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## Kinetics and Mechanism of Aquation and Formation Reactions of Carbonato Complexes. 10. Acid-Catalyzed Decarboxylation of Carbonatotetrakis(pyridine)cobalt(III) Ion<sup>1,2</sup>

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The title compound rather slowly undergoes both uncatalyzed and acid-catalyzed decomposition, in which the initial product is solely *trans*-Co(py)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, though the latter relatively rapidly undergoes a further internal redox process to yield Co<sup>II</sup>. The acid-catalyzed decarboxylation step is sensitive to ionic strength increase. It is accelerated by heavy water solvent, and the results in strongly acid solution can be correlated by the Hammett acidity function concept, consistent with a proton preequilibration mechanism. The slowness of the process relative to all other similar complexes is ascribed to unusually strong metal-oxygen bonding in the tetrapyrrolyl species, possibly related to its high degree of aromaticity.

### Introduction

Previous papers in this series<sup>2-4</sup> as well as studies in other laboratories<sup>5</sup> have involved comparisons of the kinetics of the acid-catalyzed hydrolysis of chelated carbonato complexes of the general type Co<sup>III</sup>LCO<sub>3</sub><sup>n+</sup>, where L is a tetradentate ligand or a group of simpler ligands of the same total coordinating capacity. There is a variation of about six orders of magnitude in the value of the second-order rate constant governing the proton-promoted dechelation of the carbonato group, depending on the nature of the species L. Values of this rate constant at 25 °C have now been observed to range from approximately 10<sup>-4</sup> M<sup>-1</sup> s<sup>-1</sup> for L = (bipyridine)<sub>2</sub> or (*o*-phenanthroline)<sub>2</sub> as a minimum<sup>5</sup> to a maximum of 120 M<sup>-1</sup> s<sup>-1</sup> for L = EDDA (ethylenediaminediacetate) in the  $\alpha$  configuration.<sup>2</sup> As part of our continuing effort to seek an explanation for these variations of rate with changes in the nature of the "inactive" ligand or group of ligands, we initiated the present study of the species in which L = (pyridine)<sub>4</sub>. The monodentate pyridine ligand, unlike most of the other amine ligands we have examined so far, exhibits aromaticity such as is found in the related "bpy" and "*o*-phen" ligands already mentioned,<sup>5</sup> although the (py)<sub>4</sub> complex lacks much of the structural rigidity of the triply chelated (bpy)<sub>2</sub> and (*o*-phen)<sub>2</sub> congeners. Our study now reveals that the (py)<sub>4</sub> complex is even more resistant to carbonato ring opening than are the latter species. Two other unusual and rather unexpected characteristics of the overall aquation process are noted: a relatively rapid conversion of the *cis* geometry of the original Co(py)<sub>4</sub>CO<sub>3</sub><sup>+</sup> complex such that only *trans*-diaquo product appears, and an internal redox reaction of the first-formed diaquo species to give aqueous cobalt(II). This report is concerned primarily with the dynamics of the decarboxylation process, to be followed later by a detailed consideration of the nature of the redox reaction.

### Experimental Section

The complexes carbonatotetrakis(pyridine)cobalt(III) perchlorate monohydrate, [Co(py)<sub>4</sub>CO<sub>3</sub>]ClO<sub>4</sub>·H<sub>2</sub>O, and *trans*-diaquotetrakis(pyridine)cobalt(III) perchlorate tetrahydrate, [Co(py)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O, were prepared as outlined by Springborg and Schaffer.<sup>6</sup> The purity of the two compounds was checked by chemical analysis<sup>7</sup> (Calcd. for the carbonato complex: C, 45.63; H, 4.01; N, 10.14. Found: C, 45.41; H, 4.00; N, 10.06. Calcd. for the diaquo complex: C, 30.73; H, 4.13; N, 7.17. Found: C, 30.05; H, 3.41; N, 7.25) and by comparison of the visible spectra with the literature values (Table I). The spectra were obtained with a Cary Model 14 or Model 118C instrument, those for the diaquo complex at 25 °C and for the carbonato congener at 5 °C, since at this lowered temperature its rate of decarboxylation is negligible even in 5.0 M acid. Figure 1 compares these spectra with that of a "conventional" tetraamine complex ion, carbonatobis(ethylenediamine)cobalt(III).

An alternative procedure for the preparation of the *trans*-diaquo complex made use of the corresponding dichloro complex,<sup>8</sup> *trans*-

[Co(py)<sub>4</sub>Cl<sub>2</sub>]Cl·6H<sub>2</sub>O. This is dissolved in 1 M HClO<sub>4</sub> and mercuric acetate is added. The color slowly changes from green to red-violet, and the diaquo product precipitates on the addition of 70% HClO<sub>4</sub> after cooling. Spectral measurements confirmed the identity of this product with that obtained earlier by the other method.<sup>6</sup>

All chemicals used were of reagent grade. Deionized and distilled water was used in preparing all solutions. The bis(pyridine)mercury(II) perchlorate that was used to convert the [Co(py)<sub>3</sub>CO<sub>3</sub>Cl] intermediate to the final [Co(py)<sub>4</sub>CO<sub>3</sub>]ClO<sub>4</sub>·H<sub>2</sub>O product was prepared by mixing aqueous solutions of pyridine and mercury(II) perchlorate in the stoichiometric quantities. The precipitated product was purified by recrystallization from warm water.

