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Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 15. The Acid-catalyzed Aquation of *trans*-Carbonatocyanotetraamminecobalt(III) Ion and Carbon Dioxide Uptake by *trans*-Aquocyanotetraamminecobalt(III) Ion [1]

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Introduction

Studies in this series dealing with the formation and decarboxylation of monodentate carbonate species include the pentamine complexes of Co(III) [5, 6], Rh(III) [7] and Ir(III) [7], and the tetraethylenepentamine complex of Co(III) [8]. Carbon dioxide uptake and acid-catalyzed decarboxylation in these systems only involve the formation and breakage of secondary oxygen–carbon bonds, respectively, rather than of the metal–oxygen bonds. Conversely, other studies in this series, involving diaquoamine complexes of Co(III), show that ring closing and opening of the metal–oxygen bond depends on the nature of the 'non-participating' amine group [9, 10].

The present study was undertaken to investigate the effect of substituents *trans* to the hydroxo or carbonato ligands in cobalt(III) amine complexes on the rate parameters for carbon dioxide uptake and decarboxylation reactions. Since it is well known that cyanide is a good *trans*-labilizing ligand [11] in substitution processes, its influence on the rate of C–O bond cleavage and the basicity of the hydroxo ligand was studied for the complexes *t*-$Co(NH_3)_4(CN)(OCO_2)$ and *t*-$Co(NH_3)_4(CN)(OH)^+$ respectively.

Experimental

Materials

All chemicals used were of reagent grade. Deionized and degassed water was used in preparing all solutions. *t*-$[Co(NH_3)_4(CN)(OH_2)]Cl_2$ was prepared from *t*-$[Co(NH_3)_4(CN)(SO_3)]\cdot 2H_2O$ according to standard procedures [12, 13]. All efforts to prepare *t*-$[Co(NH_3)_4(CN)(OH_2)](ClO_4)_2$ were unsuccessful and the chloride salt was used in this investigation. Its purity was checked by microanalysis [14].

Various procedures [15] were followed to isolate *t*-$[Co(NH_3)_4(CN)(OCO_2)]$. In all cases the product was contaminated with the less soluble *t*-$[Co(NH_3)_4(CN)(OH)]Cl$ species. The highest purity (~85%) was obtained by adding $NaHCO_3$ and Na_2CO_3 slowly to a saturated solution of *t*-$[Co(NH_3)_4(CN)(OH_2)]Cl_2$ until a pH of ~8.5 was reached. Cooling or addition of alcohol resulted in the precipitation of the carbonato complex along with some of the cyano hydroxo impurity.

Spectra

Absorption spectra in the UV–visible range were measured using a Cary 118 spectrophotometer. The spectra of the various species [16] involved are shown in Fig. 1. *t*-$Co(NH_3)_4(CN)(OH)^+$ was prepared in solution by dissolving *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$ in basic medium, whereas *t*-$Co(NH_3)_4(CN)(OCO_2)$ was prepared in solution as described above. The spectrum of *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$ is in good agreement with data published elsewhere [17]. Acidification of the carbonato complex solution gave a spectrum identical to that of *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$.

Determination of the Acid Dissociation Constant

The pK value for the acid dissociation of *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$ was determined at 25 °C and an ionic strength of 0.5 *M* ($NaClO_4$) by titrating a 2×10^{-3} *M* complex solution with 0.1 *M* NaOH. All pH measurements were made with a Beckman Research Model pH meter and a reference electrode filled with a saturated NaCl solution. The pK for *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$ was found to be 7.55 ± 0.05 [21].

