In c the postulated carbene may or may not be coordinated to vanadium. The c → d conversion requires a vinyl migration, which is normally not a favorable process for alkylcarbenes (hydrogen migration to yield a coordinated fulvene would have been more in line with alkyl carbene chemistry).[21] However, alkyl migrations have been observed, as in the ring expansion of cyclopropylcarbene to cyclobutene.[22] The presence of vanadium and the details of the postulated cyclopentadienylcarbene coordination may favor the vinyl migration over hydrogen migration in the present case. We also recognize the possibility of formation of (fulvene)vanadium(benzene), which could then rearrange to vanadiumbis(benzene), but we favor the vinyl migration because of its simplicity. We also note the similarity of this rearrangement to that occurring in the reaction of $(C_7H_7)Cr(CO)_3^+$ with $C_5H_5^-$, the products being $C_6H_6Cr(CO)_3$ and an unknown C_6 fragment.[23] This reaction apparently proceeds by attack of $C_5H_5^-$ on the coordinated C_7H_7 (compare b above). leading to isolable $(C_{12}H_{12})Cr(CO)_3$. The $C_{12}H_{12}Cr(CO)_3$ is converted to $C_6H_6Cr(CO)_3$ on treatment with excess $C_5H_5^-$, and the other C_6 fragment was postulated to be fulvene.

Finally, we were able to observe no rearrangement of either cpVtr or cpVtr$^+$ (prepared as in ref 5) upon heating dilute solutions to 200° in either THF or toluene for days. Evidently, considerable vibrational or electronic excitation of cpVtr$^+$ is required for production of $V(C_6H_6)_2^+$. Such an excitation may be easily accomplished by electron impact.[24]

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Carbonate Ligand Exchange Studies of *cis*- and *trans*-Carbonatodiammineethylenediamine Complexes of Cobalt(III). A Revised General Mechanism for Chelated Carbonate Ligand Exchange Reactions in Basic Aqueous Solution

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Abstract: A comprehensive set of new data on the carbonate exchange reaction of *cis*-$Co(NH_3)_2enCO_3^+$ is correlated with recently accrued results of other types of studies of the chemistry of the chelated carbonato complexes of formula $CoN_4CO_3^+$ (where N_4 represents the four coordinated nitrogen atoms of the nonexchanging NH_3 or amine ligands). At 25° and $7.5 < pH < 9.5$, only about 0.1% of the complex is in the ring-opened form produced by reaction of water with the chelated parent compound. Three monodentate carbonato species are in an equilibrium represented by

$$CoN_4(H_2O)(CO_3H)^{2+} \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} CoN_4(OH)(CO_3H)^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} CoN_4(OH)(CO_3)$$

for which the first and second pK values are approximately 5.3 and 8.7 at 25°. Carbonate exchange results from a combination of the two dissociative decarboxylations of the type $R'CO_3H \rightleftarrows R'OH + CO_2$, and the two associative carboxylations of the type $R''OH + CO_2 \rightleftarrows R''CO_3H$. The four rate constants for the *cis*-$(NH_3)_2$en species have values of 0.4 sec^{-1}, 2.5×10^{-3} sec^{-1}, 15 M^{-1} sec^{-1}, and 50 M^{-1} sec^{-1}, respectively, in good agreement with expectations based on independent data. The new mechanism is shown to offer a very satisfactory interpretation of results of analogous exchange studies extending back to 1952, and a number of the earlier discrepancies are now resolved. Comparative studies of the carbonate exchanges of the ions *cis*-$Co(NH_3)_2enCO_3^+$, *trans*-$Co(NH_3)_2enCO_3^+$, and *trans*-$Co(NH_3)_2tnCO_3^+$ (en = ethylenediamine, tn = trimethylenediamine) throw new light on some previously noted stereochemical influences of the amine ligands on carbonato ligand reactivity.

Our previous paper in this series[3] reported details of a study of the carbonate exchange reactions of the complex ion carbonatobis(propylenediamine)cobalt(III). On the basis of the evidence then available, a rational mechanism was proposed for the various chelated carbonatotetraminecobalt(III) exchanges[4,5]

(1) Work done as part of the Ph.D. requirement of the State University of New York at Buffalo, and presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. Complete dissertation available from University Microfilms, Ann Arbor, Mich.

(2) To whom correspondence concerning this paper should be addressed.

