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Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. II. Synthesis, Characterisation and Acid Hydrolysis of μ-Carbonato-bis(pentaamminecobalt(III)) Ion

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The title complex has been synthesised from the aquopentaamminecobalt(III) ion for the first time and characterised by potentiometric titration, conductometric charge determination and electronic spectra. The acid catalysed decomposition of the title complex has also been studied over the range $1 < pH < 7$ *at* $I = 0.5$ *M and 25 °C by means of stopped flow technique. The rate determining reaction is* $Co(NH_3)_5CO_3H^{2+} \rightarrow Co(NH_3)_5OH^{2+} + CO_2$. *The observed pseudo-first-order rate constant is independent of acidity for* $pH < 5$. *Above pH 5, the rate falls off rapidly and asymptotically approaches a small value beyond pH 7. The data are satisfactorily interpreted by the rate law* $k_{obs} = k_1[H^+]/([H^+] + K_1)$ *where* k_1 *is the rate constant for the above reaction and* K_1 *is the acid dissociation constant of* $Co(NH_3)_5CO_3H^{2+}$. *The values* $1.09\ s^{-1}$ *and* 4.4×10^{-7} *M found for* k_1 *and* K_1 *respectively are very similar to the values obtained for the acid catalysed decarboxylation of* $Co(NH_3)_5CO_3^+$ *ion [1–4].*

Introduction

The mechanism of decarboxylation of mononuclear carbonate complexes has been well documented [5–8]. However, there seems to be no report in the literature on the mechanism of decarboxylation of dinuclear cobalt(III) complexes containing carbonate as a bridging group. The μ-carbonato-bis(pentaamminecobalt(III)) ion is claimed to have been isolated in pure state by several workers [9–11] starting from a cobalt(II) salt. Our attempts to duplicate their methods proved futile. By modification of their method we have isolated a completely different bridged carbonato complex which we have reported recently [12]. After several unsuccessful attempts to make the μ-carbonato-bis(pentaamminecobalt(III)) salt we have finally prepared the complex salt by slight modification of the procedure followed by Abidini [13]. We now report the synthesis and characterisation of this complex salt and also the kinetic study of the carbonate bridge cleavage in acidic aqueous solution.

Experimental

Preparation of Compounds

Preparation of aquopentaamminecobalt(III) iodide

A concentrated solution of the aquopentaamminecobalt(III) nitrate which was prepared by standard procedure [14], was made in slightly acidic hot water and to this solution solid potassium iodide* was added in slight excess. The solution was cooled in ice for 30 minutes when deep red shiny crystals were collected. The purity of the complex was checked by visible spectroscopy.

Preparation of μ-carbonato-bis(pentaamminecobalt(III)) sulphate tetrahydrate

The compound was prepared by a slight modification of Abedini's method [13]. A slurry of aquopentaamminecobalt(III) iodide (32.8 mmol) and ammonium sulphate (65.7 mmol) in 200 ml of water was taken in an amber coloured bottle and cooled to 0 °C. Pure dry CO_2 gas** was passed through the solution for a period of 2 hours with slow addition of freshly prepared Ag_2CO_3 (48.9 mmol) while the mixture was stirred vigorously. During the course of the experiment a pasty solid was found to deposit on the inside of the reaction vessel. The solid was periodically scraped off and crushed. At the end of 2 hour period, the precipitated AgI was filtered off from the cherry red solution. To the filtrate about 250 ml of absolute alcohol was added and stirred for five minutes. A dark red oil which separated was converted to deep red powder by repeated treatment

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*When HI was used instead of KI only impure solid precipitated out.

**Co_2 gas was obtained in cylinder from Jamaica Oxygen and Acetylene Ltd., Kingston, Jamaica.

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with cold alcohol. The solid was found to contain some aquopentaamminecobalt(III) sulphate which was separated by repeated crystallisation from water and ethanol. The red compound was dried in a vacuum desiccator. The purity was checked by microanalysis.[†] *Anal.* Calcd. for $Co_2(NH_3)_{10}(CO_3)(SO_4)_2 \cdot 4H_2O$: C, 1.96; H, 6.21; N, 22.88. Found: C, 1.97; H, 6.17; N, 22.89.