Reaction rates were determined from absorbance vs. time data in the temperature range 30–70 °C, utilizing the time-drive chart system of the Cary Model 118C or by batch sampling with the Cary Model 14 or a Beckman DU instrument. The reaction cell was thermostated to within  $\pm 0.1$  °C. Absorbance changes were usually monitored at 530 nm, but some runs were repeated at 380 nm and verified the independence of the rate data of the monitoring wavelength. Isosbestic points were identified by a series of complete spectral scans at various intervals during the course of reaction. Except for two cases to be noted later, the rate data were analyzed by a conventional linear regression procedure<sup>9</sup> for pseudo-first-order kinetics according to the absorbance change relation  $\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{\text{obsd}}t$ .

### Results

In preliminary experiments carried out at  $I = 1.0$  M (NaClO<sub>4</sub>) and over a range of acid concentrations up to 1.0 M (HClO<sub>4</sub>), the spectral scans at various time intervals exhibited no isosbestic points in the visible region. The "infinite-time" spectrum had one minor peak at 510 nm ( $\epsilon \sim 5$  M<sup>-1</sup> cm<sup>-1</sup>), indicative of aqueous cobalt(II) as the only distinguishable product of reaction under these conditions. Plots of  $\log(A_t - A_\infty)$  vs. time were linear over at least 3 half-lives and the pseudo-first-order rate constants ( $k_{\text{obsd}}$ ) at two different wavelengths (530 and 380 nm) were identical within  $\pm 5\%$ . The results of a series of runs of this type at various temperatures and acidities are recorded in Table IIA. It is noted that these rate constants are only slightly dependent on acidity in this limited range, a fact which is made obvious on carrying out a linear regression analysis of the data according to the conventional expression<sup>2-4</sup> for hydrolysis of carbonato complexes:

$$k_{\text{obsd}} = k_0 + k_1 [\text{H}^+] \quad (1)$$

The rate constants and their standard deviations so evaluated appear at the foot of Table IIA, where the values of the conventional temperature parameters are also given. One concludes that at  $I = 1.0$  M and within the range of other conditions specified, acid catalysis plays a relatively minor role in the decomposition process and that the overall result is reduction of cobalt(III) to cobalt(II). This behavior contrasts sharply with that of the other Co<sup>III</sup>LCO<sub>3</sub><sup>n+</sup> complexes heretofore examined, all of which exhibit predominant

Table I. Spectral Data for Tetrakis(pyridine)cobalt(III) Complexes

Complex	$\lambda_{\max} (\epsilon_{\max})$ , nm ( $M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\min} (\epsilon_{\min})$ , nm ( $M^{-1} \text{ cm}^{-1}$ )	Medium	Ref
[Co(py) <sub>4</sub> CO <sub>3</sub> ](ClO <sub>4</sub> )·H <sub>2</sub> O	530 (172), 379 (190)	446 (24), 363 (167)	Water	6 <sup>a</sup>
	530 (170), 378 (189)	445 (23), 361 (171)	Water	This work
[Co(py) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	534 (163), 373 (196)	444 (24), 356 (179)	5 M HClO <sub>4</sub>	This work
	560 (44), 490 (51)	540 (43), 435 (26)	1 M HNO <sub>3</sub>	6 <sup>a</sup>
	550 (41), 490 (49)	540 (40), 440 (26)	1 M HClO <sub>4</sub>	This work
	560 (40), 488 (51)	540 (39), 435 (30)	5 M HClO <sub>4</sub>	This work

<sup>a</sup> These authors also report spectral data for the carbonato complex in other media.

Table II. Observed Rate Constants ( $s^{-1} \times 10^5$ ) for the Decomposition of Co(py)<sub>4</sub>CO<sub>3</sub><sup>+</sup> Ions in Aqueous Acidic Solution

