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Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. V*. Kinetics and Mechanism of the Reactions of the μ-Amido-μ-hydroxo-bis-[(tetraamminecobalt(III)] Complex Ion in Aqueous Solutions**

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Abstract

The kinetics of the reaction of the title complex with aqueous carbonate has been investigated by spectrophotometry at 440 nm over the range $8.00 < pH < 9.30$, $30 < \theta_t < 45$ °C and $0.05 < [CO_3]_T < 0.20$ M (where θ_t = temperature and $[CO_3]_T$ = total carbonate concentration), at an ionic strength of 0.5 M ($LiClO_4$). The reaction observed under these conditions is the unexpectedly effective substitution of CO_3^{2-} for NH_3 on one of the cobalt centres of the dinuclear species. The rate data revealed that the reaction follows a consecutive reaction pathway involving the loss of two ammonia molecules in the rate-determining steps – the value of k_1 and k_2 at 40 °C and pH = 8.62 being 5.25×10^{-3} s^{-1} and 1.48×10^{-3} s^{-1}, respectively. The rate of base hydrolysis in the absence of any carbonate also follows a consecutive reaction pattern, and the values of the rate constants are 1.36×10^{-2} s^{-1} and 2.71×10^{-3} s^{-1}, respectively. In carbonate solution the reaction product is the complex μ-amido-μ-hydroxo[tetraamminecobalt(III)] [biscarbonatocobalt(III)] which has been characterized by a previous X-ray diffraction study. The kinetic data for the formation of this compound have been explained by a mechanism involving extensive ion-pairing in solution.

Introduction

In an attempt to prepare dinuclear complexes of cobalt(III) containing a bridging carbonate group, we have shown previously [1] that the dinuclear complex ion $[(en)_2Co(\mu\text{-}OH)_2Co(en)_2]^{4+}$ undergoes complete bridge cleavage in aqueous carbonate solution leading to the sole reaction product, $Co(en)_2CO_3^+$. Although the formation of a monool $[(en)_2(OH_2)Co(\mu\text{-}OH)Co(HCO_3)(en)_2]^{4+}$ was envisaged as a kinetic intermediate during the reaction, no evidence was found for the formation of any bridged carbonato complex. This observation pointed to the need for selecting another dibridged complex which is comparatively stable in carbonate solution and containing at least one μ-OH group. The choice was the dinuclear complex ion, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ (1) which undergoes several different types of reactions with various nucleophiles without affecting the bridging amido group [2, 3]. Reactions of this complex in aqueous carbonate solution resulted in the formation of a black needle-shaped crystalline solid which was characterised unambiguously [3] by X-ray diffraction study to be $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]\cdot 5H_2O$ (2). We now report the kinetic and mechanistic details of the formation of this bis-carbonato complex.

Experimental

Preparation of μ-Amido-μ-hydroxo-bis(tetraamminecobalt(III)) Tetrachloride Tetrahydrate, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]Cl_4\cdot 4H_2O$

This complex was prepared from μ-amido-μ-sulfato-bis[tetraamminecobalt(III)] sulfate by the method published earlier [4]. The purity of the compound was checked by comparing the visible spectrum of the complex with that reported in the literature*.

Materials

All the chemicals used were of reagent grade. Ultrapure water was obtained by passing ordinary distilled water through a Milli-Q Reagent Grade Water system. The ultraviolet and visible spectral measurements were done with a Pye Unicam SP8-100 recording spectrophotometer attached to a HAAKE Model

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*Part IV, see ref. 17.

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*The absorption coefficient of complex 1 is 153 M^{-1} cm^{-1} at λ_{max} 522 nm (literature [5] ϵ = 149 M^{-1} cm^{-1} at 520 nm).

