Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. VIII*. Kinetics and Mechanism of Carbon Dioxide Uptake by the Tri-μ-hydroxo-bis((1,5-diamino-3-aza-pentane)cobalt(III)) Ion in Weakly Basic Aqueous Carbonate Solution

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Abstract

The kinetics of formation of the complex ion, μ-carbonato-di-μ-hydroxo-bis((1,5-diamino-3-aza-pentane)cobalt(III)), from the tri-μ-hydroxo-bis((1,5-diamino-3-aza-pentane)cobalt(III)) ion in aqueous buffered carbonate solution have been studied spectrophotometrically at 295 nm over the ranges $20.0 \leqslant \theta$ °C $\leqslant 34.8$, $8.03 \leqslant \text{pH} \leqslant 9.44$, 5 mM $\leqslant [CO_3^{2-}] \leqslant$ 35 mM and at an ionic strength of 0.1 M ($LiClO_4$). On the basis of the kinetic results a mechanism, involving rapid cleavage of an hydroxo bridge followed by carbon dioxide uptake with subsequent bridge formation, has been proposed. At 25 °C, the rate of carbon dioxide uptake is 0.58 M^{-1} s^{-1} with $\Delta H^{\neq} = (13.2 \pm 0.7)$ kcal mol^{-1} and $\Delta S^{\neq} = (-15.1 \pm 0.7)$ cal deg^{-1} mol^{-1}. The results are compared with those obtained for several mononuclear cobalt(III) and one dinuclear cobalt(III) complexes.

Introduction

In our earlier paper [2] in this series we have shown that the complex ion, tri-μ-hydroxo-bis(triamminecobalt(III)) ('triol') undergoes a change in weakly basic aqueous carbonate solution resulting in the formation of the μ-carbonato-di-μ-hydroxo-bis(triamminecobalt(III)) (**1**) complex. The kinetic studies [1] on the formation of the complex **1** revealed that the mechanism involves relatively rapid hydroxo bridge opening followed by the CO_2 uptake by hydroxo group as in the case of mononuclear cobalt(III) complexes [3]. It is also clear [4, 5] that the bridging hydroxide has no tendency to react with CO_2 or HCO_3^-. We have now extended our study to a dinuclear complex with a more bulky amine group to assess any steric hinderance encountered by CO_2 to react with an hydroxo group attached to the dinuclear complex. We report here a detailed kinetic study for the formation of the μ-carbonato-di-μ-hydroxo-bis((dien)cobalt(III)) ion (where dien = 1,5-diamino-3-aza-pentane) from the tri-μ-hydroxo-bis((dien)cobalt(III)) ion in aqueous bicarbonate solution.

Experimental

Preparation of Compounds

μ-Carbonato-di-μ-hydroxo-bis(dien)cobalt(III)) perchlorate hydrate (**2**) was prepared as described earlier [2]. The purity of the compound was checked by microanalysis, UV–Vis [2] and IR spectroscopy [2]. *Anal.* Calc. for $Co_2N_6H_{30}C_9O_{14}$: C, 17.01; H, 4.73; Cl, 11.18; Co, 18.6; N, 13.23. Found: C, 17.13; H, 4.69; Cl, 10.83; Co, 18.7; N, 13.24%.

Tri-μ-hydroxo-bis((dien)cobalt(III)) perchlorate ('dien-triol') was generated in situ [2] by adding appropriate quantities of di-μ-hydroxo-aquanitrato-bis(dien)cobalt(III) perchlorate to a buffer solution of pH 6. The spectrum of the solution is in agreement with that in the literature [6, 7].

Materials

All the chemicals used were reagent grade. Distilled water was further purified by passing through 'Milli-Q' ion exchange columns and was used for making up all solutions for physical measurements.

The Vis and UV spectra were obtained either with a Pye Unicam SP8-100 or with a Cary 219 recording spectrophotometer. The IR spectra were recorded with a Pye Unicam SP3-300 recording spectrophotometer.

