotometrically in the range $0.9 \text{ M} \geqslant [\text{H}^+] \geqslant 0.01 \text{ M}$ and $49.1 \,^\circ\text{C} \geqslant \theta \geqslant 40.3 \,^\circ\text{C}$ at an ionic strength (I) of 1.0 M. The k_{obs} values have been found to be completely independent of $[\text{H}^+]$ and this has been explained by a suitable mechanistic scheme. The kinetics of base hydrolysis have been studied over the range $0.7 \text{ M} \geqslant [\text{OH}^-] \geqslant 0.025 \text{ M}$ at 40 °C and $I = 1.0$ M. The results are consistent with the mechanistic scheme where there is a rapid preequilibrium followed by a rate determining step resulting in a μ-amido-dihydroxo complex species. The kinetics of formation of the title complex cation from the μ-amido-μ-hydroxobis(bis(ethylenediamine)cobalt(III)) ion in aqueous buffered carbonate solution have also been studied spectrophotometrically over the ranges $0.05 \text{ M} \geqslant [\text{CO}_3]_T \geqslant 0.02$ M and $9.11 \geqslant \text{pH} \geqslant 8.54$ at 40 °C and $I = 0.1$ M. On the basis of kinetic evidence, a mechanism is proposed in which the μ-amido-μ-hydroxo species undergoes bridge cleavage followed by an attack by aqueous CO_2 to form the μ-carbonato species. The results are compared to those of other dinuclear cobalt(III) complexes previously studied.

Introduction

In our earlier publication [1] we have shown that the reaction of the μ-amido-μ-hydroxo-bis-(tetraamminecobalt(III)) ion (1) in aqueous carbonate solution yielded a novel dinuclear complex, μ-amido-μ-hydroxo-(tetraamminecobalt(III))(biscarbonatocobalt(III)) (2). A detailed kinetic investigation [2]

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revealed that the terminal NH3 group in the complex 1 is substitutionally more labile than the bridging hydroxo group and hence the mechanism involves the gradual replacement of NH3 by HCO3⁻ followed by an extremely slow ring closure reaction. However, when the terminal NH3 groups in the complex ion 1 are replaced by the stronger chelating ligand, ethylenediamine, the bridging hydroxide can be substituted by other nucleophiles.

Hence, it is now possible for us to prepare a completely new complex, μ-amido-μ-carbonato-bis(bis(ethylenediamine))cobalt(III) perchlorate (3). We now report here the synthesis, mechanistic studies on the acid and base hydrolysis, and formation of the complex ion 3.

Experimental

Preparation of Compounds

Preparation of μ-amido-μ-carbonato-bis(bis(ethylenediamine)cobalt(III)) perchlorate
This compound has been prepared by two different methods.

Method 1. (A) Preparation of μ-amido-μ-superoxo-bis(bis(ethylenediamine)cobalt(III)) nitrate, $[(\text{en})_2\text{Co}(\mu\text{-NH}_2)(\mu\text{-O}_2)\text{Co(en)}_2](\text{NO}_3)_4$ (4) (en = ethylenediamine). This compound was synthesized following the procedure described by Stevenson and Sykes [3]. The purity of the compound was checked by ultraviolet and visible spectroscopy [4].

(B) Preparation of μ-amido-μ-carbonato-bis(bis(ethylenediamine)cobalt(III)) perchlorate, $[(\text{en})_2\text{Co}(\mu\text{-NH}_2)(\mu\text{-CO}_3)\text{Co(en)}_2](\text{ClO}_4)_3$ (3). Two g of 4 were dissolved in an aqueous suspension of 25 ml of 0.5 M Na2CO3 and 1 g SnCl2. The reaction mixture was thermostated at 50 °C for 40 min and ethanol was added to the cooled reaction mixture to complete precipitation of stannous and stannic carbonate. The reaction mixture was filtered and 2 g of Na2CO3 added to the filtrate. The filtrate

was evaporated on a water bath at 50 °C until the volume was approximately 10 ml, then neutralized with 4 M HClO₄ and ice cooled. The red crystals which separated were filtered, washed with ethanol and air dried. Yield 0.9 g. The purity of the compound was checked by elemental analysis. *Anal.* Calc. for $C_9H_{34}N_9CoCl_3O_{15}$: Co, 16.08; C, 14.54; H, 4.54; N, 17.21; Cl, 14.54. Found: Co, 15.6; C, 14.82; H, 5.23; N, 17.11; Cl, 14.38%.

