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(48) These anomalously low moments in the range 3.0–3.8 BM might be due to antiferromagnetic interactions in weakly bonded polynuclear structures. Zgadzai et al.[21] attributed a decrease in magnetic moment with increasing concentration of cobalt(II) chloride and trialkyl phosphite in ethanol solution to polymer formation. Alternatively, a referee has suggested that in the pure state the $CoCl_2L_2$ complexes exist as $[CoL_4][CoCl_4]$, with a low-spin planar cation and a high-spin tetrahedral anion; the expected moment per cobalt would then be about 3.6 BM. On dissolution, the complexes then rearrange to the high-spin $CoCl_2L_2$ structure. No evidence is yet available to test this hypothesis.
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Contribution from the Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

Studies of Labile Carbonatocobaltate(III) Complexes. 2. Kinetics of Reactions of Tris(carbonato)cobaltate(III) Species with Ethylenediamine, 1,2-Propanediamine, and 1,3-Propanediamine in Aqueous Sodium Bicarbonate Media. Unusually Stable Half-Bonded Bis(carbonato)diaminecobaltate(III) Intermediates[1,2]

GEOFFREY DAVIES* and YEN-WAN HUNG

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The kinetics of the title reactions have been investigated by stopped-flow and conventional spectrophotometry in aqueous $NaHCO_3$–$NaClO_4$ media at $8 \lesssim pH \lesssim 10.5$ and ionic strength 1.0 M. Formation of chelated $Co(CO_3)_2(diamine)^-(aq)$ complexes proceeds via unusually stable, brown, half-bonded diamine species with near-uv charge-transfer spectral characteristics. The kinetic data for rapid formation of these half-bonded diamine intermediates at 25.0 °C are consistent with an associative interchange mechanism involving unusually stable reaction precursors with ethylenediamine and 1,2-propanediamine. The rate constant for aquation of half-bonded $Co(CO_3)_2enHCO_3^{2-}(aq)$ to produce a half-bonded aquo analogue with a similar charge-transfer spectrum is $(8.9 \pm 0.1) \times 10^{-2}\ s^{-1}$ at 25.0 °C, with $\Delta H^{\ddagger}_{-2} = 18.2 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger}_{-2} = 2 \pm 4$ cal deg^{-1} mol^{-1} at 25.0 °C. Low rates of ring closure to form $Co(CO_3)_2(diamine)^-(aq)$ (lowest for 1,3-pn) are also consistent with high conformational stability in the half-bonded intermediates, presumably as a result of hydrogen bonding to chelated carbonate. Ring closure in half-bonded $Co(CO_3)_2(diamine)HCO_3^{2-}(aq)$ is considerably faster than in $Co(CO_3)_2(diamine)H_2O^-(aq)$. Available evidence indicates very different solution properties for carbonato- and aquocobalt(III) complexes containing pyridine and saturated diamine ligands.

Introduction

In part 1 of this series[2] we reported a study of the kinetics of the second-order reaction of excess pyridine, py, with solutions of $Na_3[Co(CO_3)_3]{\cdot}3H_2O$ in aqueous sodium bicarbonate. The product of the reaction was found to be *cis*-$Co(CO_3)_2py_2^-(aq)$. Dependences of the reaction rate on acidity and free bicarbonate concentration, $[HCO_3^-]$, were interpreted in terms of equilibria 1 and 2, involving monomeric

$$Co(CO_3)_3^{3-}(aq) + H_3O^+ \rightleftharpoons Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) \quad K_h \qquad (1)$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) + H_2O \rightleftharpoons Co(CO_3)_2(H_2O)_2^-(aq) + HCO_3^-(aq) \quad K_{H_2O} \qquad (2)$$

cobalt(III) species with $Co(CO_3)_2(H_2O)_2^-(aq)$ as the most rapidly substituted by py. Although it was apparent that this complex is a minor component of such solutions at $8 \lesssim pH \lesssim 10$ and analytical bicarbonate concentrations in the range 0.1–1.0 M, it was also noted that the fraction of cobalt(III) in this form would be most significant at low $[HCO_3^-]$ and low pH, conditions which sometimes obtain in syntheses involving reactions of amines with the much more soluble potassium carbonatocobaltate(III) salt in aqueous potassium bicarbonate.[3,4]

During the course of the above studies it was noticed that addition of ethylenediamine, en, 1,2-propanediamine, 1,2-pn, and 1,3-propanediamine, 1,3-pn, to green sodium carbonatocobaltate(III) solutions in 1 M $NaHCO_3$ caused a rapid color change to brown. On standing, these brown solutions slowly became purple and exhibited visible absorption spectra characteristic of carbonato(diamine)cobalt(III) complexes.[3,4] Addition of the above diamines was accompanied by an immediate increase in pH, as was also the case with the strong proton bases ammonia and 1,6-hexanediamine; however, no brown coloration was observed with the latter two ligands, indicating that the rapid initial color change was due to specific interactions of the green carbonatocobaltate(III) complexes with ethylenediamine and 1,2- and 1,3-propanediamines.

In this paper we report that the reactions of the three title ligands with aqueous solutions of $Na_3[Co(CO_3)_3]{\cdot}3H_2O$ consist of at least three separate processes, which have been kinetically resolved by stopped-flow and conventional spectrophotometry.

Experimental Section

Reagents. The preparation and standardization of solutions of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ in aqueous sodium bicarbonate was as previously described.[2] All water used was deionized and then fractionally distilled from alkaline potassium permanganate in an all-glass still. Reagent grade ethylenediamine, 1,2-propanediamine, and 1,3-propanediamine were fractionally distilled immediately prior to making up solutions in aqueous sodium bicarbonate. Standard phosphate and borate buffer solutions were used in standardizing pH measurements.[2]

Potassium Bis(carbonato)ethylenediaminecobaltate(III) Monohydrate, $K[Co(en)(CO_3)_2]\cdot H_2O$. This complex salt was prepared in impure solid form by the method of Mori,[5] except that the literature procedure[5] was modified by adding 200 ml of ethanol to the reaction mixture[5] which had been allowed to stand for 8 h at 0 °C. The initial solid product was repeatedly dissolved in the minimum amount of cold water and reprecipitated with ethanol, which eventually gave a blue-black material.[6] However, the spectrum of the product from this purification procedure exhibited a large absorption in the near-ultraviolet region which we associate with the presence of dimeric cobalt(III) species.[3,4,7] This near-uv absorption was greatly reduced by heating the blue-black solid in 1 M $NaHCO_3$ at 70 °C for 2–3 h; solutions obtained in this manner exhibited absorption spectra with maxima at 390 nm (ϵ 214 M^{-1} cm^{-1}) and 570 nm (ϵ 148 M^{-1} cm^{-1}), in good agreement with literature data for $[Co(en)(CO_3)_2]^-(aq)$.[6] The spectrum of this complex in 1 M $NaHCO_3$ was independent of acidity in the range $8 \lesssim pH \lesssim 10$ at 25 °C.

