

# Base Hydrolysis of Octahedral Complexes<sup>1</sup>

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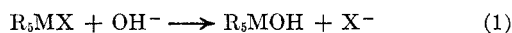
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In the past 20 years, interest in mechanisms of reactions in solution has spread from carbon as a reaction center to include most of the chemical elements. The recent increase of interest in inorganic mechanisms is partly the result of new techniques that are readily available, not the least of which is nuclear magnetic resonance spectrometry, and partly a consequence of the development of organo-transition metal chemistry and its many important ramifications.

The substitution reactions of inorganic complexes, while providing a fruitful source of new geometries, coordination numbers, and electron configurations, have not presented any fundamentally new mechanistic processes. Indeed it is surprising how limited is the range of behavior encountered. Thus, with very few exceptions, four-coordinate planar complexes undergo substitution by way of a five-coordinate trigonal-bipyramidal intermediate (an associative process). As a rule, octahedral six-coordinate complexes undergo substitution at rates that are not particularly sensitive to the nature of the entering group and, once pre-substitution equilibria have been taken into account, are independent of its concentration.

This behavior is typical of mechanisms in which the direct bonding of the entering group does not commence until after the rate-determining transition state has been passed. In certain cases where there is direct kinetic or stereochemical evidence for an intermediate of lower coordination number, a truly dissociative, "D" mechanism can be assigned, but in many situations such a species does not live long enough to equilibrate with its environment and the substitution is a dissociative interchange,  $I_d$ .<sup>2</sup>

One type of substitution that appears to contravene these rules is the base hydrolysis reaction, a process represented stoichiometrically as eq 1, and which, in



certain specific cases, obeys a rate law of form 2 and

$$-d[R_5MX]/dt = k[R_5MX][OH^-] \quad (2)$$

takes place at rates that may be many orders of magnitude faster than other substitution processes of the substrate. This reaction is the subject of this Account.

It is likely that this reaction can be generalized to any lyate ion (*i.e.*, the anionic conjugate base of a

protonic solvent) reacting in its appropriate solvent but, apart from a small amount of data for the reaction of methoxide in methanol,<sup>3</sup> little has been done in nonaqueous solvents.<sup>4</sup>

In octahedral complexes, especially those of the elements of the first row of the transition series (Ti → Cu), the spectrum is very sensitive to the nature and the relative arrangement of the groups (ligands) attached to the reaction center, and so it is possible to use visible and ultraviolet spectrophotometry to follow the course of the reaction and identify the intermediates and products. In addition the rates may be measured by monitoring the release of  $X^-$  or the uptake of  $OH^-$ .

Any mechanistic study is incomplete without a description of the stereochemistry of the process. The octahedral geometry provides considerable scope for signposting. A great deal of information can be gained with a single signpost which may be adjacent (*cis*) or opposite (*trans*) to the leaving group, but the use of multidentate ligands (attached to the central atom by more than one donor atom) provides a great deal of extra information because of the potentialities for stereoisomerism. The use of dissymmetric complexes with or without asymmetric sites in the ligand enables optical rotation and circular dichroism to be used to characterize further the relationship between the configurations of starting materials, intermediates, and products.

## Possible Mechanisms

The mechanism of base hydrolysis has been the subject of much controversy in the past. Thus, Ingold, Nyholm, and Tobe<sup>7</sup> assumed, on the basis of the kinetic form, that this was a simple bimolecular substitution at the metal atom, but the absence of similar behavior by other potentially strong nucleophiles casts doubt upon this assignment.

An attempt was made to explain the unique role of the lyate ion in terms of its mobility through the solvation shell of the complex by way of a Grotthuss chain, and some correlations between rate and steric course were proposed.<sup>8</sup> However, even this could not account for the anomalously high reactivity of com-

(3) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

(4) However, the addition of the lyate ion,  $CH_3COO^-$ , retards the solvolysis of *trans*-[Co(en)<sub>2</sub>(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup><sup>5</sup> and the *cis*-*trans* isomerization of [Co(en)<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>,<sup>6</sup> in glacial acetic acid (en = 1,2-diaminoethane).

(5) A. W. Chester, *Chem. Commun.*, 865 (1969).

(6) A. W. Chester, *Inorg. Chem.*, 8, 1584 (1969).

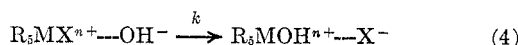
(7) (a) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956); (b) *Nature (London)*, 194, 344 (1962); (c) R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

(8) S. C. Chan and M. L. Tobe, *ibid.*, 4531 (1962).

(1) A useful review of this subject is to be found in F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 177-193 and 261-265.