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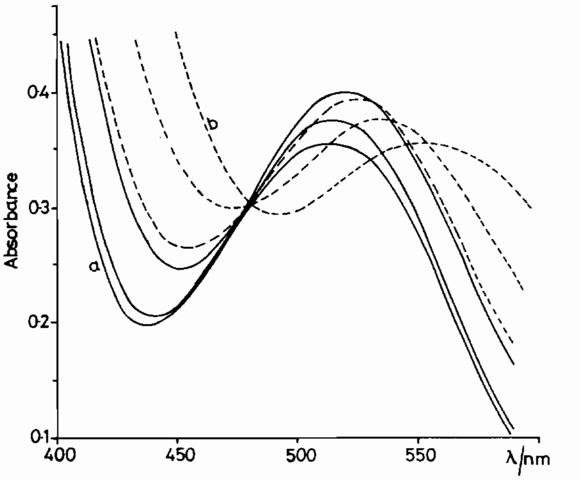

Fig. 1. Spectral changes during the reaction of the cation 1 in bicarbonate solution; [1], 2 × 10^{-3} M; [$NaHCO_3$], 0.05 M; cell, 1 cm; 35 °C. Total scan time, 3 h 10 min; - - -, first stage and ——, second stage; (a) the first spectrum; (b) the final spectrum.

KT33 circulator bath to maintain a constant temperature during measurements. Details of the UV–Vis and IR spectra for complex 1 and the final reaction product 2 have been published earlier [3].

Qualitative Observations

A family of spectra (Fig. 1) collected during the course of the reaction of 1 in aqueous carbonate solution reveals the overall pattern of the change. The series of spectra that intersect at varying wavelengths indicates the type of complexity during the kinetic run. The initial increase in absorbance at 522 nm is indicative of the first step of the reaction, and the subsequent decrease in absorbance over the same region is defined as the second step. The bathochromic effect observed during the reaction may also suggest that NH_3 ligands are being replaced by CO_3^{2-}.

Rate Measurements

All rate measurements were made at an ionic strength of 0.5 M ($LiClO_4$). Data for the formation of 2 were obtained within the range $8.00 < pH < 9.30$, $0.05 < [CO_3]_T < 0.20$ M and $30 < \theta_t < 45$ °C. The reaction of 1 with aqueous carbonate was studied under pseudo-first order conditions ([complex] = 2.0 × 10^{-3} M) by following the increase in the optical density at 440 nm. An initial check on the suitability of various buffers for the range of pH investigated revealed that the tris[§] buffer, although very widely used in the range $7 < pH < 9$, is unsuitable here as it tends to retard the reaction as compared to self-buffered carbonate or borate buffer media. Therefore, all the data presented in this work were collected in boric acid buffer [6]. The concentration of the buffer was maintained at 0.1 M in all kinetic experiments. The pH meter was calibrated with NBS standard buffer solutions [7]. The pH measurements of each solution were done before and after each kinetic run to make sure that the [H^+] remained constant during the experiment.

An initial curvature is a general feature for all kinetic plots; this behaviour is quite characteristic of systems undergoing a reversible consecutive reaction, as was found in our previous study [1]. The 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 $\ln(A_{max} - A_t)$, where A_{max} is the absorbance that the working solution would have shown at the completion of the first reaction had the second reaction not occurred. The details of this method are published elsewhere [1, 8, 9]. The A_∞ values were taken when there was no substantial absorbance change within an hour after each kinetic run. However, there was still a residual reaction occurring in the solution, which results in the final product 2. This later process is extremely slow, and it takes about two days to get the solid product 2 after each kinetic run.

Results and Discussion

The pseudo-first order rate constants for the reaction of 1 with aqueous carbonate as a function of pH at a fixed $[CO_3]_T$ are presented in Table I. It is obvious from Table I that both k_1 and k_2 values increase with an increase in pH. This increase in the values of k_1 and k_2 can be shown to be directly related to the increase in concentration of free CO_3^{2-} *; hence, both k_1 and k_2 paths are dependent on $[CO_3^{2-}]$.

To confirm this trend a second set of data was collected (Table II) by systematically changing the total carbonate concentration at a fixed pH of 8.28. A rather surprising observation here is that both k_1 and k_2 values decrease with increasing $[CO_3]_T$. A series of experiments was then carried out at $8 < pH < 10$ in which the effect of base in the absence of any carbonate was examined. Treatment of the kinetic data obtained from the base hydrolysis of the complex 1 indicates that the reaction takes place in two steps; the first step (k_3) being faster than the second (k_4). The values of k_3 and k_4 are listed in

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[§] tris = tris(hydroxymethyl)aminomethane.