(3) G. Lapidus and G. M. Harris, *J. Amer. Chem. Soc.*, **85,** 1223 (1963).

for which the stoichiometry is

$$\mathrm{CoN_4CO_3^+ + {}^{14}CO_3^{2-} \rightleftharpoons CoN_4{}^{14}CO_3^+ + CO_3^{2-}}$$

The species which we had investigated up to that time were those for which N_4 = $(NH_3)_4$,[6] bis(ethylenediamine) [$(en)_2$],[7] bis(trimethylenediamine) [$(tn)_2$],[8] as well as the bis(propylenediamine) [$(pn)_2$] analog.[3] The proposed reaction scheme was a modification of our previous hypothesis of a dual mechanism made up of an aquation path which consists of dissociative interchange with solvent water and a bimolecular associative interchange between free and complexed carbonate. Some results obtained for the N_4 = *cis*-$(NH_3)_2$en complex[9] also appeared to fit into this scheme.[3] The only significant difference observed among the various N_4 complexes mentioned was with the tn_2, for which the overall exchange reaction rate is barely one-tenth as great as for the others. This anomaly was explained stereochemically, supported by the results of a deuterium exchange study involving the amine protons of the various complexes and heavy water solvent.

The present work was undertaken with two aims in view. It was desired to expand our stereochemical influence concepts by comparing the carbonate exchange reactivity of the complexes where N_4 = *cis*-$(NH_3)_2$en or *trans*-$(NH_3)_2$en. In the first of these, the ethylenediamine chelate bridge is diagonally placed with respect to the carbonato chelate, but in the *trans* the two chelate bridges are coplanar, a factor expected to increase the strain of the O–Co–O linkage of the carbonato group. Additional information concerning this factor was sought through a limited kinetic study of the carbonate exchange reaction of the ion *trans*-$Co(NH_3)_2tnCo_3^+$. Our second aim was to reexamine our previous general mechanism,[3] the shortcomings of which have become increasingly obvious in recent years as new data accrue concerning other aspects of the chemistry of the carbonatocobalt(III) complexes. These data involve the ring opening and acid–base equilibria of the complex ions $Co(en)_2CO_3^+$ and Cotren-CO_3^+ (tren = triaminotriethylamine)[10,11] as well as the kinetics of carbonato ring-opening reactions in both acidic[12,13] and basic[14,15] solution. In the present study we obtained a considerably more comprehensive set of kinetic data than in any previous carbonate exchange work, particularly with respect to the acid dependence of the process, for which the pH range has been more than doubled. The new set of data, together with the above-mentioned related equilibrium and rate-constant information, enables us to offer a revised general mechanism of chelated carbonate ligand exchange. The obvious discrepancies in previous interpretations[3,16] are now removed, and an integration of the presently-known reaction-rate chemistry of the $CoN_4CO_3^+$ type of complex ion is provided.[17]

Experimental Section

A. Preparation of Compounds. Syntheses of *cis*- and *trans*-$Co(NH_3)_2enCO_3^+$ species have been previously described.[18,19] Our modification of the Bailar and Peppard procedure[18] is as follows. Ammonium *cis*-disulfitotetraamminecobalt(III) complex (A) is obtained by mixing 80 g of $CoCl_2 \cdot 6H_2O$ in 100 ml of water, 200 g of $(NH_4)_2CO_3$ in 1 l. of water, and 500 ml of 28% ammonia solution, bubbling ammonia-saturated air through the solution for about 8 hr, and then adding 155 g of $NaHSO_3$. After partial evaporation into the open air, the brown product precipitates on cooling to 0° and is collected and washed on a fritted-glass filter. No purification is necessary. Complex A is converted to ammonium *cis*-disulfito-*trans*-diammineethylenediaminecobalt(III) complex (B) by mixing 50 g of A with 200 ml of absolute alcohol and 7.5 ml of 92% ethylenediamine, adding 50–60 glass beads, and shaking at room temperature until the solution turns mustard yellow in color (about a week). The glass beads are removed by passage through an uncovered Büchner funnel, and the suspended product is obtained by filtering on a fine glass filter and purified by one recrystallization from water. *cis*-Dichloro-*trans*-diammineethylenediaminecobalt(III) complex (C) is obtained from B by shaking the latter for 24 hr with 90 ml of absolute alcohol previously saturated with gaseous HCl. The NH_4Cl-contaminated blue salt (C) is purified by dissolving in water, adding a slight excess of NH_4Br, and crystallizing out the bromo salt at 0° (yield about 10%). Complex C is converted to carbonato-*trans*-diammineethylenediaminecobalt(III) complex (D) by trituration with freshly prepared Ag_2CO_3 in the dark. D is obtained as the perchlorate salt by treatment of the carbonate with an equivalent of $AgClO_4$. This salt is very soluble and is obtained as the pure solid by precipitation from a 3:1:1 mixture of absolute alcohol, ether, and aqueous solution of salt, with a yield of less than 0.1% based on original starting materials. (Complex D is unstable in solution at room temperature, isomerizing to the *cis* analog on standing, as observable by nmr technique—see below.) Addition of 5 g of B to 35 ml of 40% aqueous HBr and shaking for several minutes at 80° yields *trans*-dibromo-*cis*-diammineethylenediaminecobalt(III) complex (E). The deep green solution is allowed to stand at room temperature for several hours and cooled to 0° to obtain the crystals, which can be washed with a mixture of cold water and ethanol. Conversion of E to carbonato-*cis*-diammineethylenediaminecobalt(III) complex (F) is done as for C to D. The final filtrate is concentrated on a steam bath and the pure crystals are obtained by cooling the concentrate. Carbonato-*trans*-diamminetrimethylenediaminecobalt(III) complex (G) is obtained in the same manner as its ethylenediamine analog D, substituting 100% trimethylenediamine for the ethylenediamine in the appropriate step of the synthesis.