Solutions of $Co(en)^{3+}(aq)$ were obtained by heating aqueous solutions of the above blue-black material at 70 °C and pH ~ 1 ($HClO_4$), which gave solutions with spectral maxima at 511 nm (ϵ 44 M^{-1} cm^{-1}) and 367 nm (ϵ 32 M^{-1} cm^{-1}). Attempts to isolate solid perchlorate and nitrate salts either from such solutions or by the methods used previously[7] to isolate the analogous diammineaquocobalt(III) compounds were unsuccessful due to the extremely high solubility of the ethylenediamine salts in concentrated $HClO_4$ or HNO_3 and in acetone.

Carbonatobis(ethylenediamine)cobalt(III) Chloride, $[Co(en)_2CO_3]Cl$, was prepared by the literature method.[8] The crude product was recrystallized from water and exhibited spectral properties in close agreement with literature values.[8]

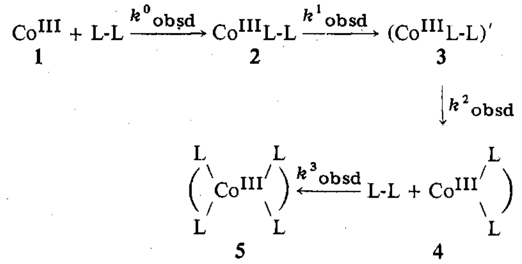
Product Identification. The products of reaction of ethylenediamine (0.45 mol) with the green reactant solution (7.28×10^{-4} mol of Co^{III} in 1 M $NaHCO_3$[2]) were characterized 6 h after mixing as follows.[9] The product mixture was added to an excess of ice-cold 2 M $HClO_4$, flushed with N_2 to remove CO_2, and then charged onto a Dowex 50W-X4 (100–200 mesh) cation-exchange column in the H^+ form. Elution with 3 M $HClO_4$ gave two fractions which were identified from their absorption spectra (see above and ref 8) as $Co(en)^{3+}(aq)$ (2.74×10^{-4} mol) and *cis*-$Co(en)_2{}^{3+}(aq)$ (4.25×10^{-4} mol). The first eluted complex was $Co(en)^{3+}(aq)$. These results account for 96% of the initial cobalt(III).

In view of the difficulty experienced in obtaining a pure $K[Co(en)(CO_3)_2]$ product (see above), no attempt was made to isolate and characterize the corresponding 1,2-pn and 1,3-pn complexes or their aquo derivatives.[4] However, it will be shown below that similar kinetic and spectral phenomena are observed in the en and 1,2-pn systems, while formation of the fully chelated complex $Co(1,3\text{-pn})(CO_3)_2{}^-(aq)$ is very slow under our experimental conditions. All other chemicals were of reagent grade and were used as supplied.

Kinetic Measurements. The kinetic processes observed on mixing the green cobalt(III) reactant with the diamines in aqueous $NaHCO_3$ were monitored by stopped-flow and conventional spectrophotometry. The following concentration ranges were employed: $[Co^{III}] = (2.31\text{–}3.99) \times 10^{-4}$ M, $[H^+] = (0.06\text{–}2.81) \times 10^{-9}$ M, $[HCO_3^-] = 0.02\text{–}0.68$ M, $[en]_T = (2.3\text{–}95.0) \times 10^{-3}$ M, $[1,2\text{-pn}]_T = (4.68\text{–}110.0) \times 10^{-3}$ M, and $[1,3\text{-pn}]_T = (2.6\text{–}150.0) \times 10^{-3}$ M. Initial formation of brown products was followed at 380–450 nm in the stopped-flow apparatus previously described.[10] Absorbance–time curves from the oscilloscope were analyzed by a combination of conventional, analog,[11] and on-line computer[12] techniques. Agreement between these alternatives was better than ±2%.

Subsequent relaxation of the initial brown product was monitored at 380 nm either in the stopped-flow apparatus (5 s/division sweep rate at 25 °C, data being treated as described above) or in a Beckman DK-1 ratio-recording spectrophotometer (at lower temperatures, pseudo-first-order rate constants were obtained from initial slopes of first-order plots).

Scheme I



Ring closure of the brown, relaxed mixture of intermediates to form $Co(CO_3)_2en^-(aq)$, $Co(CO_3)_2(1,2\text{-pn})^-(aq)$, and $Co(CO_3)_2(1,3\text{-pn})^-(aq)$ as monitored at 380 nm in the Beckman instrument gave evidence with en and 1,2-pn for higher order amine complex formation, i.e., formation of $Co(CO_3)(diamine)_2{}^+(aq)$ at 25.5 °C and above. The analysis of phenomena on the time scale of ring closure (where half-bonded intermediates are at equilibrium) was made as follows. The portion of the absorbance–time curve referring to relaxation was neglected, and the absorbance–time data were fitted either to a

$$2, 3 \xrightarrow{k^2_{obsd}} 4$$

first-order scheme[2] or, in cases where there was clear evidence for formation of $Co(CO_3)(diamine)_2{}^+(aq)$, to a

$$2, 3 \xrightarrow{k^2_{obsd}} 4 \xrightarrow{k^3_{obsd}} 5$$

first-order scheme.[13] Here **2** and **3** are the initial brown product and brown derivative thereof, **4** is the purple bis(carbonato)mono(diamine) chelate, and **5** is the red carbonatobis(diamine) chelate, respectively (see below). The rate constants k^1_{obsd}, k^2_{obsd}, and k^3_{obsd} are the computer-calculated first-order rate constants for the respective steps. In these fits the absorbance (fixed wavelength) and time were the dependent and independent variables, respectively,[13] and the computer program generated the values of the other parameters in the appropriate functions.[2,13]

In each kinetic run the free bicarbonate concentration, $[HCO_3^-]$, and the neutral amine concentrations, [L-L], were calculated from the respective total analytical bicarbonate and amine concentrations at the measured reaction acidity (unit activity coefficients assumed) by use of appropriate literature data for each species.[2,14] The concentrations of HCO_3^- and neutral ligand species were always sufficiently high to ensure pseudo-first-order conditions.[15] In all cases the ionic strength was adjusted to 1.0 M ($NaHCO_3$–$NaClO_4$) and reactant solutions were thermostated for at least 30 min before mixing. Repeated measurements under fixed concentration conditions gave pseudo-first-order rate constants, k^i_{obsd}, with a maximum uncertainty of ±6%. Activation parameters were obtained from nonlinear least-squares fitting of k^i_{obsd} as a function of temperature, as described previously.[7]