A ( <i>I</i> = 1.0 M)			B ( <i>I</i> = 5.0 M)					
[HClO <sub>4</sub> ], M	50 °C	60 °C	70 °C	[HClO <sub>4</sub> ], M	30 °C	40 °C	50 °C	60 °C
0.05		55.7	255	1.0	1.32	6.74	42.8	116
0.10		55.8	245					153
			247	2.0	2.33	11.4	64.9	194
0.20	11.2						(13.0) <sup>c</sup>	
	11.7			3.0	3.89	17.0	75.8	228
0.225		60.0					76.6	
0.30			267				(23.8) <sup>d</sup>	
0.35		61.8		4.0	5.90	24.2	97.7	288
0.40	12.1						104	
	14.1						(41.7) <sup>e</sup>	
0.60	11.0	66.8	277	5.0	7.61	32.5	103	339
	15.0					(59.4) <sup>b</sup>	111	378
0.80	12.0	72.0	273				114	381
	12.4						119	419
	12.7						(223) <sup>b</sup>	(379) <sup>b</sup>
0.99		68.7	292					
1.00	15.6	77.8	273					
	(15.5) <sup>a</sup>	(74.8) <sup>a</sup>	(267) <sup>a</sup>					
1.01	11.5							
	12.0							
	14.5							
$10^5 k_0, s^{-1}$	$11.7 \pm 1.1$	$54.9 \pm 1.7$	$250 \pm 4$		$-0.6 \pm 0.3$	$-0.9 \pm 1.4$	$28 \pm 5$	$67 \pm 21$
$10^5 k_1, M^{-1} s^{-1}$	$1.5 \pm 1.4$	$19.3 \pm 2.7$	$34.6 \pm 7.3$		$1.62 \pm 0.10$	$6.43 \pm 0.43$	$17.1 \pm 1.3$	$61.1 \pm 5.5$
$\Delta H^\ddagger_0, \text{kcal/mol}$		$33.2 \pm 0.6$						
$\Delta S^\ddagger_0, \text{cal/deg/mol}$		$25.9 \pm 1.4$						
$\Delta H^\ddagger_1, \text{kcal/mol}$		$(34 \pm 12)$					$23.2 \pm 1.0$	
$\Delta S^\ddagger_1, \text{cal/deg/mol}$		$(26 \pm 36)$					$-4.0 \pm 3.1$	

<sup>a</sup> 90% D<sub>2</sub>O. <sup>b</sup> 70% D<sub>2</sub>O. <sup>c</sup> *I* = 2.0 M. <sup>d</sup> *I* = 3.0 M. <sup>e</sup> *I* = 4.0 M.

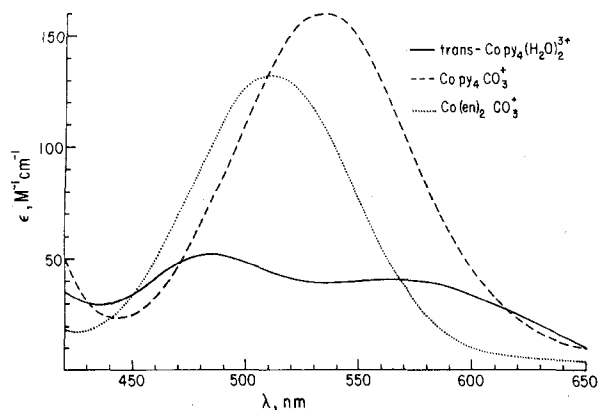


Figure 1. Spectra of tetrakis(pyridine)cobalt(III) complexes in 5 M HClO<sub>4</sub>. The spectrum of Co(en)<sub>2</sub>CO<sub>3</sub><sup>+</sup> in water is shown for comparison purposes.

acid-catalyzed decarboxylation in this range of conditions, and for none of which are cobalt(II) products obtained during relatively long periods of room-temperature storage of the resulting diaquo complexes.

Further experiments were now performed at *I* = 5.0 M (NaClO<sub>4</sub>) in order to enable a much broader acidity variation. Visible spectrum sweeps with acidities in the range 1.0 M <

[H<sup>+</sup>] < 5.0 M now indicated the existence of several isosbestic points, the positions of which and their duration in that position being somewhat dependent on [H<sup>+</sup>]. In the runs made in 5.0 M HClO<sub>4</sub>, clearly defined isosbestic points appear at 438, 478, and 622 nm and are maintained for at least 4 half-times of reaction. Reference to Figure 1 makes it apparent that direct hydrolysis to the *trans*-diaquo species is taking place under these conditions, with the cobalt(II) final product only appearing much later. At lower acid concentrations, the data could not be analyzed according to simple first-order kinetics due to partial overlap of the subsequent redox process with the initial hydrolytic reaction. With [H<sup>+</sup>] = 1.0 or 2.0 M (*I* = 5.0 M) the results were best treated as a consecutive first-order system to yield two rate constants by standard procedure,<sup>10</sup> the first of which is that of decarboxylation. At the higher acidities, the hydrolysis rate constants were readily obtained by a first-order curve-fitting method by means of which *A*<sub>∞</sub> is calculated by use of the data for approximately 90% conversion to product. Since hydrolysis is considerably more rapid in these experiments than the redox process, the latter interfered minimally and the best-fit *A*<sub>∞</sub> values differ only a few percent from the known *A*<sub>∞</sub> values calculated for complete conversion of carbonato complex to *trans*-diaquo complex (i.e., no redox).