B. Characterization of Compounds. Elemental analysis of the salts of the two $(NH_3)_2$en isomers yielded the following data.[20] *Anal.* Calcd for *cis*-$Co(NH_3)_2enCO_3ClO_4 \cdot 2H_2O$: C, 10.32; N, 16.06; H, 5.74; CO_3, 17.21. Found: C, 10.48; N, 16.31; H, 5.62; CO_3, 17.38. Calcd for *trans*-$Co(NH_3)_2enCO_3Cl \cdot H_2O$: C, 14.47; N, 18.45; H, 6.51; CO_3, 22.52. Found: C, 13.50; N, 21.02; H, 6.00; CO_3, 22.38. The visible spectra of the complexes were determined on a Cary Model 15 spectrophotometer, and the data are recorded in detail elsewhere[21] together with those for several

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(4) A reconsideration of the carbonate exchange reaction of the monodentate species $Co(NH_3)_5CO_3^+$ has been published recently as part of a study of its aquation reaction.[5]

(5) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, 90, 6360 (1968).

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(20) Carbonate determinations were made by the baryta method described previously.[8] All other analytical data provided by Galbraith Laboratories, Knoxville, Tenn.

(21) Reference 17, p 179, Table VII.

related compounds. The nmr spectra of the compounds were examined by means of a Varian A-60 unit, using D_2O as solvent. The C–H groups produce a doublet with the unsymmetrical *cis*-diammineethylenediamine isomer and a singlet with the symmetrical *trans* analog, as is to be expected from observations made[22a] with respect to the *cis* and *trans* forms of $Co(en)_2Cl_2^+$ complex ion. The *trans*-$Co(NH_3)_2enCO_3^+$ ion is thermodynamically unstable, isomerizing to the *cis* species, as is readily followed by observing the change in the C–H nmr peaks. The infrared spectra of the two diammineethylenediamine compounds were determined between 4000 and 250 cm^{-1} on a Perkin-Elmer Model 521 instrument, using Nujol mull, KBr disk, and thin-film H_2O and D_2O solution techniques. The spectra were similar to those reported by Nakamoto[23] for other chelated carbonatocobalt(III) complexes, and no meaningful differences appeared between our *cis* and *trans* isomers.

The complex *trans*-$Co(NH_3)_2tnCO_3Cl \cdot H_2O$ was analyzed for carbonate only, yielding the following data. *Anal.* Calcd for CO_3, 21.43. Found: CO_3, 21.21. Its nmr spectrum showed the expected 2:1 doublet at the C–H position, deriving from the methylenes of the amine ligand.[22b]

C. Apparatus and Technique of Exchange Rate Measurement. Enough solid complex is weighed into a 15-ml test tube to give the desired final concentration (usually 0.022 *M*). Sodium borate solution containing a known concentration of free carbonate and adjusted to the desired pH is added to give a volume of 14 ml and the solution is allowed to stand in a thermostat overnight to ensure ring-opening equilibration (see explanation in Results and Discussion section). Buffering is achieved by the combined action of borate and carbonate, or, in some experiments done in absence of the former, by carbonate alone. (The usual borate concentration was 0.05 *M*, with some runs made in nearly saturated borate.) A run is commenced by addition of 1 ml of very dilute but highly radioactive carbon-14-labeled carbonate solution to the tube containing the equilibrated reactants, from which, after rapid mixing, a 1-ml "zero-time" sample is removed as soon as possible. A series of similar samples are removed from the thermostated reaction tube at convenient time intervals. Precipitation of the free carbonate from the samples is achieved by established procedure[3] and the precipitates are collected in a geometrically reproducible form on weighted fritted-glass disks by means of a demountable filter stick assembly.[24] After drying and weighing, carbon-14 assay is made of the disks and the rate of exchange, *R*, is evaluated in the conventional manner.[3]