*Considering the equilibrium $H_2CO_3 \xrightleftharpoons{k_1} HCO_3^- \xrightleftharpoons{k_2} CO_3^{2-}$ and taking the values [10] of $k_1 = 9.33 \times 10^{-7}$ and $k_2 = 1.58 \times 10^{-10}$ (I, 0.5, 25 °C), it can be easily shown that with an increase in pH at a fixed carbonate concentration only $[CO_3^{2-}]$ increases under the pH conditions we have studied.

TABLE I. Effect of pH on the Rate Constants for the Reaction of **1** in Aqueous Carbonate Solution. [**1**] = 2 × 10^{-3} M; $[CO_3]_T$ = 0.05 M; *I* = 0.5 M ($LiClO_4$)

pH	$10^3 k_1$ (s^{-1})	$10^3 k_2$ (s^{-1})	θ_t (°C)
8.24	0.53	0.19	30
8.44	0.69	0.23	30
8.62	0.84	0.30	30
8.81	1.00	0.34	30
9.02	1.18	0.39	30
9.22	1.35	0.45	30
8.24	2.22	0.54	35
8.42	2.38	0.58	35
8.61	2.57	0.64	35
8.80	2.73	0.71	35
9.03	2.95	0.78	35
9.21	3.12	0.84	35
8.24	4.17	1.25	40
8.42	4.65	1.39	40
8.62	5.25	1.48	40
8.81	5,83	1.58	40
9.04	6.48	1.68	40
9.21	6.96	1.77	40
8.23	6.64	2.03	45
8.41	7.20	2.16	45
8.62	7.92	2.31	45
8.83	8.62	2.44	45
9.01	9.23	2.55	45
9.22	9.23	2.71	45

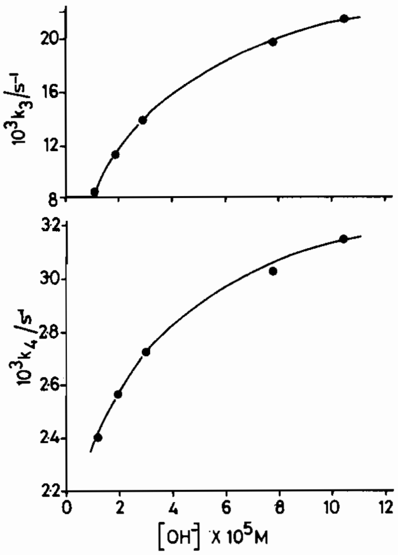


Fig. 2. Effect of pH on the hydrolysis of the cation **1** in the absence of carbonate. [**1**], 2 × 10^{-3} M, 40 °C; *I*, 0.5 M ($LiClO_4$).

TABLE II. Effect of Total Carbonate Concentration on the Rate Constants for the Reaction of **1** in Aqueous Carbonate Solution. [**1**], 2 × 10^{-3} M; pH, 8.28; *I*, 0.5 M ($LiClO_4$)

$[CO_3]_T$ (M)	$10^3 k_1$ (s^{-1})	$10^3 k_2$ (s^{-1})	θ_t (°C)
0.05	0.65	0.22	30
0.08	0.56	0.18	30
0.10	0.49	0.15	30
0.13	0.40	0.11	30
0.15	0.32	0.08	30
0.05	2.33	0.57	35
0.08	2.10	0.50	35
0.10	1.94	0.45	35
0.13	1.70	0.34	35
0.15	1.52	0.27	35
0.20	1.13	0.10	35
0.05	5.12	1.41	40
0.08	4.65	1.26	40
0.10	4.32	1.25	40
0.13	3.85	0.91	40
0.15	3.50	0.74	40
0.20	2.70	0.40	40
0.05	8.05	2.90	45
0.08	7.60	2.90	45
0.10	7.23	2.35	45
0.13	6.85	2.00	45
0.15	6.72	1.70	45
0.20	5.66	1.10	45

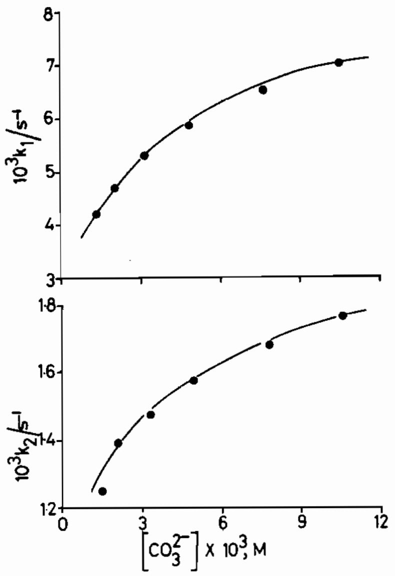


Fig. 3. Effect of $[CO_3^{2-}]$ on the reaction of the cation **1** in carbonate solution. [**1**], 2 × 10^{-3} M; 40 °C; *I*, 0.5 M ($LiClO_4$).