Results

The spectral changes observed on mixing the cobalt(III) and diamine reactants are consistent with the order of events in Scheme I. Here **1** is the initial, green carbonatocobaltate(III) reactant, L-L is the bidentate diamine ligand, **2** and **3** are postulated to be two different cobalt(III) complexes each containing a single coordinated nitrogen atom from the diamine, and **4** and **5** are chelated $Co(CO_3)_2(diamine)^-(aq)$ and $Co(CO_3)(diamine)_2{}^+(aq)$ species, respectively. The rates of the reactions **1** → **2** (hereafter called half-bonded complex formation), **2** → **3** (relaxation), and **3** → **4** → **5** (ring closure) decreased progressively with a given ligand. The ring-closure step **3** → **4** was extremely slow with L-L = 1,3-pn and data were only obtained at 25.5 °C. There was no evidence for higher order complex formation with 1,3-pn. Although a consecutive first-order kinetic absorbance–time fitting routine was applied to **3** → **4** → **5** in the reactions with en and 1,2-pn, the kinetic data for **4** → **5** were comparatively crude, since

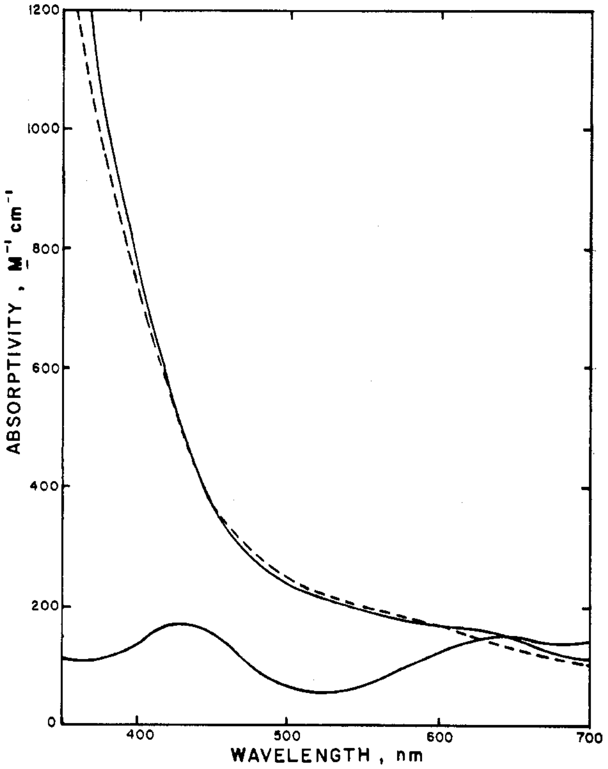


Figure 1. Spectra of green reactant (lower full line), $Co(CO_3)_2$-$enHCO_3{}^{2-}$(aq) (upper full line), and $Co(CO_3)_2enH_2O^-$(aq) (dashed line). The latter spectrum is approximate and refers to the result of extrapolation of A_∞ for relaxation to $[HCO_3^-] = 0$.

these reactions involved very small absorbance changes in the visible region over the $[Co^{III}]$ range available[2] and the reactions themselves were very slow.

Kinetics Of Half-Bonded Complex Formation Reactions with en and 1,2-pn. Stopped-flow traces obtained at fixed wavelength in the range 380–450 nm (25 °C, ionic strength 1.0 M) for **1** → **2** gave plots of log $(A_\infty - A_t)$ vs. t, where A_∞ and A_t are absorbances at "infinite" time and time t, respectively, which were linear to at least 75% reaction.[17] Extrapolation of absorbances to $t = 0$ gave spectral parameters which closely agreed with those of the green cobalt(III) reactant (the diamine ligands are essentially transparent in the wavelength-monitoring region). The molar absorptivities of **2** were found to be 1100 ± 100 M^{-1} cm^{-1} at 380 nm for both en and 1,2-pn ligands and were independent of [L-L], pH, $[HCO_3^-]$, and temperature.[18] These molar absorptivities are ca. 8 times larger than that for the green reactant at 380 nm (Figure 1).

The rate law for formation of **2** is given by eq 3 where $k^0{}_{obsd}$

$$d[2]/dt = k^0{}_{obsd}[Co^{III}] \tag{3}$$

is the observed first-order rate constant and $[Co^{III}]$ is the analytical cobalt(III) concentration. The rate constant $k^0{}_{obsd}$ was found to be independent of [L-L], $[HCO_3^-]$, and monitoring wavelength. The kinetic data are collected in Table I.[19] Variations of $k^0{}_{obsd}$ with $[H^+]$ are accounted for by the empirical equation

$$k^0{}_{obsd} = A[H^+]/(1 + B[H^+]) \tag{4}$$

According to eq 4, a plot of $1/k^0{}_{obsd}$ vs. $1/[H^+]$ should be linear, as was found to be the case for reaction with en (Figure 2) and 1,2-pn. A nonlinear least-squares fit of the data from Table I to eq 4 gave $A = (7.25 \pm 0.35) \times 10^9$ M^{-1} s^{-1} and $B = (1.21 \pm 0.13) \times 10^9$ M^{-1} for reaction with en and $A = (5.24 \pm 0.42) \times 10^9$ M^{-1} s^{-1} and $B = (0.72 \pm 0.15) \times 10^9$ M^{-1} for reaction with 1,2-pn at 25.0 °C and ionic strength 1.0 M.

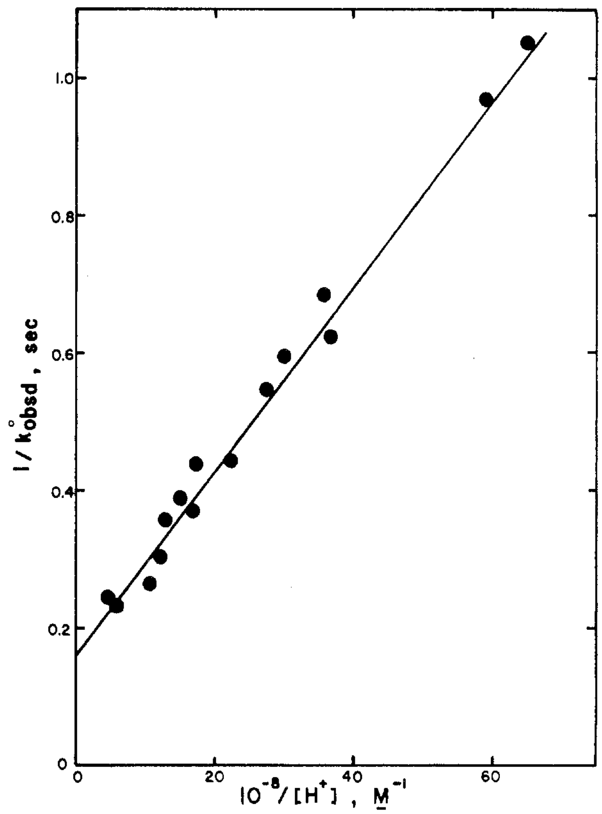


Figure 2. Plot of $1/k_{obsd}$ vs. $1/[H^+]$ for the rapid initial reaction with en at 25.0 °C and ionic strength 1.0 M.