Results and Discussion

Some preliminary studies were made of the *trans* to *cis* isomerization of the $Co(NH_3)_2enCO_3^+$ complex ion by the nmr technique. The reaction is cleanly first order, and at 50° and pH 7.5 has a rate constant of about 10^{-3} sec^{-1}, which decreases to about 2×10^{-4} at pH 10. The activation energy, based on measurements at the temperatures 30, 40, and 50° (pH 10), is 35 kcal/mol. It was found that the carbonate exchange reaction of the *trans* isomer could be studied at 25° and pH >9 without undue interference by the conversion to the *cis* form. The latter is the stable species, and no isomerization complications exist in the study of its carbonate exchange process. This has therefore been examined in much more detail than is possible for the *trans* analog, and our detailed rate constant conclusions thus apply only to the *cis* complex.

The rate of exchange, *R*, of *cis*-$Co(NH_3)_2enCO_3^+$ was determined as a function of several variables. It was shown to be first order in complex ion concentration, *a*, over the range $0.01\ M < a < 0.05\ M$, with a pseudo-first-order rate constant of $(8.9 \pm 0.4) \times 10^{-6}$ sec^{-1} at 25°, pH 8.22, free carbonate concentration, b, = 0.0144 *M*, and 0.05 *M* borate buffer. The variation of the pseudo-first-order rate constant R/a with b or with the hydrogen ion concentration, h, is shown in Figure 1. Since both types of straight-line plots have nonzero intercepts and slopes, it is clear that the reaction has free-carbonate-concentration-independent and first-order-dependent paths, as well as acid-independent and first-order-dependent paths.

Before considering a possible mechanism for the reaction, it is important that we review what is presently known concerning the aqueous equilibria involving the $CoN_4CO_3^+$ type of complex ion. In slightly basic solutions at room temperature, the following occur[25]

$$CoN_4CO_3^+ + H_2O \rightleftharpoons CoN_4(OH)(CO_3H)^+ \qquad K_1 \quad (1)$$

$$CoN_4(H_2O)(CO_3H)^{2+} + H_2O \rightleftharpoons CoN_4(OH)(CO_3H)^+ + H_3O^+ \qquad K_2 \quad (2)$$

$$CoN_4(OH)(CO_3H)^+ + H_2O \rightleftharpoons CoN_4(OH)(CO_3) + H_3O^+ \qquad K_3 \quad (3)$$

Reaction 1, ring opening by water, has an equilibrium constant, K_1, of about 10^{-3} at 25°, as is evident from measurements made on the complexes where $N_4 = en_2$ or tren.[10,11] Furthermore, the ring-opening step designated by the forward part of this reaction cannot determine the rate of carbonate exchange, since this forward rate always appreciably exceeds that of carbonate exchange for a variety of complexes of this type[12,13,15] under the conditions of the exchange studies. The magnitudes of K_2 and K_3 are also approximately known,[10,11] being about 5×10^{-6} and 2×10^{-9}, respectively, at 25°. These equilibria are, of course, continuously maintained, since they are simple acid–base proton transfers. Two free carbonate acid–base equilibria are also of significance in the exchange system

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad K_4 \quad (4)$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \qquad K_5 \quad (5)$$

for which the equilibrium constants, K_4 and K_5, have the values 4.5×10^{-7} and 5.7×10^{-11} at 25°, respectively.[26]

As in our previous studies,[3,6–8] we propose that the carbonate exchange takes place by means of a dual mechanism, partly dissociative and partly associative. However, we modify the nature of the proposed reactants in keeping with the known facts of reactions 1, 2, and 3 above, and in harmony with the now fully documented concept[4,5,12,13] of decarboxylation as the mechanism of carbonate loss from carbonato complexes. We suggest, then, a dual dissociative path consisting of decarboxylation of the ring-opened monodentate carbonato species related by reaction 2, and a dual associative path consisting of carboxylation of the ring-opened monodentates related by reaction 3. The mechanism thus consists of four equilibrations with the rate of the forward reactions (rate constants k_1, etc.) determining the rate of carbonate exchange in each instance, as follows

$$CoN_4(H_2O)(CO_3H)^{2+} \rightleftharpoons CoN_4(OH)(OH_2)^{2+} + CO_2 \qquad k_1 \quad (6)$$

$$CoN_4(OH)(CO_3H)^+ \rightleftharpoons CoN_4(OH)_2^+ + CO_2 \qquad k_2 \quad (7)$$

$$CoN_4(OH)(CO_3H)^+ + CO_2 \rightleftharpoons CoN_4(CO_3H)_2^+ \qquad k_3 \quad (8)$$

$$CoN_4(OH)(CO_3) + CO_2 \rightleftharpoons CoN_4(CO_3H)(CO_3) \qquad k_4 \quad (9)$$

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[22] (a) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963); (b) H. Yonada and Y. Morimoto, *Bull. Chem. Soc. Jap.*, **39**, 2180 (1966).