Results and Discussion

The reaction of 'dien-triol' in aqueous carbonate was studied by recording the increase in absorbance with time at 295 nm. Kinetic measurements were per-

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TABLE I. Observed Rate Constants for the Reaction of 'dien-triol' in Aqueous Carbonate Solution. [Complex], 2.5 × 10^{-4} M; I, 0.1 M ($LiClO_4$)

20 °C; $[CO_3]_T$, 0.02 M		25 °C; $[CO_3]_T$, 0.02 M		30 °C; $[CO_3]_T$, 0.01 M		34.8 °C; $[CO_3]_T$, 0.01 M	
pH	$10^5 \times k_{obs}$ (s^{-1})	pH	$10^5 \times k_{obs}$ (s^{-1})	pH	$10^5 \times k_{obs}$ (s^{-1})	pH	$10^5 \times k_{obs}$ (s^{-1})
8.63	0.84 ± 0.01	8.40	1.71 ± 0.02	8.20	2.94 ± 0.04	8.03	6.88 ± 0.07
8.73	0.76 ± 0.02	8.54	1.69 ± 0.02	8.27	2.80 ± 0.04	8.10	6.56 ± 0.04
8.80	0.72 ± 0.01	8.61	1.52 ± 0.03	8.39	2.77 ± 0.04	8.26	6.08 ± 0.02
9.04	0.61 ± 0.01	8.79	1.30 ± 0.02	8.48	2.67 ± 0.03	8.32	5.88 ± 0.08
9.22	0.51 ± 0.01	8.99	1.14 ± 0.02	8.55	2.58 ± 0.04	8.43	4.96 ± 0.08
9.44	0.30 ± 0.01	9.16	0.95 ± 0.03	8.68	2.24 ± 0.04	8.71	4.39 ± 0.06
				8.96	1.69 ± 0.02	8.98	3.35 ± 0.02
						9.11	3.08 ± 0.04

TABLE II. Observed Rate Constants for the Reaction of 'dien-triol' in Aqueous Carbonate Solution [Complex], 2.5 × 10^{-4} M; pH, 8.45; temperature, 30 °C

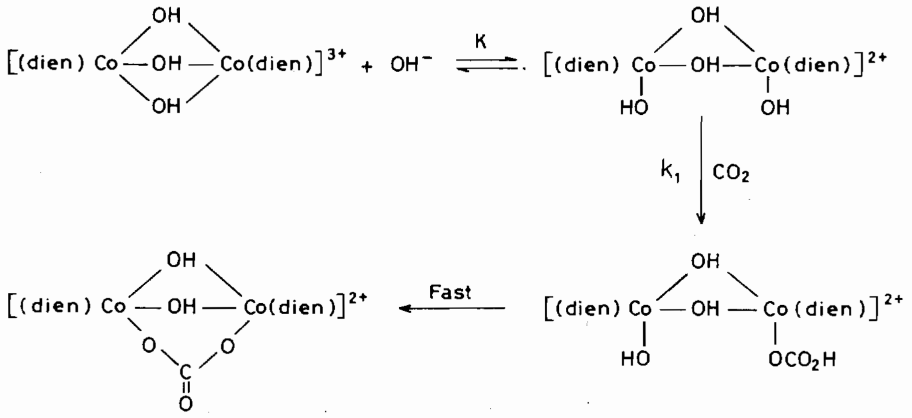
$10^3 \times [CO_3]_T$ (M)	$10^5 \times [CO_2]$ (M)	$10^5 \times k_{obs}$ (s^{-1})
5.0	3.0	0.86 ± 0.09
10.0	6.0	1.45 ± 0.02
15.0	9.0	2.28 ± 0.02
20.0	12.0	2.68 ± 0.03
25.0	14.9	3.36 ± 0.05
30.0	17.9	4.31 ± 0.04
35.0	20.9	4.40 ± 0.06

formed over the range $8.6 \leqslant pH \leqslant 9.54$ and temperature range $20.0 \leqslant \theta$ °C $\leqslant 34.8$. The total carbonate concentration was maintained constant at either 0.01 M or 0.02 M. The results obtained are collected in Table I. A series of kinetic runs, where the pH was kept constant at pH 8.45 while the total carbonate concentration was varied from 5.0×10^{-3} M to 3.5×10^{-2} M, were performed at 30 °C. These results are displayed in Table II along with the carbon dioxide concentrations in solution.