First-order rate constants from this fit of the data to eq 4 are shown in Table I for comparison with $k^0{}_{obsd}$.

Mechanism. The mechanism of eq 5–9 which is based on

$$Co(CO_3)_3{}^{3-}(aq) + H_3O^+ \overset{fast}{\rightleftharpoons} Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) \quad K_h \tag{5}$$

$$Co(CO_3)_3{}^{3-}(aq) + L\text{-}L \overset{fast}{\rightleftharpoons} [Co(CO_3)_3, L\text{-}L]^{3-}(aq) \quad K_0 \tag{6}$$

$$Co(CO_3)_2(HCO_3)(H_2O)^{2-}(aq) + L\text{-}L \overset{fast}{\rightleftharpoons} [Co(CO_3)_2(HCO_3)(H_2O), L\text{-}L]^{2-}(aq) \quad K_1 \tag{7}$$

$$[Co(CO_3)_3, L\text{-}L]^{3-}(aq) \xrightarrow[H^+]{k_0} Co(CO_3)_2(HCO_3)L\text{-}L^{2-}(aq) \tag{8}$$

$$[Co(CO_3)_2(HCO_3)(H_2O), L\text{-}L]^{2-}(aq) \xrightarrow{k_1} Co(CO_3)_2(HCO_3)L\text{-}L^{2-}(aq) + H_2O \tag{9}$$

a consideration of the cobalt(III) species believed to be present in aqueous sodium bicarbonate solution under the experimental conditions[2] and on the assumption that protonated diamine ligands are unreactive (see above) is consistent with the above kinetic dependences. Here, K_h is the protonation equilibrium constant of $Co(CO_3)_3{}^{3-}$(aq) and K_0 and K_1 are the equilibrium constants for formation of the solvent-separated reaction precursors $[Co(CO_3)_3, L\text{-}L]^{3-}$(aq) and $[Co(CO_3)_2(HCO_3)$-$(H_2O), L\text{-}L]^{2-}$(aq), respectively. Steps 8 and 9 are postulated to be rate determining. The prediction of this mechanism is that $k^0{}_{obsd}$ will be given by eq 10. Attempts to fit the data

$$k^0{}_{obsd} = \frac{(k_0K_0 + k_1K_hK_1[H^+])[L\text{-}L]}{1 + K_0[L\text{-}L] + K_h[H^+] + K_hK_1[H^+][L\text{-}L]} \tag{10}$$

in Table I to eq 10 gave a much worse fit than the that provided by eq 4, indicating that some of the terms in eq 10 are too small to be evaluated under the experimental conditions. Equation 10 reduces to the same form as eq 4 if the following assumptions are made: (i) $k_1K_hK_1[H^+] >> k_0K_0$

Table II. Mechanistic Parameters for Half-Bonded Complex Formation with Diamines at 25 °C[a]

Ligand	K_0[b]	K_1/K_0	k_0[c]	k_1[c]
py[d]	0.3	1	$\lesssim 0.01$	0.07 ± 0.01
en	$\gtrsim 3000$	0.95 ± 0.2	$\lesssim 0.1$	6.1 ± 1.0
1,2-pn	$\gtrsim 2000$	0.55 ± 0.15	$\lesssim 0.08$	7.1 ± 1.7
1,3-pn[d]	0.3	1	$\lesssim 5$	600

[a] See text for assumptions leading to estimates. [b] Units are M^{-1}. [c] Units are s^{-1}. [d] Parameters estimated from simple electrostatic theory (see text).

and (ii) $(K_1K_h[H^+] + K_0)[L\text{-}L] >> 1 + K_h[H^+]$, whereupon eq 10 reduces to eq 11. Comparison of eq 4 and 11 gives A

$$k^0_{obsd} = \frac{k_1K_hK_1[H^+]}{K_0 + K_1K_h[H^+]} \qquad (11)$$

$= k_1K_hK_1/K_0$, $B = K_1K_h/K_0$, and $k_1 = A/B = 6.1 \pm 1.0$ and 7.1 ± 1.7 s^{-1}, for reactions with en and 1,2-pn, respectively. Substitution of the previous estimate[2] $K_h = (1.31 \pm 0.12) \times 10^9$ M^{-1} into the expression for B gives $K_1/K_0 = 0.95 \pm 0.2$ and 0.55 ± 0.15 for eq 6 and 7, where L-L is en or 1,2-pn, respectively. Assumption (i) above allows an estimate of k_0 as follows. If $k_0 \lesssim 0.1(k_1K_hK_1[H^+]/K_0) = 0.1A[H^+]$ at the lowest respective experimental acidities (Table I), then the upper limits for k_0 are ca. 1×10^{-1} and ca. 8×10^{-2} s^{-1} for reaction with en and 1,2-pn, respectively. Similarly, lower limits for K_0 can be estimated from assumption (ii), since this assumption essentially rests on the requirement that $K_0[L\text{-}L] >> 1$, where [L-L] is the neutral amine ligand concentration. If $K_0[L\text{-}L] \gtrsim 10$ at the lowest calculated value of [L-L],[14] which is 3.4×10^{-3} and 4.7×10^{-3} M in the reactions with en and 1,2-pn, respectively, then K_0 is greater than ca. 3000 and ca. 2000 M^{-1} in eq 6 for reactions with en and 1,2-pn, respectively, at 25.0 °C and ionic strength 1.0 M. Estimates of rate and equilibrium constants from the above treatment of the kinetic data are collected in Table II.

Kinetics of Half-Bonded Complex Formation with 1,3-pn. The kinetic data for half-bonded complex formation with 1,3-pn at 25 °C are collected in Table III.[19] Plots of log $(A_\infty - A_t)$ vs. t were linear for at least 85% reaction,[17] indicating a first-order dependence of reaction rate on $[Co^{III}]$. The molar absorptivity of the product was found to be 1020 ± 90 M^{-1} cm^{-1} at 380 nm and was independent of $[HCO_3^-]$, $[H^+]$, and [L-L] (cf. results for en and 1,2-pn above). At fixed $[H^+]$ and $[HCO_3^-]$, the observed first-order rate constant increased with [1,3-pn]. Data obtained over the experimental [1,3-pn] and acidity ranges were best accounted for by the empirical equation