(2) See C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, pp 7-16, for a more detailed discussion of this nomenclature.

plexes such as *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. Chan<sup>9</sup> then suggested a mechanism in which there was a preequilibrium ion association between hydroxide and the substrate (eq 3 and 4) where the slow interchange step (4) could

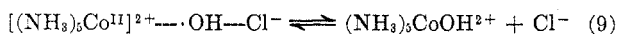
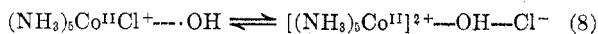
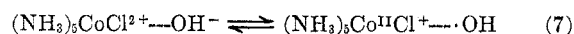
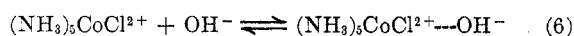


be either associative (S<sub>N</sub>2 IP) or dissociative (S<sub>N</sub>1 IP). This scheme would give the general kinetic expression

$$-d[R_5MX]/dt = \frac{K_{IP}[R_5MX][OH^-]}{1 + K_{IP}[OH^-]} \quad (5)$$

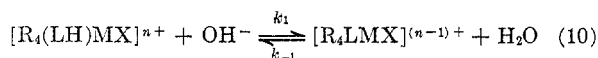
nism is to a great extent equivocal, but Chan claims to have observed departures from first-order behavior and from this has estimated values for  $K_{IP}$ .<sup>10</sup> The fact that  $K_{IP}$  is sensitive only to the charge on the complex is taken as evidence for the ion-pair mechanism. However, other workers<sup>11</sup> have been unable to repeat these observations. Recently,<sup>12</sup> Chan has suggested that the ion-pair and the conjugate-base mechanisms (see below) are similar and differ only in the extent to which the proton is transferred from the complex to the base.

A novel mechanism, proposed by Gillard,<sup>13</sup> assigns to hydroxide the role of reducing agent. It is proposed that an electron is transferred, at least in part, from the substrate to the hydroxide and that the hydroxyl radical generally remains trapped in the vicinity of the labile complex species while the latter rearranges its environment to a more stable form. Thus, for a Co(III) complex



Although this mechanism might provide a plausible explanation of why the Co(III) complexes are particularly sensitive to base hydrolysis, it is characterized by a singular lack of real experimental evidence in its favor.

Probably the closest approach to the correct mechanism is that developed by Basolo and Pearson,<sup>14</sup> who used a suggestion by Garrick<sup>15</sup> that the role of hydroxide was essentially catalytic and that it served to generate a dissociatively reactive entity by removing a proton from the substrate (eq 10–12). This mechanism was initially



(9) S. C. Chan and F. Leh, *J. Chem. Soc. A*, 126 (1966).

(10) S. C. Chan, *ibid.*, 1124 (1966).

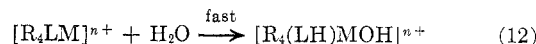
(11) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7**, 174 (1968).

(12) S. C. Chan and O. W. Lau, *Aust. J. Chem.*, **22**, 1851 (1969).

(13) R. D. Gillard, *J. Chem. Soc. A*, 917 (1967).

(14) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Inorg. Nucl. Chem.*, **1**, 341 (1955), and many succeeding papers (see ref 1).

(15) F. J. Garrick, *Nature (London)*, **139**, 507 (1937).



supported by the fact that the characteristic kinetic form of the base hydrolysis reaction was only observed when the complex substrate contained potentially acidic ligands such as H<sub>2</sub>O, NH<sub>3</sub>, ethylenediamine, and other amines. This is generally true even now, in spite of the enormous increase in the number of systems that have been studied.

If the steady-state treatment is applied to eq 10–12 kinetic expression 13 is obtained. If one assumes that

$$-d[R_4(LH)MX]/dt = \frac{k_1k_2[R_4(LH)MX][OH^-]}{k'_{-1} + k_2} \quad (13)$$

the proton-transfer steps (eq 10) are fast compared to the dissociation (eq 11), it is possible to treat eq 10 as a hydrolytic equilibrium with constant  $K$ , and then the full expression 14 obtains. The departure from a first-

$$-d[\text{substrate}]/dt = \frac{k_2K[\text{substrate}][OH^-]}{1 + K[OH^-]} \quad (14)$$

order dependence should occur when the amount of substrate in the form of the conjugate base is no longer an insignificant fraction of the total.

Of all the mechanisms proposed to date, that involving the conjugate base is closest to the truth, although it ought to be borne in mind that base hydrolysis might take place by more than one mechanism. The conjugate base mechanism is readily demonstrated when a proton can be removed from aquo oxygen. Thus, *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)Cl]<sup>2+</sup> undergoes aquation at a rate independent of acid concentration at pH ≤ 2 with  $k_{\text{aq}} = 1.6 \times 10^{-6} \text{ sec}^{-1}$  at 25°. At higher pH a term inversely proportional to [H<sup>+</sup>] (or first order in [OH<sup>-</sup>]) appears<sup>16</sup> and the rate law is of the form shown in eq 14, together with the term involving  $k_{\text{aq}}$ ,  $k_2 = 1.2 \times 10^{-2} \text{ sec}^{-1}$ , and  $K_a = 2.0 \times 10^{-7} M$ . Above pH 8,  $(K_a/K_w)[OH] \gg 1$  and the complex is entirely in the form of the conjugate base, *cis*-[Co(en)<sub>2</sub>(OH)Cl]<sup>+</sup>.