Method 2. (A) Preparation of μ-amido-μ-hydroxo-bis(bis(ethylenediaminecobalt(III)) iodide, $[(en)_2\text{-}Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]I_4$. The compound was prepared from the corresponding superoxo complex (prepared in Method 1) by the method described by Werner [5]. The purity of the compound was checked by UV—Vis spectroscopy.

(B) Preparation of μ-amido-μ-hydroxo-bis(bis-(ethylenediamine)cobalt(III)) perchlorate, $[(en)_2\text{-}Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2](ClO_4)_4$ (5). The perchlorate salt was prepared by adding 1 g of the iodide salt slowly with stirring to 10 ml of water containing 0.92 g of AgClO₄. The AgI was filtered off and 5 ml saturated NaClO₄ added to the filtrate and the reaction mixture cooled in ice. The red crystals were filtered, washed with ethanol and air dried. Yield 0.8 g. The UV—Vis spectrum is similar to the corresponding iodide salt ($\lambda_{max} = 512$ nm ($\epsilon = 188$)).

(C) Preparation of μ-amido-μ-carbonato-bis(bis-(ethylenediamine)cobalt(III)) perchlorate, $[(en)_2\text{-}Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)Co(en)_2](ClO_4)_3$. Two g of the perchlorate salt prepared in (B) were dissolved in 60 ml of 0.2 M NaHCO₃ solution. The solution was thermostated at 40 °C for 24 h. Ten ml saturated sodium perchlorate solution were then added and the solution cooled in ice. The red crystals which formed were filtered, washed with ethanol and air dried. Yield 0.8 g. The electronic spectrum of this compound is exactly the same as the one prepared by Method 1.

Materials

All the chemicals used were reagent grade. Distilled water made from a Corning distillation unit, was used for preparative work. Deionized water, obtained by passing the distilled water through the Milli-Q-Reagent grade water system (Millipore Co., Bedford, MA 01730, U.S.A.) was used to make up solutions for physical measurements.

Instrumentation

The visible and ultraviolet spectra were recorded with either a Pye Unicam model SP8-100 or a Varian-Cary 219 recording spectrophotometer. For measurements at constant temperature, the cell compartment of the SP8-100 was thermostated with a constant temperature circulator, HAAKE KT33

while that of the Cary 219 was thermostated by a Precision Circulating System. The family of spectra in repetitive scan experiments was obtained from the Cary 219 by operating it in the automatic repetitive scanning overlay mode. The infrared spectra of all the complexes were measured with a Pye Unicam SP3-300 spectrophotometer by using the KBr disc technique. The spectra were scanned in the resolution mode of the instrument between 4000 and 200 cm⁻¹. An Orion model 701 digital pH meter fitted with a Markson combination electrode and the Beckman model 3500 digital pH meter fitted with a Beckman combination electrode and a water jacketed cell was used to measure pH values of the solutions.

Kinetic Measurements

The rate of decarboxylation in acidic solution was measured by dissolving the required amount of the complex in 10 ml of solution (1 mM) containing the appropriate amounts of HClO₄ and LiClO₄ thermostated at the desired temperature. The decarboxylation in basic solution was measured exactly the same way as in acidic solution except NaOH was used instead of HClO₄. The reaction of the complex ion 5 in aqueous carbonate was studied by dissolving the required amount of complex 5 in 10 ml of solution (1 mM) containing the appropriate amount of NaHCO₃ and borate buffer.