The pseudo-first-order observed rate constant values for aquation obtained in the various experiments at *I* = 5.0 M are

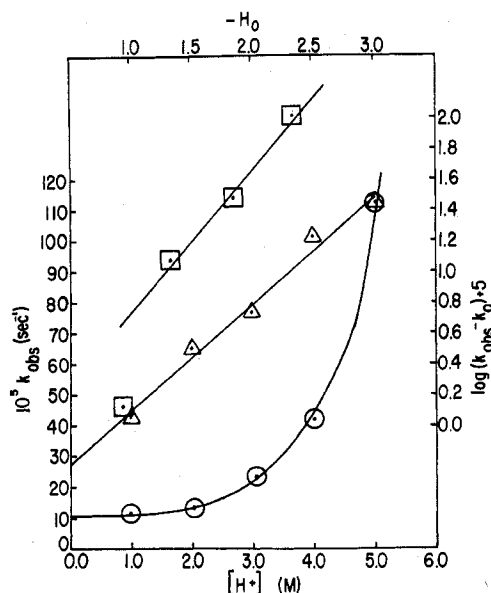
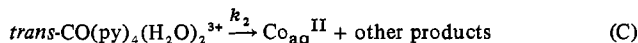
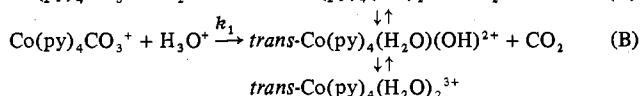
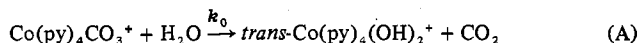


Figure 2. Variation of rate constants for acid-catalyzed decarboxylation of  $\text{Co}(\text{py})_4\text{CO}_3^+$  at  $50^\circ\text{C}$ : (▲)  $k_{\text{obsd}}$  vs.  $[\text{H}^+]$ ,  $I = 5.0$  M; (⊙)  $k_{\text{obsd}}$  vs.  $[\text{H}^+]$ ,  $I = [\text{H}^+]$ ; (⊖)  $\log(k_{\text{obsd}} - k_0)$  vs.  $-H_0$ ,  $I = [\text{H}^+]$ .

collected in Table IIB. The variation of  $k_{\text{obsd}}$  with  $[\text{H}^+]$  turns out to be linear according to the usual two-term expression of eq 1 above. Standard least-squares regression analysis yields the  $k_0$  and  $k_1$  values recorded at the foot of the table, along with the usual temperature parameters. One notes that under these conditions, in contrast to the situation when  $I = 1.0$  M, acid-catalyzed hydrolysis is the important process, while  $k_0$  is not distinguishable from zero at the lower temperatures and is only very approximately determinable at  $50^\circ\text{C}$  and above.

### Discussion

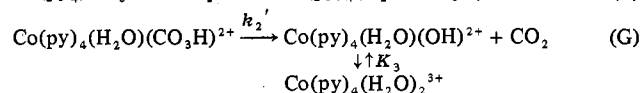
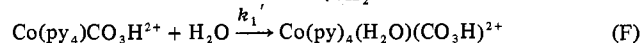
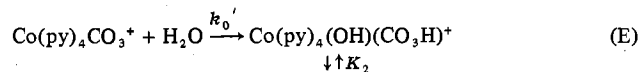
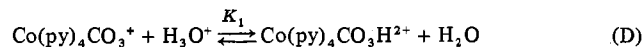
The data at  $I = 1.0$  M might appear to indicate that no diaquo intermediate exists in these reactions while it is clear that the sequence of observed events at  $I = 5.0$  M is:



Detailed studies of reaction C now in progress in our laboratory<sup>11</sup> show, however, that its rate dependence on the varied parameters is such that  $k_2$  is much too large in the  $I = 1.0$  M runs to enable detection of a *trans*-diaquo intermediate. We therefore conclude that the significant overall reactions in the present study are (A) and (B). This corresponds to the rate expression already utilized in analyzing the data (eq 1). The contrasts between the data at  $I = 1.0$  and  $5.0$  M are seen to derive from the large acceleration in reaction B as the ionic strength is increased. One notes that the values of  $k_0$  at  $50$  and  $60^\circ\text{C}$  are not very different for the data at either of these ionic strengths. However, the runs done at  $50^\circ\text{C}$  and intermediate ionic strengths in which  $I = [\text{H}^+]$  illustrate the very large effect of this factor on  $k_1$  beyond  $I = 2.0$  M, as illustrated in Figure 2. Actually, the minimal ionic strength effect on  $k_0$ , describing an ion-molecule reaction, and the large positive effect on  $k_1$ , describing a reaction between like charged ions, are as one would expect on qualitative theoretical grounds.