Materials

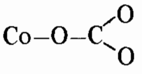
All the chemicals used were reagent grade. Distilled water, made from a Corning distillation unit, was used for preparative work. Ultra-pure water obtained by de-ionising ordinary distilled water using the Milli-Q Reagent grade water system[††] was used to make up solutions for physical measurements. The carbon dioxide gas from the cylinder was dried by P_2O_5 before using.

The visible and ultraviolet spectra were obtained with a Unicam SP8-100 recording spectrophotometer. The infrared spectra were recorded on a Perkin Elmer 735B spectrometer with KBr disc. The conductance measurements were made on a Cambridge Instrument Co. Ltd. conductivity meter using a cell of known cell constant. The pH titrations were carried out using an Orion Digital pH meter model 701 and Markson combination electrode.

The decarboxylation reactions were studied at an ionic strength of 0.5 *M* ($NaClO_4$) and over the acidity range $1 < pH < 7$. The rate measurements were made on a Durrum Model 110 stopped flow assembly [15]. For $pH > 2$ McIlvaine [16] phosphate-citric acid buffer was used. The observed pseudo first order rate constants were calculated in the usual way from the semilogarithmic plots of the data obtained from the exponential oscilloscope traces, and are reported as a mean of at least four knietic runs.

Results and Discussion

The μ-carbonato-bis(pentaamminecobalt(III)) sulphate (referred to as dimer in this section) is highly soluble in water and produces a deep red solution. The visible spectrum shows two absorption bands $\lambda_{1(max)} = 505$ nm ($\epsilon = 138\ M^{-1}\ cm^{-1}$, ${}^1T_{1g} \rightarrow {}^1A_{1g}$) and $\lambda_{2(shoulder)}$ 350 nm ($\epsilon = 152$, ${}^1T_{2g} \rightarrow {}^1A_{1g}$) which are consistent with the data expected for N_5-


$Co{-}O{-}C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$ chromophore. The extinction coefficient of the binuclear compound at λ_1 is significantly different[*] from an equimolar mixture of $Co(NH_3)_5CO_3^+$ and $Co(NH_3)_5H_2O^{3+}$. This observation eliminates the possibility that such a mixture is being confused with the dimer. An aqueous solution of the dimer has a pH of 6.47 at 25 °C while the equimolar mixture of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5CO_3^+$ produced a pH of 5.73. A highly alkaline value should be expected for a mixture of $Co(NH_3)_5OH^+$ and $Co(NH_3)_5HCO_3^{2+}$ as the latter is unstable [5] and decomposes to $Co(NH_3)_5OH^{2+}$ and CO_2. However, the dimer is believed to have been produced during the synthesis by the condensation of $(NH_3)_5CoCO_3H^{2+}$ and $(NH_3)_5CoOH^{2+}$ as follows:

$$(NH_3)_5CoHCO_3^{2+} + OHCo(NH_3)_5^{2+} \rightleftharpoons (NH_3)_5Co{-}OCO_2{-}Co(NH_3)_5^{4+} + H_2O.$$

This reaction occurs when a high concentration of CO_2 is maintained in the solution. The visible spectrum is also in accordance with such a mechanism [17].

The bridging nature of the carbonate in the dimer has been demonstrated by its infrared spectrum. The vibrational frequencies obtained for the dimer are in perfect agreement with the C–O frequencies obtained for another well characterised μ-carbonato complex of cobalt(III) [3] (see Table I). pH titrations have been used to study the stoichiometry of the reactions of bimolecular species with acid in comparison with its counterpart $Co(NH_3)_5CO_3^+$. It has been found from the titration curves that the ratio of mol of H^+ to mol of cobalt is 0.99 for the dinuclear complex and 1.90 for the carbonato pentaammine complex ion. Thus the dinuclear complex needs 1 mol of H^+ per mol of cobalt(III) for decarboxylation while the mononuclear carbonato complex needs 2 mol of H^+ per mol of cobalt(III). If the dimer is treated with excess dilute acids, brisk effervescence of CO_2 is observed and the visible spectrum of the acidic solution reveals two new peaks at 490 and 340 nm respectively, showing that all the complex is quantitatively converted into $Co(NH_3)_5H_2O^{3+}$. These observations enable us to write the stoichiometric equation:

$$(NH_3)_5CoCO_3Co(NH_3)_5^{4+} + 2H_3O^+ \rightarrow 2Co(NH_3)_5H_2O^{3+} + CO_2 + H_2O.$$

Another striking evidence for the dinuclear nature of the complex was obtained from conductometric measurements using the Onsager equation: $\lambda_c = \lambda_o - B\sqrt{C}$ as modified by Feltham and Hayter [18] for complex ions. In the equations λ_c and λ_o are the equivalent conductances at concentrations C and zero

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

[††] Milli-Q deioniser was purchased from Millipore Co., Bedford, Mass. 01730, U.S.A.

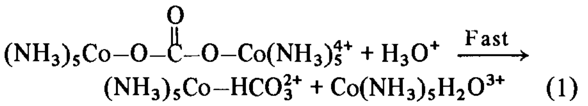
[*] The extinction coefficient of the binuclear compound is 138 M^{-1} cm^{-1} at 505 nm whereas a value of 126 was found for an equilibrium mixture of $Co(NH_3)_5CO_3^+$ and $Co(NH_3)_5H_2O^{3+}$ at the same wavelength. It is also worth noting that the experimental mixture has an absorption maximum at 502 nm.

TABLE 1. Vibrational Frequencies of Carbonato Complexes.

Complexes	Frequency (cm^{-1})			
	$\nu_3{}^a$	$\nu_1{}^b$	$\nu_2{}^c$	ν_4
$[(NH_3)_3Co(\mu\text{-}OH)(\mu\text{-}OH)(\mu\text{-}CO_3)Co(NH_3)_3]SO_4$	1270 1340,1480 1600	1050	830	620 750
$[(NH_3)_5Co(\mu\text{-}CO_3)Co(NH_3)_5](SO_4)_2$	1268 1337,1470 1620	1050	850	630 720

respectively. The value of B which can be obtained from the slope of the plot λ_c *vs.* $\sqrt{C}$ indicates the charge of the complex ion. Such a plot (as shown in Fig. 1) of the dimer gives a slope of 562.5. This value is in reasonable agreement with the value of 525 obtained [18] for a 4:1 type of electrolyte.

The pseudo first order rate constants (obtained from stopped-flow experiments) for the decarboxylation of the dimer at 25 °C are presented in the form of a k_{obs} *vs.* pH plot in Fig. 2. Below pH 5, k_{obs} is constant at 1.09 s^{-1} except for some experimental scatter. In the range of $5 < pH < 7$ there is a rapid decline in the rate to reach a low value at pH ~7. This observation is very similar to what is observed in the comparable study of carbonatopentaamminecobalt(III) ion [5]. Clearly the same type of preprotonation/CO_2 release mechanism is operative here, according to the reactions:



$$(NH_3)_5Co{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}Co(NH_3)_5^{4+} + H_3O^+ \xrightarrow{\text{Fast}} (NH_3)_5Co{-}HCO_3^{2+} + Co(NH_3)_5H_2O^{3+} \qquad (1)$$

$$(NH_3)_5Co{-}HCO_3^{2+} \overset{K_1}{\rightleftharpoons} (NH_3)_5CoCO_3^+ + H^+ \qquad (2)$$

$$(NH_3)_5Co{-}HCO_3^{2+} \xrightarrow{k_1} (NH_3)_5CoOH^{2+} + CO_2 \qquad (3)$$

$$(NH_3)_5Co{-}OH^{2+} + H^+ \overset{K_2}{\rightleftharpoons} (NH_3)_5Co(H_2O)^{3+} \qquad (4)$$