Rate Measurements

The kinetics of the acid-catalyzed aquation of the carbonato complex were studied at an ionic strength of 0.5 *M* ($NaClO_4$), between 9 and 30 °C and over an acidity range of $0.3 \leqslant pH \leqslant 7.6$. The rate of carbon dioxide uptake by *t*-$Co(NH_3)_4(CN)(OH)^+$ was measured within the temperature range 5 to 30 °C, at acidities of $8 \leqslant pH \leqslant 9.5$, and at an ionic strength of 0.5 *M* ($NaClO_4$), by the 'acidification method' described earlier [6]. Both reactions were monitored at a wavelength of 330 nm where the difference in absorption between reactant and product is at a maximum (see Fig. 1). The rate measurements were made on a Durrum Model 110 stopped-flow assembly. For $pH \geqslant 2$ the following buffers were used: McIlvaine phosphate–citric acid [22]; phosphate–NaOH [23]; and boric acid–NaOH [23]. pH measurements were made on the above mentioned pH meter using a water-jacketed sample holder thermostated at the reaction temperature. The observed pseudo-first-order rate constants were calculated in the usual way using a least-squares program and are reported in the Results as the mean of at least six kinetic runs. For the decarboxylation experiments at

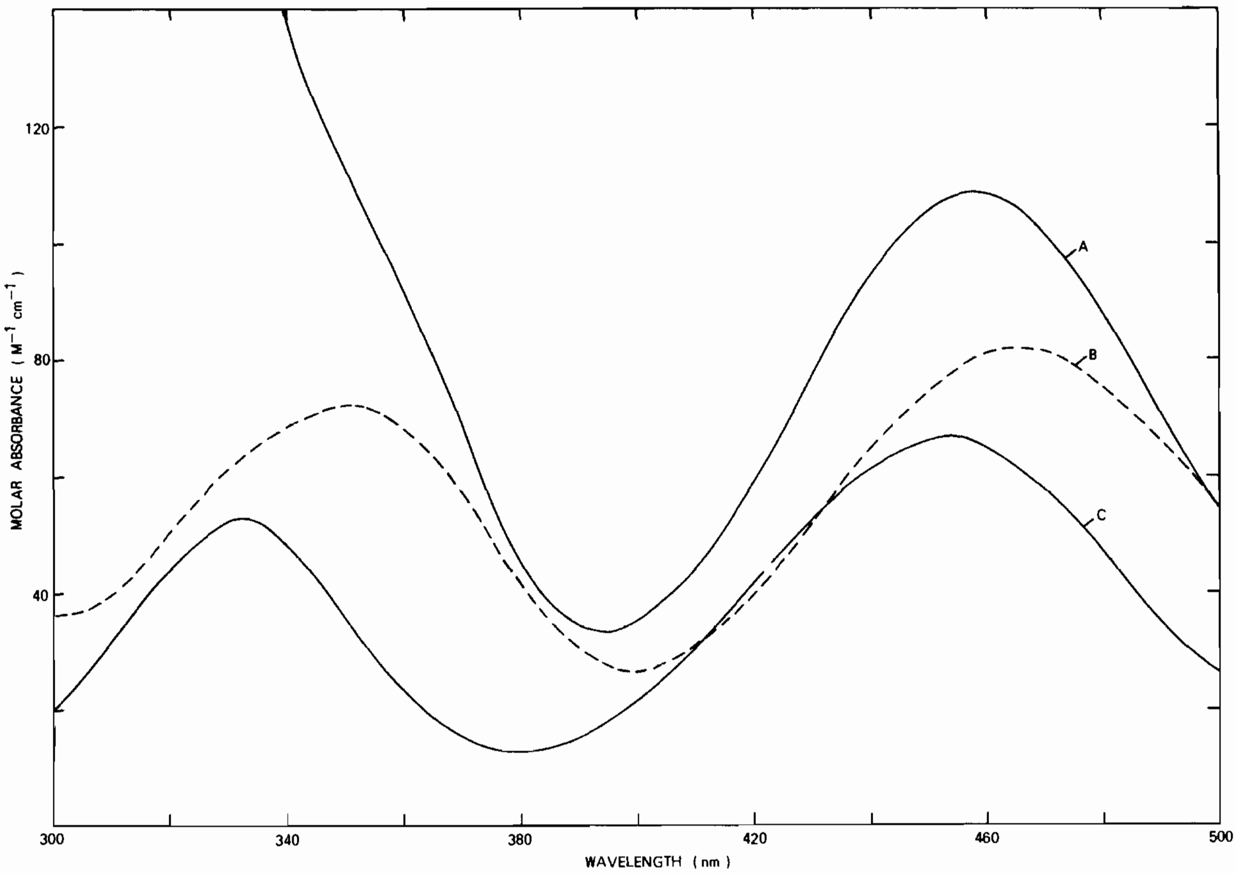

Fig. 1. Absorbance spectra of various complex ions: A, *t*-$Co(NH_3)_4(CN)(OCO_2)$; B, *t*-$Co(NH_3)_4(CN)(OH)^+$; C, *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$.