[23] K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

[24] W. Robb, Ph.D. Dissertation, University of Melbourne, 1963.

[25] (a) Ring opening promoted by OH^- ion need not be considered since it is an extremely slow process[14,15] below pH 10; (b) see ref 17, footnote 268, concerning preference for $CoN_4(OH)(CO_3H)^+$ over $CoN_4(OH_2)(CO_3)^+$.

[26] D. M. Kern, *J. Chem. Educ.*, **37**, 14 (1960).

Since K_1 is small, $(CoN_4(OH)(CO_3H)^+) = K_1a$, $(CoN_4(H_2O)(CO_3H^{2+}) = K_1ah/K_2$, and $(CoN_4(OH)(CO_3)) = K_1K_3a/h$. The CO_2 concentration is given by $bh^2/(h^2 + K_4h + K_4K_5)$, since the amount of CO_2 formed by dissociation in reactions 6 and 7 or used up by association in reactions 8 and 9 is very small relative to the total. Also, under the conditions of the present study, $7.5 < pH < 9.5$, $(CO_2) = hb/K_4$ within a 10% error. Combining the above facts, one can write the pseudo-first-order rate constant for the exchange reaction in the form

$$R/a = k_1K_1h/K_2 + k_2K_1 + k_3K_1hb/K_4 + k_4K_1K_3b/K_4 \quad (10)$$

Employing the quoted approximations for K_1 K_2, K_3, and K_4, one can derive two sets of figures for the rate constants by using the intercepts and slopes of the *R/a vs. b* plots at the two different acidities and the *R/a vs. h* plots at the two different *b* values (Figure 1). This procedure leads to the following results at 25°.

	k_1, sec^{-1}	10^3k_2, sec^{-1}	k_3, M^{-1} sec^{-1}	k_4, M^{-1} sec^{-1}
R/a vs. b plots	0.45	2.5	16	47
R/a vs. h plots	0.30	2.6	10	58

The agreement is seen to be very satisfactory, considering the errors inherent in the analysis and the fact that the paths governed by k_1 and k_3 make only minor contributions to the total rate.

Support for our proposed mechanism is available from a number of sources. A good estimate of k_1, obtained from direct studies of the decarboxylation of $Co(NH_3)_4CO_3^+$, is about 1 sec^{-1} at 25° and ionic strength 0.5 *M*,[12a] which agrees as well as can be expected with the figures deduced from the exchange data, since it is for a different compound under somewhat different conditions. There is no experimental value available for comparison with k_2, but the k_1/k_2 ratio of about 150 is quite reasonable in view of the nearby location of the extra proton to the reaction site in (6), which undoubtedly facilitates decarboxylation. Reactions 8 and 9 are comparable to one recently studied by Sargeson[27] using stopped-flow technique

$$Co(NH_3)_5OH^{2+} + CO_2 \rightleftharpoons Co(NH_3)_5CO_3H^{2+} \quad (11)$$

The observed second-order forward rate constant of (11) is 56 M^{-1} sec^{-1} at 25° and ionic strength 0.2 *M*, agreeing rather well with k_4 above at a somewhat lower ionic strength (which, in any case, should be of little consequence—see below). The value of k_3 is somewhat smaller, and this is reasonable since here the extra proton on the monodentate carbonato reactant can reduce the hydroxyl group's reactivity to carboxylation through hydrogen bonding. However, the effect is not great since the bicarbonato proton is rather remote from the reaction site, the oxygen atom of the hydroxyl group.

The doubly monodentate carbonato intermediates proposed in reactions 8 and 9, for which we have as yet no direct experimental evidence of any kind, are nevertheless well supported by analogies to other systems. For example, part of the exchange of free glycine with trisglycinatonickel(II) is attributed[28] to the formation of a bisbidentate–bismonodentate species of formula $Ni(NH_2CH_2COO)_2(NH_2CH_2COOH)_2$. Also, direct evidence is reported[29] for the existence of the complex $Co(en)_2(HPO_4)_2^-$ in equilibrium with free phosphate and $Co(en)_2PO_4$ under suitably controlled conditions.