When sodium bicarbonate is dissolved in water, the following equilibrium is established fairly rapidly.

$$H_2CO_3 \overset{K_1}{\rightleftharpoons} HCO_3^- \overset{K_2}{\rightleftharpoons} CO_3^{2-}$$

The equilibrium concentrations of CO_2, HCO_3^- and CO_3^{2-} at a particular concentration of $NaHCO_3$ and at a constant pH can be determined from the experimentally determined K_1 and K_2 values*. An examination of the results in Table I shows that for a fixed $[CO_3]_T$, the k_{obs} values decrease with increasing pH. It can also be shown that with increasing pH, $[CO_3^{2-}]$ increases, $[CO_2]$ decreases, while $[HCO_3^-]$ decreases only marginally. Thus the results suggest that CO_2 is the reactive species in the formation of the μ-carbonato complex 2. At constant pH, the reaction rate increases with increasing $[CO_2]$ as shown in Table II. On the basis of these results, a mechanism similar to the one proposed [1] for the formation of complex 1 is outlined in Scheme 1. This



Scheme 1.

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*The value of pK_1 and pK_2 for carbonic acid are 6.03 and 9.8 at 25 °C and I = 0.5 M [8].

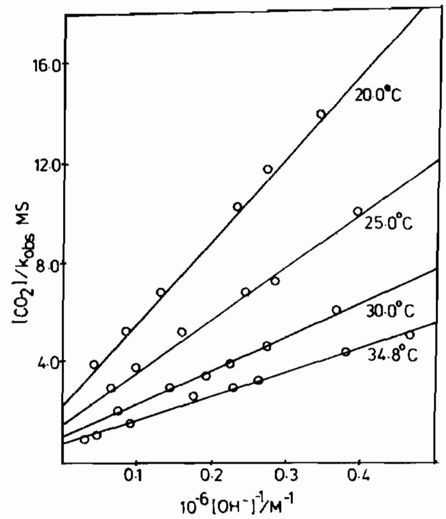

Fig. 1. Plot of $[CO_2]/k_{obs}$ *vs.* $[OH^-]^{-1}$ for the CO_2 uptake by 'dien-triol' at different temperatures.

mechanism proposes that in aqueous buffered carbonate solution 'dien-triol' equilibrates rapidly with the dihydroxo species II which then picks up CO_2 from the solution to form the μ-carbonato complex. The mechanism proposed in Scheme 1 leads to the rate law.

$$k_{obs} = \frac{k_1K[OH^-][CO_2]}{1 + K[OH^-]} \tag{1}$$

which can be arranged to give

$$\frac{[CO_2]}{k_{obs}} = \frac{1}{k_1K[OH^-]} + \frac{1}{k_1} \tag{2}$$

A plot of $[CO_2]/k_{obs}$ *versus* $1/[OH^-]$ should therefore be linear with a slope of $1/k_1K$ and intercept $1/k_1$. These plots obtained at four different temperatures are shown in Fig. 1. It is also clear from eqn. (1) that at constant pH a plot of k_{obs} *versus* $[CO_2]$ should be linear passing through the origin. This plot utilising the data in Table II is shown in Fig. 2. The values of k_1 and K obtained from the least square treatment of the data in Table I and the corresponding temperature parameter are shown in Table III. The plot in Fig. 2 gives a value of 0.80 M^{-1} s^{-1} which agrees very well with the value of 0.91 M^{-1} s^{-1} obtained from the plot in Fig. 1.