The intimate mechanism of the acid catalysis requires consideration. Our previous kinetic studies of chelated

carbonato complex decomposition have been interpreted in terms of rate-determining proton transfer from hydronium ion to carbonato moiety in the transition state, leading to ring opening by metal-oxygen bond cleavage.<sup>2-4</sup> An alternative view<sup>5</sup> suggests proton preequilibration followed by rate-determining ring opening. Accepting this view, and ignoring for the moment the question of the geometry of the aquocarbonato and diaquo products, the mechanism for the  $(\text{py})_4$  system may be symbolized:



The rate expression corresponding to eq D thru G, making the reasonable assumptions that reaction G is much more rapid than reactions E or F and that the equilibria described by  $K_1$ ,  $K_2$ , and  $K_3$  are continuously maintained, takes the form:

$$k_{\text{obsd}} = (k_0' + k_1'K_1[\text{H}^+]) / (1 + K_1[\text{H}^+]) \quad (2)$$

The earlier spectral studies<sup>6</sup> as well as our own (see Table I) suggest the possibility of observable protonation of the  $\text{Co}(\text{py})_4\text{CO}_3^+$  ion, possibly on the carboxyl group as indicated in reaction D. In fact, equilibrium constant estimates based on solubility data have been reported<sup>6</sup> as  $K_1 = 3.3$  ( $I = 8.0$  M) and  $K_1 = 1.4$  ( $I = 4.5$  M), so that  $K_1$  should have a value of  $\sim 2$  at  $I = 5.0$  M. There is, however, no sign of deviation from second-order kinetics in the acid-catalyzed hydrolysis in the range  $1.0 \text{ M} < [\text{H}^+] < 5.0 \text{ M}$  at  $I = 5.0$  M (see Figure 2). It follows that  $K_1$  must be much smaller than the value estimated if this mechanism is to be correct, unless specific medium effects resulting from the substitution of  $\text{H}^+$  for  $\text{Na}^+$  as the acidity is increased modify the observed rate constant in such a manner as to maintain the observed linearity of the plot. However, carbonyl groups in general have very low basicities, and the high value of the acid dissociation constant represented by  $K_3$  in reaction G (see Table III) is consistent with a similar low basicity for the oxygens attached to the metal. The mechanism proposed is, moreover, supported by two other lines of reasoning.

One notes from Table IIB that in  $5.0$  M acid there is a positive  $\text{D}_2\text{O}$  solvent effect such that the ratio  $k_{\text{obsd}}^{\text{D}}/k_{\text{obsd}}^{\text{H}}$  has the values 1.8, 1.9, and 1.7 at  $40$ ,  $50$ , and  $60^\circ\text{C}$ , respectively, in runs where between 80 and 90% of the reaction is by the acid-catalyzed path. By contrast, in  $1.0$  M acid ( $I = 1.0$  M, see Table IIA), the  $\text{D}_2\text{O}$  effect is very small, with  $k_{\text{obsd}}^{\text{D}}/k_{\text{obsd}}^{\text{H}}$  having values of 0.99, 0.96, and 0.98 at  $50$ ,  $60$ , and  $70^\circ\text{C}$ , respectively, under conditions such that only a small fraction ( $< 15\%$ ) is acid catalyzed. These solvent isotope effects are just as expected for the type of mechanism suggested.<sup>12</sup> The other supporting evidence is provided by application of the Hammett acidity function concept<sup>13</sup> to the data with variable ionic strength, i.e., with  $I = [\text{H}^+]$ . If one subtracts the apparently constant value of  $k_0 = 12 \times 10^{-5} \text{ s}^{-1}$  from the  $k_{\text{obsd}}$  values at each acidity and plots the data in the form  $\log(k_{\text{obsd}} - k_0)$  vs.  $-H_0$ , a good straight line through the points for  $[\text{H}^+] > 2.0$  M with close to unit slope is obtained (see Figure 2),<sup>14</sup> which is the expectation for this type of process. We conclude, therefore, that the proton-preequilibration reaction scheme is operative in this system, despite the possibly contradictory evidence with respect to the magnitude of  $K_1$  already discussed.

Table III. Rate Properties of  $\text{CoCO}_3^+$  Complexes Most Resistant to Acid-Catalyzed Decarboxylation ( $T = 25^\circ\text{C}$ ,  $I = 1.0\text{ M}$ )

L	$10^4 k_1$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\text{p}K_{\text{av}}$	$\text{p}K_3$	Ref	Remarks
$\beta$ -trien <sup>a</sup>	2000	$17.0 \pm 1.0$	$-5.0 \pm 3.0$	$7.3^h$	$5.3^h$	4	
$\alpha$ -dmtr <sup>b</sup>	180			6.4		15	
<i>trans</i> -14-dien <sup>c</sup>	80	$24.2 \pm 0.7^d$	$13.0 \pm 2.1^d$			16	$I = 0.25\text{ M}$
$\beta$ -dmtr <sup>b</sup>	5.6			6.4		15	
(bpy) <sub>2</sub>	$1.7^e$	$22.3 \pm 1.7$	$-1.5 \pm 4.8$	4.5	4.5	5	
( <i>o</i> -phen) <sub>2</sub>	$1.1^e$	$20.4 \pm 1.9$	$-8.6 \pm 5.1$	5.0	4.7	5	
tet-b <sup>f</sup>	$\sim 1^g$			$6.3^h$		16	$I = 0.25\text{ M}$
(py) <sub>4</sub>	0.1	$23.2 \pm 1.0$	$-4.0 \pm 3.1$	$\sim 5^i$	$\sim 1.2^i$	This work	$I = 5.0\text{ M}$