$$k^0_{obsd} = \frac{C[H^+][L\text{-}L]}{1 + K_h[H^+]} \qquad (12)$$

which predicts that a plot of $k^0_{obsd}(1 + K_h[H^+])/[H^+]$ vs. [L-L] will be linear with a zero intercept, as was observed within experimental error. A linear least-squares fit of the data in Table III[19] with $K_h = 1.3 \times 10^9$ M^{-1} [2] gave $C = (2.7 \pm 0.2) \times 10^{11}$ M^{-2} s^{-1} at 25.0 °C and ionic strength 1.0 M. A relationship of the same form as eq 12 can be obtained if it is assumed that the mechanism consisting of reactions 5–9 applies for L-L = 1,3-pn, with (i) $k_0K_0 << k_1K_hK_1[H^+]$ (see above) and (iii) $(1 + K_h[H^+]) >> [K_0 + K_1K_h[H^+]][L\text{-}L]$ in eq 10. These assumptions lead to $C = k_1K_hK_1 = (2.7 \pm 0.2) \times 10^{11}$ M^{-2} s^{-1}. Substitution of K_h[2] into this relationship for C gives $k_1K_1 = (2.05 \pm 0.15) \times 10^2$ M^{-1} s^{-1} for reaction with 1,3-pn. Assumption (i) is valid if $k_0K_0 \lesssim 0.1k_1K_1K_h[H^+] = 0.1C[H^+]$ at the lowest experimental acidity. Thus, $K_0k_0 \lesssim 1.7$ M^{-1} s^{-1} at 25 °C. If it is further assumed that $K_0 \approx K_1$ (as appears to be the case for en and 1,2-pn, Table II), then assumption (iii) amounts to $0.1 \gtrsim K_0[L\text{-}L]$ at the highest experimental [L-L] (Table III); thus $K_0 \approx K_1 \lesssim 0.7$ M^{-1} at 25 °C. It thus appears that very weak reaction precursors are formed in the carbonatocobaltate(III)–1,3-pn system, consistent with the simple, first-order dependence of k^0_{obsd} on [1,3-pn], eq 12. Electrostatic theory[20] for precursors formed with neutral ligands predicts $K_0 \approx K_1 \approx 0.3$ M^{-1} at 25 °C, which leads to $k_0 \lesssim 5$ s^{-1} and $k_1 \approx 6 \times 10^2$ s^{-1} for reaction with 1,3-pn. These estimates are collected in Table II for comparison with corresponding data for en and 1,2-pn reactions. The corresponding reaction[2] with py is also first order in [py], and if it is assumed that the first Co–py bond is formed by an analogous mechanism, then, with $K_0 \approx K_1 = 0.3$, we may obtain the values for k_0 and k_1 shown in Table II from our earlier work.[2]

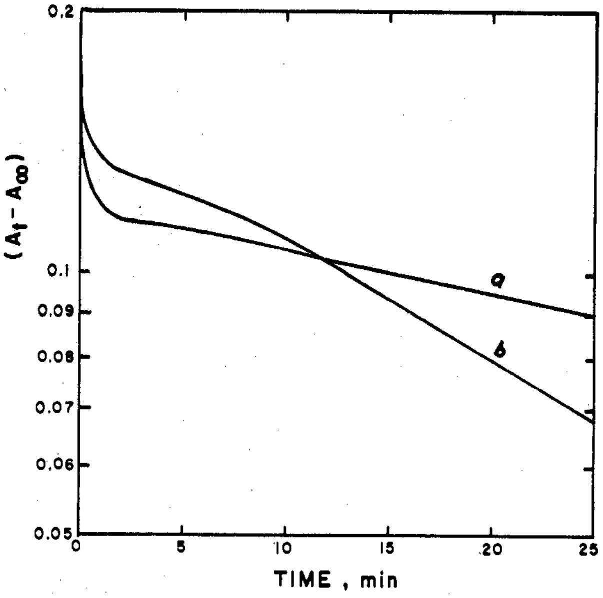


Figure 3. First-order plot for relaxation–ring closure of the en system at 10 °C and ionic strength 1.0 M: (a) $[HCO_3^-] = 0.26$ M, pH 9.30, $[en]_T = 0.08$ M; (b) $[HCO_3^-] = 0.84$ M, pH 8.20, $[en]_T = 0.08$ M. The time-dependent absorbance changes refer to relaxation and ring closure (see text).

Kinetics of Relaxation and Ring Closure. Figure 3 shows examples of plots of log $(A_t - A_\infty)$ vs. time for conversion of the brown intermediate **2** with en to chelated $Co(en)(CO_3)_2^-(aq)$ in aqueous sodium bicarbonate solution. The initial deviation of each plot indicates the occurrence of a kinetic process (a relaxation phenomenon) prior to ring closure, as supported by stopped-flow traces obtained at longer times than are necessary for formation of the initial brown intermediate **2** (Figure 4). The initial deviations in first-order plots like those in Figure 3 for ring closure in the three diamine systems were found to increase with decreasing $[HCO_3^-]$, while the spectra of the intermediates **3** always differed little from those of **2**, suggesting that **3** is also half-bonded for each diamine system. The largest deviations in first-order ring-closure plots were obtained in the en system at low $[HCO_3^-]$; even under these conditions, the deviations in plots of log $(A_t - A_\infty)$ vs. time for the 1,2- and 1,3-pn ring-closure reactions were too small to give accurate kinetic data, although similar kinetic processes are indicated by the spectral changes observed for all three systems.

Relaxation in the Ethylenediamine Systems. Analysis of the initial slopes of first-order plots for ring closure in the en system gave the set of first-order rate constants for relaxation in Table IV.[19] The observed first-order rate constant at fixed temperature was essentially independent of $[HCO_3^-]$, pH, and [en], suggesting the empirical rate law

$$k^1_{obsd} = D \qquad (13)$$

Table VI. Empirical Parameters and Activation Parameters for Ring Closure in Carbonatodiaminecobaltate(III) Systems at Ionic Strength 1.0 M ($NaHCO_3$-$NaClO_4$)

Ligand	Temp, °C	10^5E[a]	10^5F[b]	$\Delta H^{\ddagger}_E$[c]	$\Delta S^{\ddagger}_E$[d]	$\Delta H^{\ddagger}_F$[c,e]	$\Delta S^{\ddagger}_F$[d,e]
en	10.5	2.8 ± 1	42 ± 1	33 ± 2	38 ± 8	21.2 ± 0.7	0 ± 2
	25.5	92 ± 3	208 ± 8				
	32.2	210 ± 10	800 ± 33				
1,2-pn	11.5	4 ± 3	88 ± 4	47 ± 8	84 ± 30	11.7 ± 1.9	−31 ± 6
	25.5	30 ± 13	300 ± 30				
	31.5	180 ± 17	400 ± 30				
1,3-pn	25.5	19 ± 0.5	71 ± 3				

[a] Units are s^{-1}. Errors shown are one standard deviation. [b] Units are $M^{-1}\ s^{-1}$. Errors shown are one standard deviation. [c] Units are kcal mol^{-1}. [d] Units are cal $deg^{-1}\ mol^{-1}$. [e] These are composite quantities (see text).