The corresponding rate equation is

$$k_{obs} = k_1[H^+]/([H^+] + K_1)$$

This equation can be further written as

$$1/k_{obs} = 1/k_1 + K_1/k_1[H^+]$$

A replot of the data in Fig. 2 in the double reciprocal form of the above equation where the limiting value $k_{obs} = k_1$ at high acidity is taken as 1.09 s^{-1} (an average of all the k_{obs} values below pH 4) gives a straight line. The slope of the straight line yields a value of $K_1 = 4.40 \times 10^{-7}$ *M* ($pK_1 = 6.4$). The solid curve of Fig. 2 was calculated by use of these k_1 and K_1 values. Both of these constants are in excellent agreement with those obtained by Dasgupta and Harris [5].

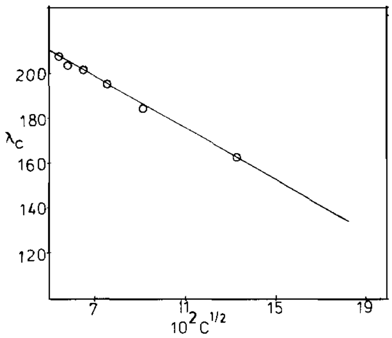


Fig. 1. Plot of equivalent conductance, λ_c *vs.* $C^{1/2}$ at various concentrations, C.

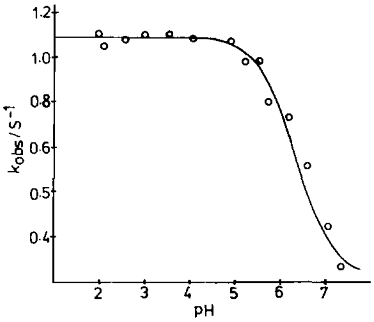


Fig. 2. Observed decarboxylation rate constant for $(NH_3)_5Co(\mu\text{-}CO_3)Co(HN_3)_5^{4+}$ as a function of pH at 25 °C and I = 0.5 *M*.

Although the decomposition of the dimer in acid solution is very fast (eqn. 1), in neutral solution the dimer remains stable for about 24 hours. This suggests that the equilibrium

$$(NH_3)_5CoCO_3Co(NH_3)_5^{4+} + H_2O \rightleftharpoons Co(NH_3)_5HCO_3^{2+} + Co(NH_3)_5OH^{2+} \qquad (5)$$

favours the dimer formation. However, an equilibrium mixture of $Co(NH_3)_5CO_3^+$ and $Co(NH_3)_5H_2O^{3+}$ at pH 6.5 does not produce [19] any appreciable quantity of the dimer. This means the reverse reaction in eqn. 5 is slower than the decomposition* of $Co(NH_3)_5HCO_3^{2+}$. Hence during the synthesis of the dimer a continuous passage of CO_2 is necessary in order to build up an appreciable concentration of $Co(NH_3)_5HCO_3^{2+}$ in the reaction mixture, and this will in turn force the above equilibrium to the direction of the dimer formation.

Finally, it is interesting to note that the bridged carbonate in the dinuclear complex μ-carbonato-bis-(pentaamminecobalt(III)) behaves like reactive mononuclear carbonato complexes of cobalt(III) whereas the carbonate in the complex ion μ-carbonato-di-μ-hydroxo-bis(triamminecobalt(III) and in other related μ-carbonato complex ions we recently prepared [20] are effectively inert to acid hydrolysis. This is, however, in contrary to the recent observations [21] made on some Cr(III) and Rh(III) complexes where the bridged carbonate behaves almost like a bidentate carbonate in mononuclear complexes [22]. A detailed study on the nature and reactivity of binuclear complexes containing carbonate ligand is in progress in our laboratory.

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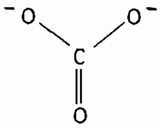

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*The mechanism of the reverse reaction in eqn. 5 is obviously different from the one established for the reaction [7] of $Co(NH_3)_5OH^{2+}$ with CO_2. This is contrary to what has been predicted by Abedini, Ref. 13).