<sup>a</sup> Triethylenetetramine (in  $\beta$  geometry). <sup>b</sup> 4,7-Dimethyltriethylenetetramine ( $\alpha$  and  $\beta$  geometries, respectively). <sup>c</sup> 5,7,7,12,14,14-Hexamethyl-1,4,8,11-azacyclotetradecane-4,11-diene. <sup>d</sup> Recalculated from the published rate data at 24.8, 40.8, and 72.5  $^\circ\text{C}$ . <sup>e</sup> Recalculated from the published temperature parameters. <sup>f</sup> 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane. <sup>g</sup> Estimated from data at 73.5  $^\circ\text{C}$  by use of the same  $\Delta H^\ddagger$  as for the *trans*-14-diene complex. <sup>h</sup> As quoted in ref 5. <sup>i</sup>  $\text{p}K$  of pyridine is 5.2 (ref 17) and  $\text{p}K_3$  is 1.4 (ref 6) at  $I = 1.0\text{ M}$ , 25  $^\circ\text{C}$ . These are estimated to be decreased by about 0.2 unit at high ionic strength.

A number of further questions are raised by the above analysis. One wonders first why the (py)<sub>4</sub> complex is more stable to decomposition than other carbonatocobalt(III) complexes, even the closely related (bpy)<sub>2</sub> and (*o*-phen)<sub>2</sub> species mentioned before. Data concerning the several complexes which are most resistant to decarboxylation are presented in Table III. The rate constants given are deduced according to the simple two-term analysis of eq 1. It is seen that acceptance of the proton preequilibrium mechanism with  $K_1[\text{H}^+] \ll 1$  leads to the equalities  $k_0 = k_0'$  and  $k_1 = k_1'K_1$  (see eq 2). The contrasts in  $k_1$  values thus can arise either from changes in the basicity of the chelated  $\text{CO}_3$  moiety or changes in the rate at which the protonated chelate undergoes ring opening according to reaction F. It is of interest that, at least for the olefinic or aromatic ligand systems, the kinetic differences are not the result of substantial variations in the enthalpies of activation, which are in fact equal within experimental error. Previous discussions of the rate contrasts have sought to explain the effects in terms of solvation phenomena as in the comparison of the  $\beta$ -trien and  $\beta$ -dmtr complexes.<sup>2</sup> Steric factors have also been invoked, as in the comparisons between  $\alpha$  and  $\beta$  forms of the trien<sup>4</sup> or dmtr<sup>15</sup> complexes, or in the comparison of the complexes containing the cyclic *trans*-14-diene or tet-b ligands with simpler tetramine species.<sup>16</sup> The third approach<sup>5</sup> considers the relative stabilities of the Co-O bond in the compounds as evidenced by the magnitude of the average of the  $\text{p}K$ 's for acid dissociation of the amine ligand group or of the first acid dissociation constant ( $K_3$ ) of the diaquo product complex. The  $\text{p}K_{\text{av}}$  figures provide no clear-cut correlation for the restricted group of complexes of Table III and are even less satisfactory if one includes other types of ligands such as the amino acetates.<sup>2</sup> However, the limited  $\text{p}K_3$  figures show that the *trans*-Co(py)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> complex is very much more acidic than are the *cis*-diaquo (bpy)<sub>2</sub> and (*o*-phen)<sub>2</sub> congeners. This is consistent with much stronger Co-O bonding in the (py)<sub>4</sub> species than in the latter two complexes and consequently much weaker basicity of the carbonato group in the parent Co(py)<sub>4</sub>CO<sub>3</sub><sup>+</sup> ion, i.e., a lower value of  $K_1$ . One can thus account for the greater resistance to acid-catalyzed hydrolysis by the (py)<sub>4</sub> complex than by the other two, though if the relative magnitudes of  $K_3$  parallel those of  $K_1$  one might expect a much greater contrast than the observed factor of 10–20. The steric argument cannot therefore be unequivocally ruled out, particularly as molecular models tend to show a considerable degree of protection of the  $\text{CO}_3$  moiety from H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> attack in the case of all the resistant complexes, and we must note also such sizable rate differences as exist between the  $\alpha$  and  $\beta$  dmtr isomers. It appears likely that a combination of solvation shell, steric, and electronic structure effects determines the degree of reactivity in a manner not amenable to simple correlation.

We consider now the very rapid geometrical rearrangement which occurs during the course of the decarboxylation of Co(py)<sub>4</sub>CO<sub>3</sub><sup>+</sup> so that only *trans*-diaquo product is observable.