TABLE I. pH Dependence of k_{obs} for the Aquation of *t*-$Co(NH_3)_4(CN)(OCO_2)^a$. [Co(III)] = 2.3×10^{-3} *M*, Temp. = 25 °C, wavelength = 330 nm, Ionic strength = 0.5 *M*.

pH	k_{obs}, sec^{-1}
0.30	0.363 ± 0.019
0.30	0.367 ± 0.016
0.60	0.383 ± 0.016
1.30	0.367 ± 0.023
1.60	0.375 ± 0.024
1.60	0.387 ± 0.025
2.00	0.364 ± 0.017
2.54	0.388 ± 0.030
3.10	0.399 ± 0.034
3.38	0.390 ± 0.018
4.36	0.407 ± 0.024
4.37	0.388 ± 0.023
5.42	0.320 ± 0.027
6.04	0.269 ± 0.009
6.44	0.270 ± 0.010
6.77	0.201 ± 0.013
6.94	0.168 ± 0.006
7.01	0.136 ± 0.009
7.59	0.062 ± 0.002

[a]Prepared in solution as described in the Experimental.

pH > 6.5, the first-order plots showed deviation from linearity at longer reaction times, an effect which became more pronounced with increasing pH. Such deviations have been observed before [7] and were attributed to interference by the slower rate of hydration of the released CO_2, resulting in significant CO_2-uptake under such conditions. Addition of micromolar quantities of carbonic anhydrase [7], which catalyzes CO_2 hydration, to the reaction solution resulted in normal linear first-order plots.

Results and Discussion

Preliminary experiments indicated that under the experimental conditions used in this investigation isomerization did not interfere with any of the reactions involving *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$, *t*-$Co(NH_3)_4(CN)(OH)^+$, or *t*-$Co(NH_3)_4(CN)(OCO_2)$.

Rate data for the acid-catalyzed decarboxylation of *t*-$Co(NH_3)_4(CN)(OCO_2)$ as a function of acidity and temperature are summarized in Tables I and II, respectively. A plot of k_{obs} *versus* pH for the data in Table I exhibits the same sigmoid pH dependence as was observed in earlier studies of monodentate

TABLE II. Temperature Dependence of k_{obs} for the Aquation of t-$Co(NH_3)_4(CN)(OCO_2)^a$. [Co(III)] = 2.3×10^{-3} *M*, pH = 0.30 ([H^+] = 0.5 *M*), wavelength = 330 nm. Ionic strength = 0.5 *M*.

Temperature °C	k_{obs}, sec^{-1}
9.7	0.043 ± 0.003
13.9	0.073 ± 0.005
19.1	0.173 ± 0.003
24.5	0.331 ± 0.012
25.0	0.365 ± 0.017
29.3	0.494 ± 0.009
$\Delta H^{\neq}$ kcal mol^{-1}	21.5 ± 1.0
$\Delta S^{\neq}$ cal deg^{-1} mol^{-1}	+11.4 ± 3.5

[a] Prepared in solution as described in the Experimental.

TABLE III. Rate Data for the CO_2 Uptake by t-$Co(NH_3)_4(CN)(OH)^+$. [Co(III)] = 1×10^{-3} *M*, wavelength = 330 nm, $[CO_2]^a$ = 0.01 *M*. Ionic strength = 0.5 *M*.