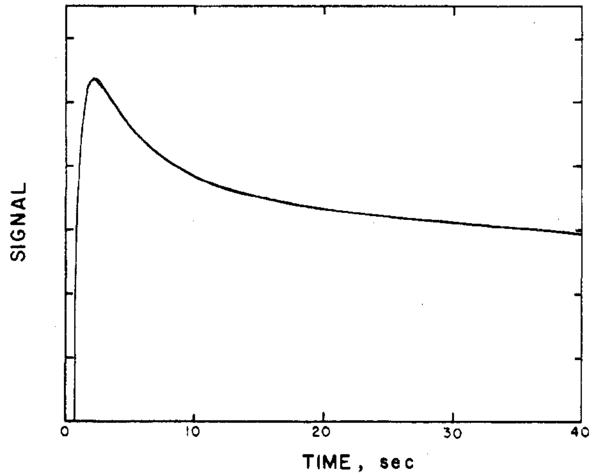


Figure 4. Formation and relaxation of half-bonded intermediate $Co(CO_3)_2enHCO_3{}^{2-}(aq)$ in a stopped-flow trace at 450 nm for the reaction with en at 25.0 °C, $[HCO_3{}^-] \approx 0.1$ M and ionic strength 1.0 M. The signal scale (arbitrary) is proportional to transmittance.

Mechanism. The mechanism shown by eq 14, which is

$$\underset{2}{Co(en)(CO_3)_2HCO_3{}^{2-}(aq)} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \underset{3}{Co(en)(CO_3)_2H_2O^-(aq)} + HCO_3{}^- \qquad (14)$$

based on a consideration of data for equilibria 1 and 2 under the experimental conditions along with the above mechanism for formation of **2**, is consistent with the kinetic data for relaxation. Here, the observed relaxation phenomenon is attributed to equilibration of the primary half-bonded intermediate **2** (formed predominantly from reaction of $Co(CO_3)_2(HCO_3{}^-)(H_2O)^{2-}(aq)$ with en; see above) to give an equilibrium mixture of **2** and **3**; species **3** will be favored over **2** at low $[HCO_3{}^-]$, as observed (Figure 3). The observed relaxation time, τ, for equilibrium 14 is given by

$$1/\tau = k^1{}_{obsd} = k_2([3] + [HCO_3{}^-]) + k_{-2} \qquad (15)$$

$$\approx k_2[HCO_3{}^-] + k_{-2} \qquad (16)$$

since $[3] << [HCO_3{}^-]$. Comparison of eq 13 and 16 suggests that $k_2[HCO_3{}^-] << k_{-2}$, in which case $D = k_{-2}$ in eq 13. The data in Table IV give a linear plot of log D vs. $1/T$, supporting the above assumptions. The activation parameters[7] for conversion of **2** to **3** are $\Delta H^{\ddagger}{}_{-2} = 18.2 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger}{}_{-2} = 2 \pm 4$ cal $deg^{-1}\ mol^{-1}$ at 25.0 °C. An $[HCO_3{}^-]$ independence of the relaxation time at the three experimental temperatures is consistent with $k_2[HCO_3-] \lesssim 0.1k_{-2}$ at the highest respective $[HCO_3{}^-]$ (Table IV), which gives upper limits for 10^2k_2 of 0.05, 0.25, and 4 $M^{-1}\ s^{-1}$ at 1, 10.5, and 25.0 °C, respectively. Thus, the equilibrium constant for formation of **2** from **3**, $K_2 = k_2/k_{-2}$ (see below), has upper limits of ca. 0.1_6, 0.1_2, and 0.4_5 M^{-1} at 1, 10.5, and 25.0 °C, respectively. The spectrum of **3** obtained from extrapolation of A_∞ for relaxation to $[HCO_3{}^-] = 0$ (i.e., the hypothetical situation where **3** is the only half-bonded complex present) is given in Figure 1.

Kinetics of Ring Closure. The kinetic data for conversion of half-bonded diamine complexes to fully chelated $Co(CO_3)_2(diamine)^-(aq)$ are collected in Table V.[19] At fixed temperature, $[H^+]$, and $[HCO_3{}^-]$, the first-order rate constant $k^2{}_{obsd}$ was independent of [L-L], while at fixed [L-L] and $[HCO_3{}^-]$, $k^2{}_{obsd}$ was independent of $[H^+]$. However, the data at fixed $[H^+]$ and [L-L] indicated that $k^2{}_{obsd}$ increases with $[HCO_3{}^-]$, consistent with the empirical equation

$$k^2{}_{obsd} = E + F[HCO_3{}^-] \qquad (17)$$

where E and F are empirical parameters with units of s^{-1} and $M^{-1}\ s^{-1}$, respectively. Empirical parameters E and F and their associated activation parameters obtained from a nonlinear least-squares fit[7] of the data to eq 17 are collected in Table VI.

Mechanism of Ring Closure. A mechanism consisting of equilibrium 14 together with the rate-determining steps 18 and 19 is postulated to account for the kinetic data in Table V.

$$2 \xrightarrow{k_3} (CO_3)_2Co(diamine)^-(aq) + HCO_3{}^- \qquad (18)$$

$$3 \xrightarrow{k_4} (CO_3)_2Co(diamine)^-(aq) + H_2O \qquad (19)$$

Here **2** and **3** are the bicarbonato- and aquo-coordinated half-bonded diamine complexes, respectively (see above), and $(CO_3)_2Co(diamine)^-(aq)$ is the chelated bis(carbonato)-mono(diamine)cobaltate(III) product. This mechanism, with **2** and **3** always at equilibrium on the time scale of ring closure (see above), predicts that the observed rate constant for ring closure will be given by eq 20.

$$k^2{}_{obsd} = \frac{k_3K_2[HCO_3{}^-] + k_4}{1 + K_2[HCO_3{}^-]} \qquad (20)$$

Comparison of eq 17 and 20 suggests that $K_2[HCO_3{}^-] << 1$ in eq 20 (consistent with the above interpretation of the relaxation data), in which case $E = k_4$ and $F = k_3K_2$. The assumption that $K_2[HCO_3{}^-] \lesssim 0.1$ at the highest calculated $[HCO_3{}^-]$ gives the following upper limits for K_2: en, $K_2 \lesssim 0.1_3$ M^{-1} (10.5 °C); 1,2-pn, $K_2 \lesssim 0.1_3$ M^{-1} (11.5 °C); 1,3-pn, $K_2 \lesssim 0.2_2$ M^{-1} (25.5 °C). Thus, $10k_3 \gtrsim 2$, 4, and 2 s^{-1} for ring closure with the three respective diamines at these same temperatures.

Higher Order Amine Complex Formation. As noted earlier, there is evidence for formation of $Co(CO_3)(diamine)_2{}^+(aq)$ products at 25.5 °C and higher temperatures. However, because of experimental difficulties arising from small absorbances, small absorbance changes, and the very low rates of such processes (see above), the kinetic data for

$$4 \xrightarrow{k^3{}_{obsd}} 5$$

are too crude for mechanistic analysis. The observed rate constant $k^3{}_{obsd}$ was, on the average, about 200 times smaller than k^2_{obsd} with both en and 1,2-pn under any particular set of experimental conditions.