The ionic strength for all these experiments was adjusted to 0.5 M by adding the required amount of LiClO₄. The solutions were allowed to equilibrate at the selected temperature for at least 20 min before addition of the complex. The progress of the reactions was followed spectrophotometrically as the change in absorbance at selected wavelengths utilizing the time-drive chart mechanism of the spectrophotometer. All experiments were done under pseudo-first-order conditions and the rate constants along with the corresponding standard deviations were obtained from the slope of the $\ln(A_t - A_\infty)$ versus time plot, using a standard least-squares computer programme. Some rate constants were obtained by the Guggenheim method [6].

Results and Discussion

Complex ion 3 reacts in dilute perchlorate acid solution to give a solution whose UV—Vis spectra correspond to an equilibrium mixture of complex ion 5 and $[(en)_2(H_2O)Co(\mu\text{-}NH_2)Co(H_2O)(en)_2]^{5+}$. The spectral changes observed during the reaction are shown in Fig. 1. It is clear from the Figure that the λ_{max} at 514 nm immediately shifts to 512 nm and this is followed by a slow decrease in absorbance over this region of the spectrum. The rate of
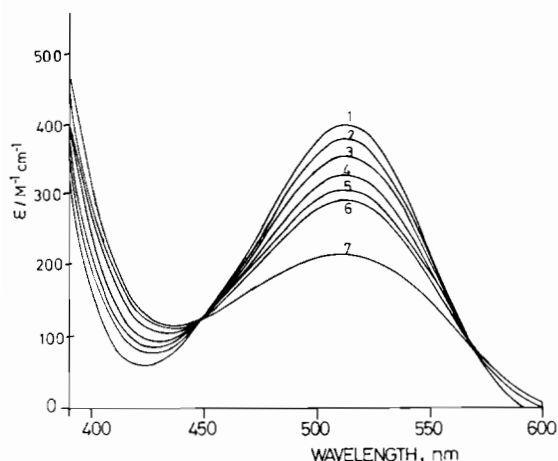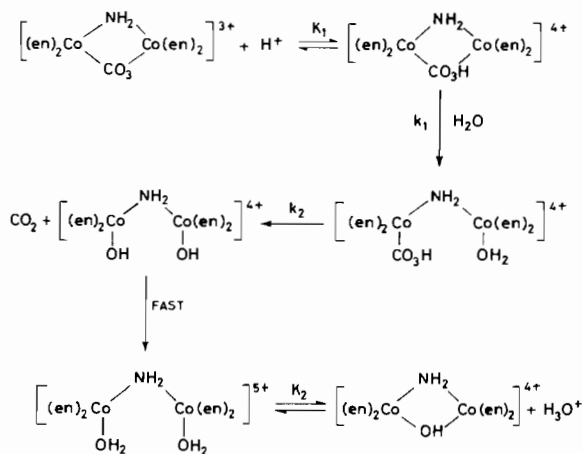
Fig. 1. Spectral change during the decarboxylation of $[(en)_2$-$Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)Co(en)_2]^{3+}$ in 0.1 M $HClO_4$ at 50 °C. The spectra (1 to 6) were recorded at 30 min intervals and spectrum 7 was recorded after 24 h.

TABLE 1. Pseudo-first-order rate constants for the decarboxylation of complex **3** in perchloric acid solution. [Complex], 1×10^{-3} M; $I = 1.0$ M