Temperature °C	pH	k_{obs}, sec^{-1}	$k_2^b = \frac{k_{obs}([H^+] + K_2)}{K_2[CO_2]}$ M^{-1} sec^{-1}
25	8.16	3.27 ± 0.07	407
	8.48	3.24 ± 0.09	362
	8.66	3.03 ± 0.07	327
	8.88	2.95 ± 0.04	309
	9.04	3.02 ± 0.05	312
	9.20	3.11 ± 0.05	318
	9.36	3.25 ± 0.04	330
	9.50	3.39 ± 0.15	343
		Average	338 ± 32
5.9	8.66	0.385 ± 0.009	41.4
10.3		0.547 ± 0.019	58.9
15.7		0.941 ± 0.050	101
20.1		1.24 ± 0.06	133
25.0		3.03 ± 0.07	327
29.2		3.32 ± 0.03	357
$\Delta H^{\neq}$ kcal mol^{-1}			15.7 ± 1.4
$\Delta S^{\neq}$ cal K^{-1} mol^{-1}			+5.3 ± 4.8

[a] From 'acidification method' – see ref. 6. [b] $K_2 = 2.82 \times 10^{-8}$ *M* ($pK_2 = 7.55$ at $\mu = 0.5$ *M*).

carbonato complexes [5–8]. The same type of preprotonation/CO_2 release mechanism appears to be operative in this system involving the following equations:

$$t\text{-}Co(NH_3)_4(CN)(OCO_2) + H^+ \rightleftharpoons t\text{-}Co(NH_3)_4(CN)(OCO_2H)^+ \qquad 1/K_1 \qquad (1)$$

$$t\text{-}Co(NH_3)_4(CN)(OCO_2H)^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} t\text{-}Co(NH_3)_4(CN)(OH)^+ + CO_2 \qquad (2)$$

TABLE IV. Comparison of Rate Parameters for Carbon Dioxide Uptake and Decarboxylation Reactions of Various Metal Amine Complexes[a].

ML_5	pK_1 [b]	pK_2	Decarboxylation			CO_2 Uptake			Ref.
			k_1 sec^{-1}	$\Delta H^{\neq}$ [c]	$\Delta S^{\neq}$ [d]	k_2 M^{-1} sec^{-1}	$\Delta H^{\neq}$ [c]	$\Delta S^{\neq}$ [d]	
$Co(NH_3)_5^{3+}$	6.70 ± 0.02	6.6	1.10 ± 0.05	16.8 ± 0.2	−2 ± 1	220 ± 40	15.3 ± 0.9	+4 ± 3	6
$Co(tetren)^{3+}$	6.4	6.3 ± 0.1	0.28 ± 0.03	15.6 ± 1.9	−9 ± 4	166 ± 15	15.4 ± 1.2	+3 ± 4	8
t-$Co(NH_3)_4(CN)^{2+}$	6.89 ± 0.04	7.55 ± 0.05	0.36 ± 0.04[b]	21.5 ± 1.0	+11 ± 3	338 ± 32	15.7 ± 1.4	+5 ± 5	this work
t-$Co(en)_2(Cl)^{2+}$	6.52 ± 0.03[e]	5.9	1.02[f]	17.4 ± 1.1	0 ± 4	64[e]	–	–	24
$Rh(NH_3)_5^{3+}$	6.95 ± 0.03	6.78 ± 0.03	1.13 ± 0.06	17.0 ± 0.5	−1 ± 1	490 ± 120	17 ± 1	+12 ± 3	7
$Ir(NH)_3)_5^{3+}$	6.79 ± 0.02	6.70 ± 0.03	1.45 ± 0.07	19.0 ± 0.5	+6 ± 1	590	–	–	7

[a] Rate and equilibration constants refer to reactions similar to those presented in reactions (1) to (3). Temp. = 25 °C, ionic strength = 0.5 *M*. [b] Calculated from the double reciprocal plot of the kinetic data – see Discussion. [c] kcal mol^{-1}. [d] cal deg^{-1} mol^{-1}. [e] Temp. = 15 °C. [f] Estimated from the temperature dependence of k_1.

$$t\text{-Co(NH}_3)_4\text{(CN)(OH)}^+ + \text{H}^+ \rightleftharpoons t\text{-Co(NH}_3)_4\text{(CN)(OH}_2)^{2+} \quad 1/K_2 \qquad (3)$$

Reactions (1) and (3) are rapid acid–base equilibria, whereas reaction (2) is the rate-determining step for both the decarboxylation (k_1) and CO_2 uptake (k_2) processes. The overall rate law for this mechanism is [6]:

$$k_{obs} = \frac{k_1[H^+]}{[H^+] + K_1} + \frac{k_2K_2[CO_2]}{[H^+] + K_2} \qquad (4)$$