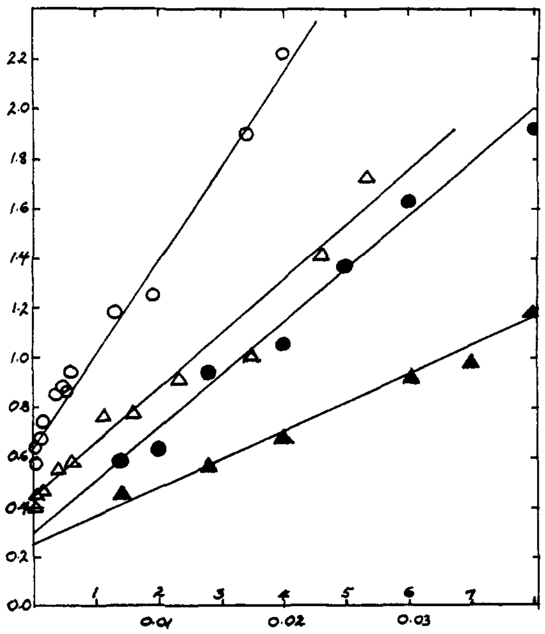

Figure 1. Variation of pseudo-first-order carbonate exchange rate constant, *R/a*, of 0.022 *M cis*-$Co(NH_3)_2enCO_3^+$ complex ion with carbonate concentration and with acidity in 0.05 *M* aqueous borate buffer at 25°: ●, with carbonate at pH 8.22; ▲, with carbonate at pH 9.33; ○, with acidity at *b* = 0.0144 *M*; △, with acidity at *b* = 0.0072 *M*.

Some experiments were done with the *cis*-$Co(NH_3)_2enCO_3^+$ complex in which information was obtained concerning the effects of variation of borate buffer concentration (and thus ionic strength) and temperature. The data were obtained in the form of *R/a vs. b* plots, all of which are linear and yield intercept and slope values in a manner similar to that illustrated in Figures 1 and 2. A summary is given in Table I. It is noted that the ionic strength changes have a rather small effect on both slope and intercept values at 25°, with

Table I. Effect of Variation of Buffer Concentration and Temperature on the Pseudo-First-Order Carbonate Exchange Rate Constant of Carbonato-*cis*-diammineethylenediaminecobalt(III) Complex Ion

pH	Borate concn,[a] *M*	Temp, °C	Intercept,[b] 10^6 sec^{-1}	Slope,[b] 10^4 M^{-1} sec^{-1}
8.22		25	3.5	5.0
8.22	0.05	25	3.0	4.3
8.22	Satd	25	2.0	2.8
8.22	0.05	30	4.4	5.8
8.22	0.05	35	6.4	6.6
9.33		25	2.5	2.3
9.33	0.05	25	2.5	2.3
9.33	Satd	25	2.0	1.8
9.33	0.05	30	5.0	3.3
9.33	0.05	35	8.0	6.0

[a] With no borate (buffering provided by free carbonate only), the ionic strength is about 0.03–0.06 *M*; with 0.05 *M* borate, ionic strength is about 0.05–0.08 *M*; with saturated borate, ionic strength is about 0.4 *M*. [b] Obtained from the linear plots of *R/a vs. b*.

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(27) A. M. Sargeson, personal communication.

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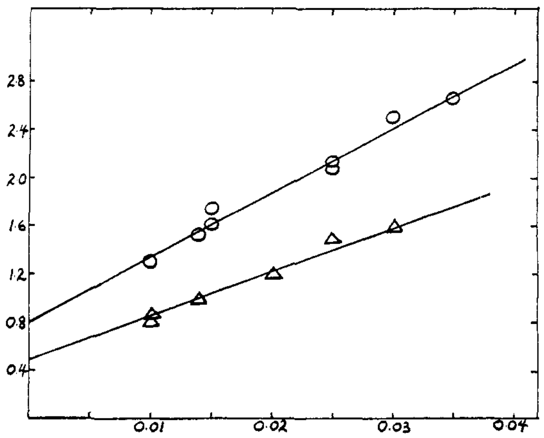

Figure 2. Variation of pseudo-first-order carbonate exchange rate constant, R/a, of 0.022 M *trans*-diamminecarbonatocobalt(III) complex ions with carbonate concentration in 0.05 M aqueous borate buffer at pH 9.33 and 25°: ○, *trans*-$Co(NH_2)enCO_3^+$; △, *trans*-$Co(NH_3)_2tnCO_3^+$.

the effect more pronounced in the more acidic systems. The net result is a modest decrease in exchange rate as the ionic strength is increased, as previously noted for $(NH_3)_4$[6b] and $(tn)_2$[8] complexes. Consideration of the form of the rate law, eq 10, and the magnitudes of the various constants already deduced, shows that at pH 9.33 the first and third terms contribute very little to the magnitude of R/a, and the pseudo-first-order exchange rate constant may thus be approximated by the expression

$$R/a = k_2K_1 + k_4K_1K_3b/K_4 \qquad (12)$$

In these circumstances, the intercept and slope figures can be equated to k_2K_1 and $k_4K_1K_3/K_4$. Ionic strength variation should not have much effect on the rate constants, nor on K_1 and K_3, but K_2 should decrease slightly and K_4 increase. Whence at pH 9.33, where eq 12 applies, the intercept of the R/a plot should be only slightly affected by increase of ionic strength and the slope moderately decreased, as observed. At pH 8.22, the full eq 10 applies and the slope should decrease more steeply with increased ionic strength, since both the third and fourth terms of the rate equation are affected by K_4. Again, this is in keeping with observation.