$[H^+]$ (M)	$10^5 \times k_{obs}$ (s^{-1})	Temperature (°C)
0.01	2.15	40.3
0.05	2.58	40.3
0.10	2.41	40.3
0.40	2.54	40.3
0.90	2.64	40.3
0.01	3.93	45.2
0.05	4.24	45.2
0.10	3.97	45.2
0.40	4.13	45.2
0.90	4.31	45.2
0.50	8.40	49.1
0.60	8.37	49.1
0.70	8.75	49.1

decomposition was measured at 512 nm where there is a maximum change in absorbance. The results obtained at 40.3, 45.2 and 49.1 °C are recorded in Table 1. Attempts were made to obtain the rates in the pH range 3.3–5 but they were unsuccessful due to the interference by the buffer used as a result of the formation of $[(en)_2Co(\mu\text{-}NH_2)$-$(\mu\text{-}X)Co(en)_2]^{5-n}$ where X^{n-} is the anion present in the buffer system [7, 8]. The mechanism proposed for the decarboxylation reaction is outlined in Scheme 1. This mechanism leads to the rate expression

$$k_{obs} = \frac{k_1 K_1 [H^+]}{1 + K_1[H^+]} \qquad (1)$$

At high $[H^+]$, $K_1[H^+] \gg 1$ and hence $k_{obs} = k_1$, i.e. k_{obs} would be independent of $[H^+]$. This is what we observed experimentally as is evident from

the data in Table 1. The assumption that the k_2 path is much faster than the k_1 path is quite justifiable, since the decarboxylation of monodentate carbonate in the mononuclear cobalt(III) complexes is fast [9].

It is of interest now to compare the reactivity of various bridging carbonate groups in dinuclear cobalt(III) complexes. The monobridged complex, $[(NH_3)_5Co(\mu\text{-}CO_3)Co(NH_3)_5]^{4+}$ was found [10] to react rapidly in acidic solutions ($k = 1.09$ s^{-1} at 25 °C), the rate of decomposition being controlled by the rate of decarboxylation of $[(NH_3)_5Co\text{-}HCO_3]^{2+}$. This is in contrast to the behaviour of several tribridged μ-carbonato cobalt(III) complexes [11] where the rate of acid hydrolysis is relatively slow. The rate of decomposition of the μ-carbonato-di-μ-hydroxo-bis(triamminecobalt(III)) ion in 1 M $HClO_4$ at 60 °C is 10^{-5} s^{-1}. Considering that the protonation of the bridging carbonate is much more difficult in the tribridged complex, its specific rate of decomposition may be as much as two orders of magnitude less than the rate of decarboxylation of complex **3**. Experimental observation so far has shown that the order of reactivity of the bridging carbonate ligand is as follows:

single bridged complex $\gg$ double bridged complex

$\gg$ triple bridged complex

Weighardt *et al.* [8] observed that the bridged carbonate in the μ-carbonato-di-μ-hydroxo-bis(1,4,7-triazacyclononane)chromium(III) cation and its rhodium(III) analogue behave almost like a bidentate carbonate in mononuclear complexes in acidic solutions. The rate expression obtained for the acid catalysed decomposition of these ions in solution is of the form $k_{obs} = k_0 + k_1[H^+]$. The values

Scheme 1.

of k_1 at 30 °C and $I = 1.0$ M for the rhodium(III) and chromium(III) complexes are 2.73×10^{-4} M^{-1} s^{-1} and 6×10^{-5} M^{-1} s^{-1} respectively. Thus it is abundantly clear that the behaviour of tribridged cobalt(III) complexes is completely different from that of the corresponding chromium(III) and rhodium(III) complexes [11]. A detailed mechanistic investigation on this particular problem is now being pursued in our laboratory.

It is to be noted here that the reactions of complex 3 with dilute HCl and dilute H_2SO_4 are different from its reaction with $HClO_4$. With dilute HCl the final product is a mixture of complex 5 and $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}Cl)Co(en)_2]^{4+}$ and with dilute H_2SO_4 the final product is a mixture of complex ion 5 and $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}SO_4)Co(en)_2]^{3+}$, the equilibrium position in both cases being dependent on the concentration of acids used. The rate constant for these reactions is calculated to be nearly the same and is approximately 8×10^{-5} s^{-1}. It is obvious, therefore, that the mechanism involves the cleavage of the carbonate bridge in complex 3 as shown in Scheme 1 followed by the rapid anation by Cl^- or SO_4^{2-}. The hydroxo bridge cleavage of the complex ion 5 by several acids to form bridged complexes has been investigated by Garbett and Gillard [12]. The rate of formation of these complexes is significantly faster than the decarboxylation of the complex ion 3. The occurrence of isosbestic points in Fig. 1 further provides evidence that the decarboxylation step is indeed the rate determining step.