It is now possible to compare the rate constants for the CO_2 uptake by mononuclear and binuclear hydroxo complexes of cobalt(III). These data are shown in Table IV. It is clear that the rate of CO_2 uptake by the dinuclear complexes is significantly lower than that of the mononuclear species. This result has previously [1] been explained in terms of the stereochemical hinderance offered by the dinuclear structure. This is now clearly evident especially when one compares the rate constant for CO_2 uptake by 'triol' with that of 'dien-triol' (see Table III). This considerable difference in rate constant can only be rationalised in terms of steric congestion due to the bulky 'dien' ligand which most likely imposes obstruction in the direct associative activation of CO_2 by the hydroxo group of the dinuclear complex. This is also reflected in the values of the activation parameters. The enthalpy factor went up by about 2 kcals while the entropy factor went up nearly 4 units as a result of a somewhat disordered transition state. It should also be noted at this point that the equilibrium constant for the opening of hydroxo bridge of the 'dien-triol' is 7.9 X 10^4 M^{-1} compared to that of 2.2 X 10^4 M^{-1} for the 'triol'. This high equilibrium constant value accompanied with lower $\Delta H°$ and $\Delta S°$ values again suggest the facile bridge opening process due to the presence of the bulky 'dien' ligand. We are now in the process of examining various 'triol' complexes differing in bulkiness of the terminal amine group.

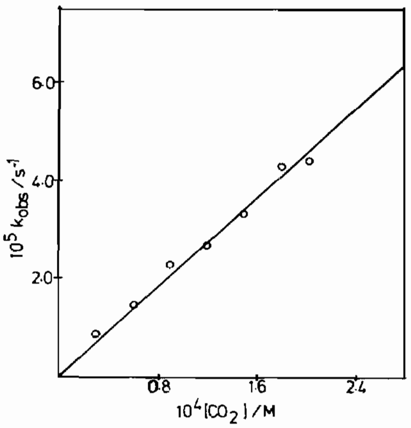

Fig. 2. Plot of k_{obs} *vs.* $[CO_2]$ for the CO_2 uptake by 'dien-triol' at 30 °C.

TABLE III. Rate Parameters for the CO_2 Uptake by 'dien-triol'

Temperature (°C)	k_1 (M^{-1} s^{-1})	$10^{-4} \times K$ (M^{-1})
20.0°	0.42 ± 0.06	6.8 ± 2.0
25.0	0.58 ± 0.05	7.9 ± 0.5
30.0	0.91 ± 0.12	8.4 ± 2.0
34.8	1.30 ± 0.08	9.2 ± 2.0

$\Delta H^{\neq}$ = 13.2 ± 0.7 kcal/mol
$\Delta H°$ = 3.6 ± 0.5 kcal/mol
$\Delta S^{\neq}$ = −15.1 ± 2.4 cal deg^{-1} mol^{-1}
$\Delta S°$ = 34 ± 2 cal deg^{-1} mol^{-1}

TABLE IV. Rate Constants for CO_2 Uptake by Mononuclear and Binuclear Hydroxo Complexes of Cobalt(III)

Complex ion^a	k (M^{-1} s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal deg^{-1} mol^{-1})	Reference
$Co(NH_3)_5OH^{2+}$	220	15.3 ± 0.9	3.6 ± 3.0	8
$Co(tren)(OH_2)(OH)^{2+}$	44	14.7 ± 0.1	−1.9 ± 0.2	9
cis-$Co(cyclam)(OH_2)(OH)^{2+}$	57	14.8 ± 1.0	0.8 ± 3.5	3
cis-$Co(cyclam)(OH)_2{}^+$	196	15.2 ± 0.5	3.0 ± 1.9	3
trans-$Co(cyclam)(OH_2)(OH)^{2+}$	37	29.0 ± 0.1	46.2 ± 0.4	3
trans-$Co(cyclam)(OH)_2{}^+$	70	29.3 ± 0.6	44.6 ± 1.9	3
$(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3{}^{3+}$	4.3	11.1 ± 1.1	−18.1 ± 3.8	1
$(dien)Co(\mu\text{-}OH)_3Co(dien)^{3+}$	0.58	13.2 ± 0.7	−15.1 ± 2.4	this work

^{a}tren = 2,2′,2″-triaminotrethylamine; cyclam = 1,4,8,11-triazacyclotetradecane.

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