Table III. Both k_3 and k_4 values increase with an increase in $[OH^-]$, and at high $[OH^-]$ a tendency to level off is indicated (Fig. 2). This behaviour is quite characteristic of systems which exhibit ion-pairing phenomena. The data in Table I also show the same behaviour when k_1 and k_2 values are plotted against free carbonate concentration (Fig. 3) suggesting an ion-pair mechanism operating for both

TABLE III. Effect of pH on the Rate Constants for the Hydrolyis of 1. [1], 2×10^{-3} M; temperature, 40 °C; *I*, 0.5 M ($LiClO_4$)

pH	$10^3 k_3$ (s^{-1})	$10^3 k_4$ (s^{-1})
8.23	8.32	2.40
8.44	11.1	2.56
8.62	13.6	2.71
9.05	19.3	3.01
9.18	21.1	3.14

k_1 and k_2 path. It is also easy to visualise even stronger ion-pairing in the latter case since in solution a 4+ complex cation is surrounded by anions like OH^-, CO_3^{2-} and HCO_3^-.

Further evidence for the existence of an ion pair was obtained from the charge transfer spectrum of the amidohydroxo complex **1**. The intensity of the 292 nm peak of **1** is very sensitive to the concentration of carbonate ion in the solution. Figure 4 is obtained by immediately scanning the spectrum of complex **1** each time after the addition of successive amounts of $NaHCO_3$. The changes in the absorbance at this wavelength with the change in $[CO_3]_T$ are too large in magnitude and occurs too fast to be ascribed to any chemical reaction, and are in direct contrast to the absorbance changes during the kinetic run at 292 nm. The strength of these Linhard–Weigl bands [11] is dependent on the formation constant of the ion-pair complex. The calculated ion-pair constant *cf.* 1050 M^{-1} for $X \cdot CO_3$ species (see Scheme 1) strongly suggests a high concentration of this ion-pair in solution. Ion-pair formation of similar complexes with anions like SCN^-, SO_3^{2-} and CO_3^{2-} have been reported previously [12].

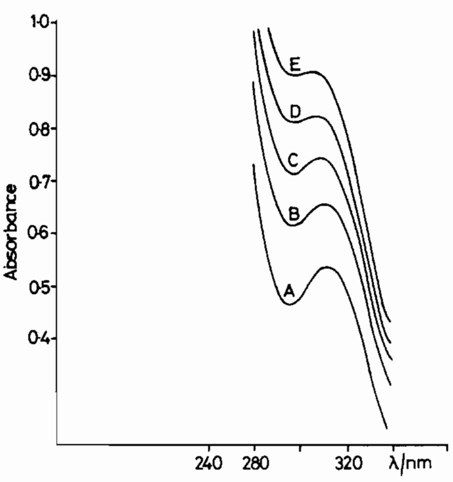
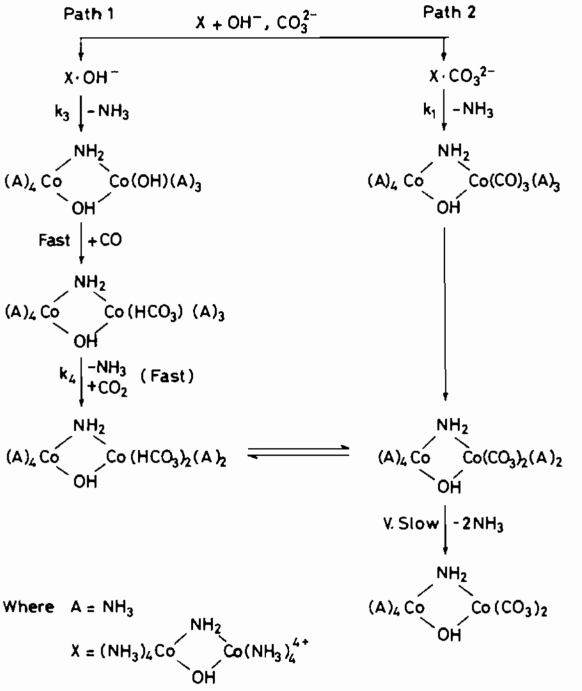