The behaviour of complex ion 3 in basic solution has also been investigated and mechanistically it is very similar to its behavior in acidic solution. When complex 3 is treated with excess dilute sodium hydroxide the visible spectrum shows a fairly rapid increase in absorbance followed by a slow decrease in absorbance with a shift in λ_{max} from 514 to 520 nm and retention of the isosbestic point at 441 nm. The final spectrum has been found to be identical to the spectrum obtained when complex ion 5 is dissolved in basic solution*. Our findings are also in agreement with the results obtained by Garbett and Gillard [12]. The kinetics of base hydrolysis were carried out at 40 °C over the concentration range 0.025 M $\leqslant$ [OH$^-$] $\leqslant 0.700$ M. The initial small and fast increase in absorbance at low [OH$^-$] is interpreted as an equilibrium step for the carbonate bridge cleavage reaction and no attempt was made to study this reaction in detail. Plots of

*When the complex ion $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2]^{4+}$ is dissolved in 0.1 M NaOH solution the solution shows a spectrum with a λ_{max} of 520 nm and extinction coefficient of 298 M^{-1} cm^{-1} which is comparable to the value of 300 M^{-1} cm^{-1} at the same wavelength obtained from the final base hydrolysis solution of complex 3.

$\ln(A_t - A_\infty)$ versus time account for the final 90% of the reaction. The results obtained by least-squares calculations of these data are tabulated in Table 2.

TABLE 2. Observed rate constants for the base hydrolysis of complex 3. [Complex], 1×10^{-3} M; I, 1.0 M (LiClO$_4$); temperature, 40 °C

[OH$^-$] (M)	$10^4 \times k_{obs}$ (s^{-1})
0.025	0.09
0.050	0.18
0.100	0.27
0.250	0.76
0.350	1.16
0.500	1.42
0.600	1.80
0.700	2.16

The plot of k_{obs} versus [OH$^-$] is completely linear and the results can be interpreted in terms of the mechanism outlined below where R = Co(en)$_2$.
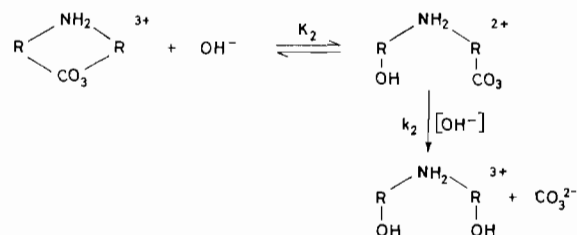
The rate expression obtained for the mechanistic scheme shown above is

$$k_{obs} = \frac{k_2 K_2 [OH^-]^2}{1 + K_2 [OH^-]} \qquad (2)$$

Assuming $K_2[OH^-] \gg 1$ at the conditions of our experiments, $k_{obs} = k_2[OH^-]$. The least-squares analysis of the data in Table 2 gave k_2 as $(3.01 \pm 0.12) \times 10^{-4}$ M^{-1} s^{-1}.

The absence of non-linearity in the plot of k_{obs} versus [OH$^-$] confirms that the magnitude of K_2 is quite big. It was not possible to determine K_2 directly from our kinetic experiments, but one can assume the K_2 value [12] to be between 10^2 to 10^3. At lower [OH$^-$] a slight curvature in the first-order plot and also slight deviation from clear cut isosbestic point indicate the presence of an intermediate.