The only other parallel case so far reported is that of Co(*trans*-14-dien)CO<sub>3</sub><sup>+</sup>, which differs in structure from its tet-b congener only in the introduction of two olefinic bonds into the tet-b ligand.<sup>16</sup> A possible explanation is that the expected five-coordinate reactive intermediates<sup>18</sup> formed in the ring-opening reactions E and F for the (py)<sub>4</sub> and *trans*-14-diene complexes shift quickly into the square-pyramidal form, with the amine nitrogens grouped meridially, thus resulting in total *cis*  $\rightarrow$  *trans* conversion on attachment of the water molecule. This behavior may well be favored by the crowded geometry of the *trans*-14-diene and (py)<sub>4</sub> groupings, as is evident for the latter species from its crystal structure.<sup>19</sup> Presumably, in all other cases a trigonal-bipyramidal intermediate conducive to *cis* retention is formed.

Finally, one must question the adoption of the proton preequilibrium mechanism in the present study, since this concept is contradictory to the mechanism adopted in all our previous investigations of carbonato complex decomposition. In these, direct proton attack in the rate-determining step is assumed, an assumption based on an early solvent D<sub>2</sub>O study.<sup>20</sup> This assumption is now brought seriously into question and is presently under reinvestigation. Also, the special properties of *trans*-Co(py)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup> which lead to the rapid internal redox process require explanation and will constitute the subject of a forthcoming communication.<sup>11</sup>

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**Registry No.** Co(py)<sub>4</sub>CO<sub>3</sub><sup>+</sup>, 47597-86-4; *trans*-Co(py)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, 51830-14-9.

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but such data for perchloric acid solutions are not available. However, it is well known that both  $H_+$  and  $H_-$  functions generally parallel the  $H_0$  function (Rochester, pp 92-95).

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## Proton Exchange and Base Hydrolysis of

### $\beta$ -*cis*-Dichloro(1,9-diamino-3,7-diazanonane)cobalt(III) Cations

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The kinetics of proton exchange of  $\beta$ -*cis*-[Co(*R,R(S,S)*)-2,3,2-tet]Cl<sub>2</sub>]<sup>+</sup> (2,3,2-tet = 1,9-diamino-3,7-diazanonane) have been studied in buffered aqueous solution. One primary and one secondary amine proton exchange rapidly ( $k_1 = 2.7 \times 10^6$  and  $3.6 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> at 20.0 °C,  $\mu = 0.070$ ) and another primary amine proton exchanges somewhat more slowly ( $k_1 = 9.5 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup> at 20.0 °C,  $\mu = 0.070$ ). It is presumed that these are the three protons on nitrogens that are *trans* to the chlorines. No exchange can be observed of the other three protons before the complex undergoes base hydrolysis. One of the labile protons must be involved in forming the reactive conjugate base, presumably the secondary amine proton since the immediate product is *trans*-[Co(*R,S*)-2,3,2-tet]OH(Cl)]<sup>+</sup>. Exchange of the remaining three protons occurs after base hydrolysis, the secondary amine proton exchanging during or rapidly after the pH-independent loss of the second chlorine, while the primary amine protons exchange in the *trans*-[Co(*R,S*)-2,3,2-tet]OH(H<sub>2</sub>O)]<sup>2+</sup> - *trans*[Co(*R,S*)-2,3,2-tet](OH)<sub>2</sub>]<sup>+</sup> product at rates that do not depend strongly upon pH. The base hydrolysis of  $\beta$ -*cis*-[Co(*R,R(S,S)*)-2,3,2-tet]Cl<sub>2</sub>]<sup>+</sup> follows the usual second-order rate law with  $k_B = 1.6 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> at 20.0 °C,  $\mu = 0.04$ ;  $\Delta H^\ddagger = 17.5 \pm 1.0$  kcal/mol and  $\Delta S^\ddagger = +19 \pm 3$  cal K<sup>-1</sup> mol<sup>-1</sup>. The  $\beta$ -*cis*-dichloro complex is compared with the *trans*-dichloro isomer where deprotonation is the rate-limiting step of base hydrolysis.

## Introduction

The three known isomeric forms of [Co(2,3,2-tet)Cl<sub>2</sub>]<sup>+</sup> (2,3,2-tet = 1,9-diamino-3,7-diazanonane), namely, the *trans-R,S*, the *trans-R,R(S,S)*, and the  $\beta$ -*cis-R,R(S,S)* species, have all been shown to give the *trans-R,S*-[Co(2,3,2-tet)-OH(Cl)]<sup>+</sup> cation as the first product of base hydrolysis<sup>1,2,3</sup>. In the case of the two *trans* isomers it has been shown that the base hydrolysis involves the removal of the secondary amine proton in a slow, rate-determining step, followed by a rapid dissociative solvolysis of the amido conjugate base, in the course of which the deprotonated nitrogen becomes planar.<sup>2,3</sup> This is an unusual reversal of the normal pattern for the base hydrolysis of cobalt(III) amine complexes where proton transfer is usually fast compared to the overall rate of hydrolysis. The rate-determining deprotonation leads to general-base catalysis and the activation parameters of the reaction correspond to those expected for proton-exchange reactions.<sup>4</sup> It has long been known that proton exchange in octahedral cobalt(III) amine complexes is very sensitive inter alia to the nature of the *trans* ligand and that protons on nitrogens *trans* to chlorine could be some 2-3 orders of magnitude more labile than those on nitrogens *trans* to amine ligands<sup>5-7</sup> and so it was of some interest to see why the  $\beta$ -*cis* isomer, in spite of having one secondary amino group *trans* to a chlorine, did not undergo base hydrolysis significantly faster than the two *trans* isomers, where all amine groups are *trans* to nitrogen. This paper reports the proton-exchange rates of the amine groups of the  $\beta$ -*cis*-[Co(*R,R(S,S)*)-2,3,2-tet]Cl<sub>2</sub>]<sup>+</sup> cation and their relation to the base hydrolysis.