Discussion

To our knowledge, this and our previous work[2] are the only sources of kinetic data for reactions of cobalt(III) centers which are predominantly coordinated by carbonate ligands. The limited ligand-exchange data for the present cobalt(III) system, coupled with the lack of data for analogous reactions of tris(carbonato)metalate(III) complexes in the first transition series, restrict the extent to which we can draw firm mechanistic conclusions. However, the results of the present work do seem to support our earlier observations,[2] while at the same time providing additional evidence concerning the nature of this labile cobalt(III) system.

Formation of the First Co–N Bond. The first-order rate dependence on [py] and [1,3-pn] for formation of the first Co–N bond with these ligands is consistent with an interchange (I_d or I_a) mechanism involving "normal" reaction precursors (Table II).[20] A simple electrostatic model[20] predicts that $K_0/K_1 \approx 1$ for an ion–neutral molecule precursor interaction, as assumed for py and 1,3-pn and indicated by the data for en and 1,2-pn. However, it is evident from the independence of the substitution rate on [en] and [1,2-pn] that unusually stable precursors must be invoked in an interchange mechanism for substitution by these latter ligands.[21] If an I_d or I_a mechanism is appropriate, then precursor stabilities might reasonably be related to the basicity and conformation of the ligand. However, 1,3-pn is much more basic than py,[14] but 1,3-pn forms a "normal" precursor, which points to specific conformational interactions of 1,2-diamines in the formation of precursors with $Co(CO_3)_3^{3-}$ (K_0) and $Co(CO_3)_2HCO_3H_2O^{2-}(aq)$ (K_1). It is notable that K_0 and K_1 are both large for 1,2-diamines, suggesting a very favorable general interaction with inner-sphere carbonate, perhaps through hydrogen bonding. It would seem that the conformational requirements of the 1,3-pn ligand itself, where the N ligand atoms are presumably more widely separated than in 1,2-diamines, are sufficient to outweigh the energetic advantages of interaction with inner-sphere carbonate.[22]

The vast majority of ligand substitution reactions of cobalt(III) centers are dissociatively controlled.[23] When an I_d mechanism is invoked to take account of reaction precursors, it is also usually assumed that the slow step of the overall substitution process is breaking of the bond from the metal to the ligand being displaced and that the presence of the substituting ligand in the reaction precursor has little influence on the rate of this slow step.[20,23] This latter assumption does not appear to be valid for substitution at $Co(CO_3)_2HCO_3H_2O^{2-}(aq)$, the rate constants increasing roughly in proportion to ligand basicity (Table II). Thus, an associative interchange (I_a) mechanism appears appropriate at least for substitution reactions of $Co(CO_3)_2(HCO_3)H_2O^{2-}(aq)$.

Spectral Properties of Half-Bonded Intermediates. The constant molar absorptivities for primary half-bonded diamine products $Co(CO_3)_2(HCO_3)(diamine)^{2-}(aq)$ under all reaction conditions with en, 1,2-pn, and 1,3-pn as substituting ligands indicate that formation of such species is quantitative even at the lowest [L-L] employed. Unusually large molar absorptivities[24] are not apparent in the corresponding reactions with monodentate NH_3 or py or bidentate 1,6-hexanediamine, 1,6-hn. Since a similar Co–N bond presumably is formed with one end of all four diamines, it must be that the other end of 1,6-hn cannot interact strongly with the metal center through coordinated carbonate groups. Similar observations with NH_3 and py also implicate specific interactions of the noncoordinated amine groups of 1,2- and 1,3-diamines with inner coordination sphere carbonate ligands in the half-bonded products. The unusual spectral characteristics of half-bonded complexes with these latter ligands suggest efficient charge transfer between the nitrogen atoms of the ligand through an N↔Co↔carbonate↔N route. Our observation that half-bonded $Co(CO_3)_2enHCO_3^{2-}(aq)$ and $Co(CO_3)_2enH_2O^{-}(aq)$ species have similar spectra (Figure 1) indicates that predominant involvement of *chelated* carbonate–amine interactions gives rise to this charge-transfer process. The direct involvement of the Co atom in charge-transfer interactions between the two N ligand atoms is implicated by the lack of evidence for significant spectral changes before the first Co–N bond has formed (i.e., reaction precursors and carbonatocobaltate(III) reactants have very similar visible spectra). Coordination of one end of 1,3-pn to the metal center would, of course, increase its ability to interact effectively with chelated carbonate in the half-bonded complex, leading to the same kind of charge-transfer interactions as those for en and 1,2-pn.

The pH independence of the molar absorptivity of $Co(CO_3)_2(diamine)HCO_3^{2-}(aq)$ suggests that the noncoordinated nitrogen atom is not protonated in these half-bonded species (protonation to form NH_3^+ would presumably interfere with charge transfer and lead to variation of ϵ_2 with pH). This conclusion is mildly supported by the pH independence of the rates of ring closure (see below).

Relaxation Phenomena. The extent of relaxation of the primary substitution product $Co(CO_3)_2(diamine)HCO_3^{2-}(aq)$ increases with decreasing $[HCO_3^-]$ (Figure 3) supporting the assignment of the relaxation phenomena to inner-sphere bicarbonate loss to give an equilibrium mixture of $Co(CO_3)_2(diamine)HCO_3^{2-}(aq)$ and $Co(CO_3)_2(diamine)H_2O^{-}(aq)$. The equilibrium constant for bicarbonate coordination at $Co(CO_3)_2(H_2O)_2^{-}(aq)$ has been estimated[2] as $1/K_{H_2O} \geq 17\ M^{-1}$ at 25 °C (eq 2), which is substantially larger than the corresponding equilibrium constants K_2 for coordination of HCO_3^- by half-bonded $Co(CO_3)_2(diamine)H_2O^{-}(aq)$ obtained from the relaxation and ring-closure data. The presence of an inner-sphere cobalt–diamine bond thus significantly reduces the stability of cis $Co^{III}–HCO_3^-$ interactions.

Ring-Closure Reactions. No evidence was found[2] for formation of $Co(py)_3(CO_3)X^{n-}(aq)$ ($X = H_2O$ or HCO_3^-) or higher pyridine complexes[25] in the reaction of the green cobalt(III) reactant with excess py within a period of 100 h at 25 °C, whereas substantial proportions of $Co(CO_3)(en)_2^+(aq)$ are formed in much shorter times in the reaction with en under similar experimental conditions (see Experimental Section). This observation indicates that the presence of inner-sphere N atoms from saturated diamine ligands reduces the affinity of the cobalt(III) center for coordinated carbonate.