Fig. 4. Absorption spectra of the cation **1** at different concentrations of $NaHCO_3$. The total concentration of carbonate in A, B, C, D and E are 0.0 M, 0.05 M, 0.10 M, 0.15 M, and 0.20 M, respectively.



Scheme 1.

Hence, under the pH conditions prevailing in our experiments one can envisage the existence of three different types of ion pairs, $X \cdot OH^-$, $X \cdot CO_3^{2-}$, $X \cdot HCO_3^-$ (where X = complex ion **1**), all of which undergo a two-step reaction resulting in the loss of two molecules of NH_3. Subsequent loss of the other two NH_3 molecules with concurrent ring closure of carbonate occurs much more slowly, as indicated before. The effect of $X \cdot HCO_3^-$ in the system is almost negligible since the concentration of free HCO_3^- in the pH range examined is very small. It is also obvious from the data in Table I and III that $X \cdot OH^-$ eliminates NH_3 molecules much faster than $X \cdot CO_3^{2-}$. Therefore, it is now possible to rationalise the observed increase in the rate with an increase in pH at a constant $[CO_3^{2-}]_T$. As the pH increases, so does the concentration of $X \cdot OH^-$; hence, the reaction proceeds predominantly via Path 1 (Scheme 1). Once an ammonia is lost, direct anation of CO_3^{2-} to the pentacoordinate cobalt(III) might be one possibility, or if a OH^- ion takes up that site prior to any carbonate reaction, the rest of the chemistry must be akin to the now well-understood mechanism [13, 14] of fast CO_2 uptake by the coordinated hydroxide. It is reasonable to assume that the first coordinated carbonate labilizes an NH_3 molecule *trans* to it causing the k_2 path to occur. However, when the $[CO_3]_T$ is increased systematically the species $X \cdot OH^-$ is largely replaced by the more unreactive $X \cdot CO_3^{2-}$, resulting in a gradual decrease in the values of both k_1 and k_2 as presented in Table II. Under these conditions Path II becomes more predominant. The involvement of two ion-pairs and their simultaneous reactions make any rigorous treatment of the kinetic data very difficult.

An essential feature of the mechanism proposed in Scheme 1 is the loss of NH_3 molecules in the rate-determining steps. These reactions are of considerable interest since NH_3 ligands are generally very inert when coordinated to cobalt(III). The rate of loss of NH_3 from $Co(NH_3)_6^{3+}$ in water, for example, is reported [15] to be $\sim 10^{-10}$ s^{-1} and $\Delta H^{\ddagger}$ is 35 kcal mol^{-1}. The decomposition [16] of μ-amino-bis(pentaamminecobalt(III)) complex in aqueous solution is also slow ($k = 1.3 \times 10^{-4}$ s^{-1} at 65 °C) and it involves no loss of NH_3. In contrast to all of these, the reaction observed here is the unexpectedly effective substitution of CO_3^{2-} for NH_3. It must also be noted that the elimination of NH_3 occurs only from one of the cobalt centres, whereas in other studies [3] in acidic solutions it has been proposed that loss of NH_3 occurs from both the cobalt atoms.

Finally, it is interesting to note that the loss of NH_3 is about five times slower if NH_4HCO_3 is used instead of $NaHCO_3$ as the source of carbonate in the present reaction. This suggests that the free ammonia or primary ammine stabilises the terminal ammonia. This also explains the general retardation of the overall reaction when tris buffer was used in some initial runs. Thus, if the terminal ligands are sufficiently stabilised then the hydroxide cleavage might become the rate determining step and this, in turn, will facilitate the formation of a complex with a bridging carbonate group. This theory has been tested in our laboratory and, in fact, a bridging carbonato complex $[(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)Co(en)_2]^{4+}$ has been isolated and characterized.

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