The temperature variation data at pH 9.33 enable us to conclude that the activation energies for k_2 and k_4 are about 21 and 18 kcal/mol, respectively, neglecting the contribution to the temperature dependence from the various equilibrium constants. These numbers are in reasonable agreement with those deduced in previous work for the dissociative and associative exchange paths at high pH.[3] At pH 8.22, the activation energies related to the intercept and slope values are somewhat lower, but the number of constants involved is too large to enable any sensible conclusions to be drawn.

We turn now to the results we have obtained concerning the carbonate exchange rates of the complexes *trans*-$Co(NH_3)_2enCO_3^+$ and *trans*-$Co(NH_3)_2tnCO_3^+$. These are presented as R/a plots *vs.* carbonate concentration in Figure 2. Comparison of the data for the *trans*-$(NH_3)_2$en species with those for the *cis* analog (Figure 1) shows that for the former the intercept and slope values are close to three times the corresponding values for the latter. Inspection of eq 10 suggests that this probably results from an increase of the one constant, K_1, which is common to all four terms in the rate equation. Support for this hypothesis is provided by X-ray structural studies of related cobalt(III) complexes. Reflecting the limited span of the four-membered carbonato chelate ring, it is known[30] that the O–Co–O bond angle in the carbonatotetraammine complex is reduced from the ideal octahedral value of 90 to 70.5°. The coplanar N–Co–N angle is enlarged to 94.5° and the two coplanar O–Co–N angles to 97.7°. A similar study of the trisethylenediaminecobalt(III) complex[31] shows that the preferred N–Co–N angle within the five-membered ethylenediamine chelate is 87.4°. If these values are relatively undisturbed in aqueous solution and applicable to related cobalt(III) complexes, one can explain the increase in K_1, the ring-opening equilibrium constant, of *trans*-$Co(NH_3)_2enCO_3^+$ as compared to *cis*. With the latter, it is possible to keep the O–Co–O angle of the carbonato chelate at 70.5°, enlarge the other three coplanar angles, and still maintain the N–Co–N angle of the ethylenediamine chelate at the preferred 87.4°. However, the *trans* analog must have both carbonate and ethylenediamine rings in the same plane, increasing the strain in the carbonato group and encouraging it to open to a greater extent than in the *cis* case, to give the relatively strain-free monodentate intermediate, as shown in reaction 1. A test of this explanation is provided by our experiments with the *trans*-$Co(NH_3)_2tnCO_3^+$ complex (see Figure 2). While the exchange rates for this species are faster than for *cis*-$Co(NH_3)_2enCO_3^+$, they are significantly slower than for *trans*-$Co(NH_3)_2enCO_3^+$ under comparable conditions. X-Ray studies of $Co(tn)_3Br_3$[32] show that the preferred N–Co–N angle for the six-membered trimethylenediamine ring is about 94°. Thus, when such a ring is coplanar with a carbonato ring, the strain in the latter should be substantially reduced from the ethylenediamine analog. This kind of an argument has been used previously[33] in discussing the contrast in the ORD properties of $Co(en)_3I_3$ and $Co(tn)_3I_3$. The former compound exhibits a large rotational strength, which is reduced five- to tenfold in the latter. This effect is attributed to the strain inherent in the five-membered ethylenediamine chelate as compared to its six-membered homolog.

Finally, there remains to make an assessment of the earlier studies of carbonate exchange with the various chelated carbonatocobalt(III) complexes in the light of our revision of the general mechanism. These previous studies have not been made over a wide enough range of variables to enable evaluation of the various rate constants as has been possible in our work with the *cis*-$(NH_3)_2$en complex. However, since most of the studies were made within the limited range $9 < \text{pH} < 10$, the simplified rate equation (12) is approximately applicable. We have therefore converted the previous data into a form comparable with ours at 25°, pH 9.33, and 0.05 M borate by evaluating the intercepts and slopes of the various straight-line R/a *vs.* b plots and equating these constants to the appropriate terms of eq 12. This treatment enables the comparisons presented in Table II. The only complex which varies

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Table II. Comparison of Carbonate Exchange Rates for Various $CoN_4CO_3^+$ Complexes (25°; pH, 9.33; 0.05 *M* borate)