The mechanism of base hydrolysis of a bridged carbonate in the dinuclear cobalt(III) complex thus seems to be different from that of the chelated carbonate in mononuclear cobalt(III) complexes. So far, detailed studies of the base hydrolysis of a chelated carbonato complex have been reported only for three complexes [13, 14] (en)$_2$Co(CO$_3$)$^+$, (tren)Co(CO$_3$)$^+$ and (cyclam)Co(CO$_3$)$^+$ (tren =

TABLE 3. Pseudo-first-order rate constants for the formation of complex species **3** in aqueous carbonate solution. [Complex], 1×10^{-3} M; temperature, 40 °C; $I = 0.1$ M (LiClO$_4$)

pH	$[CO_3]_T$ (M)	$10^5[OH^-]$ (M)	$10^4[CO_2]$ (M)	$10^5 \times k_{obs}$ (s^{-1})
8.29	0.02	0.57	1.96	1.09
8.29	0.03	0.57	2.95	1.44
8.29	0.04	0.57	3.93	2.36
8.29	0.06	0.57	5.39	3.02
8.29	0.07	0.57	6.87	3.52
8.54	0.05	1.02	2.75	2.63
8.58	0.05	1.14	2.50	2.47
8.71	0.05	1.51	1.84	2.27
8.87	0.05	2.18	1.26	2.23
9.01	0.05	3.01	0.89	2.33
9.11	0.05	3.78	0.72	1.88

2,2',2''-triaminotriethylamine and cyclam = 1,4,8,11-tetraazacyclotetradecane). Except for last complex, a clear cut mechanism in which a ring-opening process is followed by the formation of dihydroxo products, has been established. In the tren case, the intermediate Co(tren)(OH)(CO$_3$) has been isolated and the base hydrolysis of this intermediate has been studied separately [13]. The intermediate hydroxocarbonato species has not been identified for Co(cyclam)(CO$_3$)$^+$ due to the stronger nephelauxatic effect of the ligand. It is now possible to compare the reactivity of the bridging carbonate with that of the bidentate carbonate in the mononuclear complexes in strongly basic conditions. It is clear from Table 3 that the rate constant for replacement of the carbonate ligand by [OH$^-$] in a dinuclear complex is of the same order of magnitude as that for the mononuclear complex and hence, probably, requires [13] Co–O bond cleavage during substitution.

The reaction of complex species **5** in an aqueous solution of carbonate was studied by measuring the increase in absorbance with time at 520 nm where there is an appreciable absorbance change between the complex species **5** and **3**. The pseudo-first-order rate constants for the formation of complex ion **3** were determined at a fixed total carbonate concentration, $[CO_3]_T$, of 0.05 M and over the pH range of $8.54 \leqslant pH \leqslant 9.11$ at 40 °C. The results obtained are listed in Table 3. A series of kinetic runs were performed at a fixed [H$^+$] (pH, 8.29) and temperature (40 °C) by varying the total carbonate concentration over the range 0.02 M $\leqslant$ $[CO_3]_T \leqslant 0.07$ M. These results are displayed in Table 3. The equilibrium concentrations of CO$_2$, HCO$_3^-$ and CO$_3^{2-}$ have been calculated for each kinetic run from the known pK values of carbonic acid as discussed before [14]. It is clear from the

data in Table 3 that at a fixed $[CO_3]_T$ the k_{obs} values decrease with increasing pH, i.e. with decreasing $[CO_2]$. Similarly, at constant pH the reaction rate increases with increasing $[CO_2]$. On the basis of these results a mechanism similar to the one proposed earlier [15, 16] for the formation of the complex ion, (NH$_3$)$_3$Co(μ-CO$_3$)(μ-OH)$_2$-Co(NH$_3$)$_3^{3+}$, is presented in Scheme 2. The rate expression derived from Scheme 2 takes the form