## Experimental Section

**$\beta$ -*cis*-Dichloro(*R,R(S,S)*)-1,9-diamino-3,7-diazanonane]cobalt(III) Chloride.** Finely powdered  $\beta$ -*cis*-[Co(*R,R(S,S)*)-2,3,2-tet]CO<sub>3</sub>]ClO<sub>4</sub>, prepared by the method of Ahmed and Tobe<sup>3</sup> (0.6 g), was suspended in dry ethanol (15 ml) that was saturated with dry hydrogen chloride. The mixture effervesced and, when its color had changed from dark red to violet, it was cooled in ice and the violet product was filtered off and washed with ethanol and ether and dried in a stream of air (0.45 g, 78%).

Anal. Calcd for C<sub>7</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>3</sub>Co: C, 25.8; H, 6.19; N, 17.2; Cl, 32.7. Found: C, 25.8; H, 6.22; N, 17.1; Cl, 32.4.

$\beta$ -*cis*-Dichloro[*N,N,N',N'',N''',N''''*-<sup>2</sup>H<sub>6</sub>](*R,R(S,S)*)-1,9-diamino-3,7-diazanonane]cobalt(III) chloride was prepared from the fully N-deuterated  $\beta$ -*cis*-[Co(*R,R(S,S)*)-2,3,2-tet]CO<sub>3</sub>]ClO<sub>4</sub><sup>3</sup> by the method described above for the normal complex. The peaks at 3255, 3180, and 3090 cm<sup>-1</sup> found in the <sup>1</sup>H<sub>6</sub> complex were absent and replaced by a new set at 2440, 2370, and 2285 cm<sup>-1</sup>.

Anal. Calcd for C<sub>7</sub>H<sub>14</sub>D<sub>6</sub>N<sub>4</sub>Cl<sub>3</sub>Co: C, 25.4; N, 16.9. Found: C, 25.3; N, 16.8.

All other reagents were AR or reagent grade and purified by recrystallization or distillation where necessary.

**Proton-Exchange Kinetics.** Buffer solutions were prepared by adding sufficient nitric acid (0.05 M) to a 0.1 M solution of 2,6-lutidine (pH 6.74 buffer) or 2,4,6-trimethylpyridine (pH 8.21 buffer) until the desired pH was reached. A weighed amount of  $\beta$ -*cis*-dichloro[*N,N,N',N'',N''',N''''*-<sup>2</sup>H<sub>6</sub>](*R,R(S,S)*)-1,9-diamino-3,7-diazanonane]cobalt(III) chloride was dissolved in 10<sup>-3</sup> M hydrochloric acid (sufficient for a 0.03 M solution of the complex) previously brought to the reaction temperature and this was added as soon as possible to the thermostated buffer solution. After the required period of time the reaction was stopped by adding an excess of ice-cold perchloric acid and the mixture was set aside for 30 min in an ice bath. The  $\beta$ -*cis*-[Co(2,3,2-tet)Cl<sub>2</sub>]ClO<sub>4</sub> was filtered off, washed with ethanol and ether, and dried in a stream of air, and the <sup>1</sup>H NMR spectrum of the amine protons was measured in the way previously described.<sup>2,3</sup> The solubility of the *cis*-dichloro perchlorate in dilute perchloric acid is not low enough for this separation to be completely quantitative (only about 85% is precipitated under these conditions) but this only causes difficulties when one wishes to examine the nature and extent of isotopic exchange in the reaction product recovered in the early stages of base hydrolysis. Even there it is possible, with sufficient care, to minimize the interference to negligible amounts. In the experiments where the base hydrolysis was negligible the filtrate was discarded; otherwise a few milliliters of concentrated hydrochloric acid was added and the mixture was set aside at room temperature. Crystals of *trans*-[Co(*R,S*)-2,3,2-tet]Cl<sub>2</sub>]ClO<sub>4</sub> separated slowly and were filtered off from time to time until sufficient sample was obtained for the subsequent examination. The *R,R(S,S)* *trans* isomer, formed by the anation and isomerization of the *cis*-[Co(2,3,2-tet)H<sub>2</sub>O(Cl)]<sup>2+</sup> species left behind after the separation of the *cis*-dichloro complex, separated more slowly and when this was detected in the recovered