N_4	$10^6 k_2 K_1$, sec^{-1}	$10^4 k_4 K_1 \cdot K_3/K_4$, $M^{-1}\ sec^{-1}$	$10^3 K_1$[g]	$10^7 k_4 K_3$[h]
$(NH_3)_4$[a]	10.4	5.4	4.2	0.6
$(en)_2$[b]	5.9	2.5	2.4[i]	0.5
$(pn)_2$[c]	3.7	4.3	1.5	1.3
$(tn)_2$[d]	0.5	0.2	0.2	0.5
cis-$(NH_3)_2en$[e]	3.7	3.5	1.5	1.0
cis-$(NH_3)_2en$[f]	2.5	2.3	1.0	1.0
trans-$(NH_3)_2en$[f]	8.0	5.5	3.2	0.8
trans-$(NH_3)_2tn$[f]	5.0	3.6	2.0	0.8

[a] Deduced from "best fit" values for rate constants given in ref 6a along with reported temperature dependence. [b] Deduced from "best fit" values for rate constants given in ref 7. [c] Deduced from ref 3, Table I. [d] Deduced from ref 8, Table IIB. [e] Deduced from plot of data in ref 9, Table I, first five entries; *no added borate* in these runs. [f] This work. [g] Calculated by assuming k_2 has the same value (2.5×10^{-3} sec^{-1}) for all complexes, as found in this work for the *cis*-$(NH_3)_2en$ complex. [h] Calculated using K_1 of the preceding column and $K_4 = 4.5 \times 10^{-7}$. [i] Recent data on the base hydrolysis of the $(en)_2$ complex[15] suggest that $K_1 = 50K_w/K_3$ at 25° in 1.0 *M* $NaClO_4$, where k_w is the ion product of water and has a value of about 2×10^{-14} under these conditions.[27] Assuming our quoted value of K_3 to be independent of salt concentration, one deduces $K_1 = 5 \times 10^{-4}$, in reasonable agreement with our tabulated value, considering the manifold approximations involved.

drastically from the average pattern of the other species is the $(tn)_2$ analog, which exchanges considerably more slowly. The explanation based on the magnitude of K_1, as already invoked in comparing the *cis*- and *trans*-$(NH_3)_2en$ compounds, seems to provide a reasonable answer. This is illustrated by making the logical assumption that the magnitude of k_2 does not change much in going down the series, since it refers to the decarboxylation of ring-opened bicarbonato hydroxo complexes of very similar geometry. One can thus make estimates of the values of K_1 for the various species, as given in the third column of Table II. Also, since K_4 is known, estimates can be given of k_4K_3 for each of the complexes, as shown in the last column of the table. It is seen that K_1 for $(tn)_2$ is less than one-tenth of the average value for the others. It has been shown[3] that the rate of amine hydrogen exchange for $(tn)_2$ is about one-tenth as great as for the $(en)_2$ analog, suggesting a greater extent of hydrogen bonding in the former, perhaps in the form of N–H–O–C bridging which might assist in retention of the chelate structure of the carbonato group. This would show up as a reduction in K_1, but not in a decrease of the forward rate constant of (1), since this is known to be only slightly smaller for the $(tn)_2$ than for the $(en)_2$ complex.[13] Clearly what reduces K_1 for the $(tn)_2$ species must be an increase in the rate constant of the reverse of (1), possibly as a result of the H-bonding propensity already mentioned. The presence of the two tn chelates may, of course, substantially reduce the strain in the O–Co–O linkage of the carbonato chelate, in line with arguments presented earlier. However, this apparently shows up kinetically as an increase in the reverse rate constant of (1) rather than a decrease of the forward.

The modest divergence of the *trans*-$(NH_3)_2en$ species from the standard pattern has already been discussed and ascribed to a threefold increase of K_1 as compared to its *cis* isomer. This is, in fact, the result of an approximately threefold increase in the forward rate constant of (1).[12b] The $(NH_3)_4$ species diverges slightly more from the average pattern than does the *trans*-$(NH_3)_2en$, again as a result of an increased K_1. Its forward rate constant for (1) is, however, only slightly greater than for $(en)_2$ or $(pn)_2$.[13] Perhaps in this instance the lack of any rigid geometry enforced by amine chelation in some way inhibits the carbonato ring closure by the reverse of (1), thus increasing K_1.

It is of interest that there appears to be no great variation in the magnitude of k_4K_3 in going down the series in Table II. This is indicative of a cancelling out of variations one might expect in k_4 by a reverse trend in K_3, or perhaps a virtual constancy of both. In conclusion, we note that our data for the *cis*-$(NH_3)_2en$ complex are in as good agreement with those of Pratt, *et al.*,[9] as can be expected of work done in two different laboratories under different buffer conditions.

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