$$k_{obs} = \frac{k_3 K_3 [OH^-][CO_2]}{1 + K_3[OH^-]} \qquad (3)$$

which then rearranged to

$$\frac{[CO_2]}{k_{obs}} = \frac{1}{k_3 K_3 [OH^-]} + \frac{1}{k_3} \qquad (4)$$

A plot of $[CO_2]/k_{obs}$ versus $1/[OH^-]$ is shown in Fig. 2. The values of k_3 and K_3 obtained from a least-squares treatment of such a plot are listed in Table 4. It is clear from the rate expression (3) that at constant pH a plot of k_{obs} versus $[CO_2]$
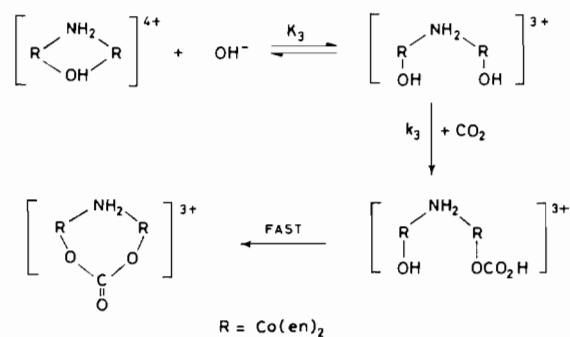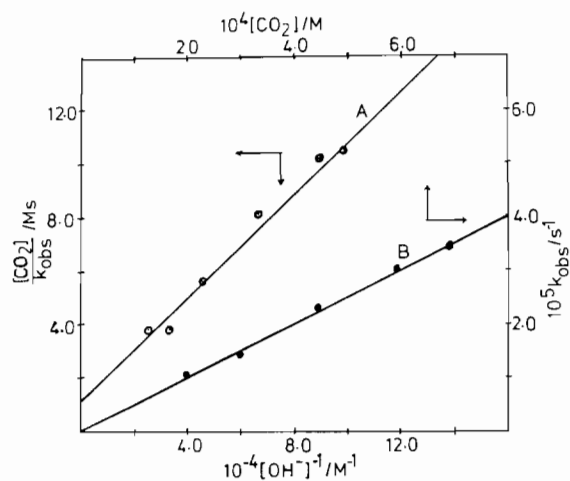
Scheme 2.

Fig. 2. Formation of [(en)$_2$Co(μ-NH$_2$)(μ-CO$_3$)Co(en)$_2$]$^{3+}$ in aqueous solution. (A) Plot of $[CO_2]/k_{obs}$ vs. $1/[OH^-]$; (B) plot of k_{obs} vs. $[CO_2]$. Temperature, 40 °C; I, 1 M (LiClO$_4$).

TABLE 4. Rate and equilibrium constants for CO_2 uptake by dinuclear cobalt(III) complexes (temperature, 40 °C)

Complex[a]	k (M^{-1} s^{-1})	$10^4 \times K$ (M^{-1})	Reference
$(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3^{3+}$	11.1	4.42	13
$(dien)Co(\mu\text{-}OH)_3Co(dien)^{3+}$	1.78	10.6	16
$(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2^{4+}$	0.90	1.13	this work

[a]dien = 1,5-diamino-3-aza-pentane.

should be linear passing through the origin. Such a plot is also shown in Fig. 2. The value of 0.89 M^{-1} s^{-1} obtained for k_3 from the data in Table 3 is in excellent agreement with the value 0.90 M^{-1} s^{-1} obtained from the earlier plot derived from expression (4).

It is now possible to compare the CO_2 uptake rates for at least three dinuclear complexes and those are listed in Table 4. The rate and equilibrium constant values are surprisingly similar to each other in spite of the differences in the number of bridging groups. It is, therefore, obvious that the CO_2 uptake rate is dominated by the available concentration of complex with terminal hydroxo group which, in turn, is controlled by the equilibrium constant in the first step of Scheme 2. The differences in the rate constants for the CO_2 uptake by mononuclear and dinuclear hydroxo complexes of cobalt(III) were discussed previously [15] in terms of the stereochemical hinderance cause by the latter complexes. The present result provides further support to this argument. We are now in the process of investigating the mechanism of CO_2 uptake by dinuclear complexes of metal ions other than cobalt(III).

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