Formation of *cis*-$Co(CO_3)_2(py)_2^{-}(aq)$ from reaction of py with $Co(CO_3)_2pyX^{n-}$ ($X = HCO_3^-$ or H_2O)[2] is much faster than is ring closure to form chelated diaminecobalt(III) species, again indicating unusually stable half-bonded diamine intermediates. The rate of ring closure for diamine ligands is greater when $X = HCO_3^-$ than when $X = H_2O$, irrespective of whether a five- or six-membered chelate ring is being formed. This may be due in part to the weakness of the $Co–OCO_2H$ bond as compared to that of $Co–OH_2$ when the cis position is occupied by a diamine nitrogen atom (see above). The relative magnitudes of E and F in eq 17 are such that E always makes a minor contribution to the rate of ring closure. As a result, the data for E, ascribed to ring closure in $Co(CO_3)_2(diamine)H_2O^{-}(aq)$, are crude in comparison to those for F. Nevertheless, the enthalpies of activation for ring closure in $Co(CO_3)_2(en)H_2O^{-}(aq)$ and $Co(CO_3)_2(1,2\text{-}pn)H_2O^{-}(aq)$ species are very large (Table VI), indicating considerable conformational stability in these half-bonded intermediates.

The decrease in ring-closure rates when X = H_2O in going from en to 1,2-pn to 1,3-pn suggests that larger conformational barriers to ring closure exist for the latter two ligands.

In preliminary experiments we have noticed that addition of X = NCS^- or $Fe(CN)_6{}^{4-}$ has a large retarding effect on the rates of ring closure; the simplest explanation for our observations is that $Co(CO_3)_2$(diamine)X complexes (formed from reaction of labile [$Co(CO_3)_2$(diamine)HCO_3, H_2O]$^{2-,-}$ with X) undergo very slow ring closure.

The formation of $Co(CO_3)_2$(diamine)$_2{}^+$ from reaction of excess en or 1,2-pn with $Co(CO_3)_2$(diamine)$^-$(aq) is a very slow process and is accompanied by a very small absorbance decrease at 380 nm. An intermediate with three coordinated nitrogen atoms is presumably involved in this process but has not been detected.

Finally, we wish to comment on the very different rates of aquation–reduction of half-bonded and chelated diamine-aquocobaltate(III) species. Addition of solutions of brown $Co(CO_3)_2$(diamine)X^{n-}(aq) (X = $HCO_3{}^-$ or H_2O) to excess acid very rapidly produces Co^{2+}(aq) and protonated free amine,[9] whereas Co(en)$^{3+}$(aq) and *cis*-Co(en)$_2{}^{3+}$(aq) are quite stable under acidic conditions (see above). However, unlike its half-bonded diamine analogues, Co(py)$^{3+}$(aq) is quite stable in moderately strong perchloric acid,[2,26] and it has been concluded that the slowest step in the aquation of Co(py)$_4{}^{3+}$(aq) actually involves reduction of Co(py)$^{3+}$(aq) by water.[27] These observations again point to very substantial differences in the properties of carbonato- and aquocobalt(III) centers which also carry coordinated N atoms derived from pyridine or saturated diamine ligands, respectively.

Registry No. en, 107-15-3; 1,2-pn, 78-90-0; 1,3-pn, 109-76-2; $Co(CO_3)_3{}^{3-}$, 12602-46-9; $(CO_3)_2Co$(en)$(HCO_3)^{2-}$, 58815-48-8; $(Co_3)_2Co$(1,2-pn)$(HCO_3)^{2-}$, 58814-72-5; $(CO_3)_2Co$(1,3-pn)$(HCO_3)^{2-}$, 58815-49-9; $CO_3{}^{2-}$, 3812-32-6.

Supplementary Material Available: Table I (first-order constants for half-bonded complex formation with en and 1,2-pn at 25 °C), Table III (first-order rate constants for half-bonded complex formation with 1,3-pn), Table IV (kinetic data for relaxation of $Co(CO_3)_2enHCO_3{}^{2-}$(aq), and Table V (kinetic data for ring-closure reactions of half-bonded complexes with the title ligands) (5 pages). Ordering information is given on any current masthead page.

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(1) This work was supported by a Cottrell Grant from the Research Corp., which is gratefully acknowledged.

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(14) The carbonate equilibrium data used in this work are from the literature cited in ref 2. The logarithmic stability constants for protonation of py, en, 1,2-pn, and 1,3-pn are 5.2, 10.24, 10.13, and 10.81 at 25.0 °C and ionic strength 1.0 M ($NaClO_4$): see L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes", Chemical Society, London, 1964 and 1971.

(15) Decreasing pH reduces the ratio [L-L]/[diammine]$_T$. Runs at [L-L]/[Co^{III}] < 10 give nonlinear first-order kinetic plots for the initial rapid reaction, indicating that the process (diamine)$H^+ \rightarrow$ L-L + H^+ is not sufficiently rapid to maintain a constant excess of L-L, the reactive form. The rate constants for substitution of protonated diamine ligands are much lower than are those for the neutral forms in other systems.[16]

(16) See, e.g., L. J. Kirschenbaum and K. Kustin, *J. Chem. Soc. A*, 684 (1970); R. W. Taylor, H. K. Stepien, and D. B. Rorabacher, *Inorg. Chem.*, **13**, 1282 (1974).

(17) Linearity in first-order plots for half-bonded complex formation in each system is limited solely by the subsequent relaxation processes which are accompanied by a decrease in absorbance (Figure 1) (largest for the en system at low [$HCO_3{}^-$]; see text). First-order data for the initial complex formation were obtained by successive approximations of first-order plots.

(18) Molar absorptivities for the half-bonded intermediates $(CO_3)_2Co$(en)$(HCO_3)^{2-}$(aq) and $(CO_3)_2Co$(en)H_2O^-(aq) were obtained as parameters from computerized fits of absorbance–time data to a successive first-order kinetic scheme (for equations see ref 13). Molar absorptivities for $(CO_3)_2Co$(en)$^-$(aq) from this treatment were in good agreement with ref 6, but subsequent substitution to form $(CO_3)Co$(diamine)$_2{}^+$(aq) was too slow and resulted in too small absorbance changes to give accurate molar absorptivities or kinetic data for these latter processes (see text).

(19) Supplementary material.

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(21) The possibility remains that the reactions with en and 1,2-pn proceed via a dissociative (D) mechanism.[20]

(22) We know of no other cobalt(III) centers which form precursors of the order of stability indicated by the data for en and 1,2-pn in equilibria analogous to eq 6 and 7 (see text and Table II).

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(24) As indicated in Figure 1, the molar absorptivities of the half-bonded complexes greatly exceed those of the initial green reactant in the near-uv region. Molar absorptivities of this order of magnitude at wavelengths longer than ca. 300 nm are very unusual for monomeric cobalt(III) complexes.

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