In the absence of any added CO_2, equation (4) simplifies to

$$k_{obs} = k_1[H^+]/\{[H^+] + K_1\} \qquad (5)$$

The decarboxylation data in Table I can be plotted according to eqn. (5) in the double reciprocal linear form of k_{obs}^{-1} *versus* $[H^+]^{-1}$, and yield $k_1 = 0.36 \pm 0.04$ sec^{-1} and $pK_1 = 6.89 \pm 0.04$. This value of k_1 is in good agreement with the average limiting value for k_{obs} at pH < 4.5 of 0.38 ± 0.01 sec^{-1} (at high $[H^+]$ eqn. (5) reduces to $k_{obs} = k_1$). The temperature dependence of k_{obs} at $[H^+] = 0.5$ *M* enables the calculation of the activation parameters for k_1 and these values are included in Table II.

At pH > 8, where CO_2 uptake by t-Co(NH$_3$)$_4$(CN)(OH)$^+$ was studied (see Table III), the contribution from the decarboxylation process towards k_{obs} becomes so small that eqn. (4) simplifies to

$$k_{obs} = \frac{k_2K_2[CO_2]}{[H^+] + K_2} \qquad (6)$$

Since pK_2 is known (see Experimental), k_2 could be calculated from eqn. (6) for the CO_2 uptake data over the pH and temperature ranges shown in Table III. The average value of k_2 and its activation parameters are also included.

A comparison of the decarboxylation and CO_2 uptake rate parameters for a series of metal amine complexes is given in Table IV. pK_2 for t-Co(NH$_3$)$_4$(CN)(OH$_2$)$^{2+}$ is significantly higher than for any of the other systems quoted and illustrates the *trans*-effect of the cyano ligand. The strengthening of the O–H bond cannot be ascribed to the difference in net charge on the complex since this is not observed for t-Co(NH$_3$)$_4$(Cl)(OH$_2$)$^{2+}$ [24]. The *trans*-effect also shows up to a lesser extent in the pK_1 values, which are all very similar although somewhat higher for t-Co(NH$_3$)$_4$(CN)(OCO$_2$H)$^+$. This is within expectation since the strengthening of a secondary O–H bond is involved in the latter case. Furthermore, similar reasons account for the higher activation parameters reported for the cleavage of the –O–C– bond (decarboxylation step) in t-Co(NH$_3$)$_4$(CN)(OCO$_2$H)$^+$. Although k_1 for this complex is not the lowest in the series, it certainly has the highest activation parameters.

Although k_2 for t-Co(NH$_3$)$_4$(CN)(OH)$^+$ is higher than for the other Co(III) complexes quoted, the difference is not very significant since the activation parameters are almost equal, within experimental error. The increase in k_2 down the series to the Rh(III) and Ir(III) amine complexes was previously ascribed to a decreasing basicity of the coordinated oxygen of the M–O–H group in conjunction with the increasing M–O bond strength in the series Co $<$ Rh $<$ Ir [7]. The large errors involved in the measurements of k_2 do not allow any reasonable comparison to be made between these quantities. The value of k_2 for t-Co(NH$_3$)$_4$(CN)(OH)$^+$ fits the linear relationship between $\log k_2$ and the pK of the corresponding aquo complex (pK_2 in this study) as discussed before in detail [25].

Thus the *trans* effect appears to play only a minor role in affecting the reactivity of bonds which are not directly at the metal centre, at least for cobalt(III) complexes.

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16 λ_{max} and ϵ_{max} (given in brackets) for the different complex species are *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$–453 (67), 333 (53); *t*-$Co(NH_3)_4(CN)(OH)^+$–465 (82), 352 (72); *t*-$Co(NH_3)_4(CN)(OCO_2)$–458 (109).

17 λ_{max} and ϵ_{max} (given in brackets) for *t*-$Co(NH_3)_4(CN)(OH_2)^{2+}$ quoted in the literature are: 451 (–) [18]; 455 (67.5), 334 (52.1) [19]; 446 (68), 330 (55) [20].

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