### Conjugate Base Mechanism

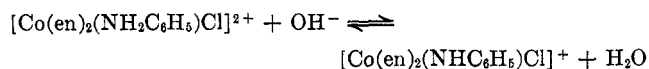
The major part of this Account will examine the validity of an S<sub>N</sub>1cb mechanism in terms of three aspects that can be considered separately, namely, (i) the acid–base behavior of the amine or aquo complex; (ii) the labilizing power of the amido or hydroxo group; and (iii) evidence for a reactive five-coordinate intermediate. The bulk of the systematic information relates to cobalt(III) complexes, and it will be of interest to compare this with the sparse data for octahedral complexes of other transition elements in order to see to what extent the behavior of Co(III) is unique.

**Acid–Base Properties of Amine and Aquo Complexes.**  $pK_a$  of the Conjugate Acid. As a rule base hydrolysis in aqueous solution is specifically catalyzed by hydroxide ions. This would suggest that the proton

(16) S. C. Chan, *J. Chem. Soc.*, 5137 (1963).

transfer steps in eq 10 are fast compared to the dissociation in eq 11. It is possible therefore to consider eq 10 as a preequilibrium with  $k_1/k_{-1} = K = K_a/K_w$ , where  $K_a$  is the acid dissociation constant of the conjugate acid (the complex substrate) and  $K_w$  is the ionic product of water. Although  $K_a$  values for aquo complexes are easily determined by standard methods, attempts to determine  $K_a$  for amine complexes of Co(III) have either been unsuccessful or else have given equivocal answers. Spectrophotometric changes accompanying the addition of strong base to  $[\text{Co}(\text{en})_3]^{3+}$  are better explained in terms of ion association.<sup>17</sup>

The absence of departure of the base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  from first-order dependence, even when  $[\text{OH}^-] = 0.1 \rightarrow 1.0 \text{ M}$ ,<sup>9</sup> suggests that  $K < 0.05$ , but how much less is difficult to say. Erickson<sup>18</sup> has determined  $\text{p}K_a$  values for Pt(II)-amine complexes from the dependence of <sup>1</sup>H nmr chemical shifts of the ligand protons on the concentration of strong alkali. He reports values of  $K$  in the range 0.01–0.20. This method has not been applied to the Co(III) complexes. However, the pH dependence of the hydrolysis of complexes of the type  $[\text{Co}(\text{en})_2(\text{am})\text{Cl}]^{2+}$ , where am = aniline, *m*- or *p*-toluidine, or 3,4-dimethylaniline, has recently been examined.<sup>12,19</sup> The observed second-order rate constants are extremely high for this type of complex,  $2 \times 10^8$  to  $6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  at 0°, and it is suggested that this is due to the potential acidity of the coordinated aniline



An estimate of the value of  $K$  for this equilibrium ( $10^8 \text{ M}^{-1}$ )<sup>12</sup> would suggest a departure from a first-order dependence at pH  $\sim 10$ . Unfortunately the study was not extended to this region.

**Kinetics of Proton Transfer.** In contrast to the dearth of quantitative data about the acidity of amino complexes, a great deal is known about rates of proton exchange in these compounds. Much of the earlier work is fully tabulated and discussed in ref 1 and can be summarized by saying that the rate is very sensitive to the nature of the complex. For identical ligand environments,  $\text{Ir(III)} \ll \text{Rh(III)} < \text{Co(III)} \sim \text{Cr(III)} \ll \text{Ru(III)} < \text{Pt(IV)}$ , and this sequence parallels the anticipated acidity. Insofar as it is possible to make an independent distinction between the variation of the charge and the nature of the ligands, the rate of exchange decreases with decreasing charge. Certainly for a constant central atom there is clear evidence that the different amine protons within the complex exchange at widely differing rates. The original methods, which used changes in infrared spectra, were not able to identify various processes satisfactorily, but the information can be obtained with relative ease using <sup>1</sup>H nmr techniques.

It appears that the nature of the trans ligand is of utmost importance. Thus it is reported that in *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]^{2+}$ <sup>20</sup> the protons on the nitrogen trans to the chloride exchange some 100–300 times faster than the others, irrespective of whether they are on  $\text{NH}_3$  or ethylenediamine. Also, the exchange rate constants for the amine protons in *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$  are  $5.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$  (25°) for those trans to  $\text{NO}_2$  (in the *cis* complex)<sup>21</sup> and  $7.2 \times 10^4$  and  $6.8 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$  (25°) for those cis to the nitro groups (in the *cis* and *trans* complexes, respectively).

There is also apparently a marked *cis* effect as seen in the comparison of *trans*- $[\text{Co}(\text{en})_2\text{F}_2]^+$  ( $k = 1.0 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  at 25°)<sup>21</sup> with *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$  ( $k = 6.8 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}$  at 25°). Examination of the data in the literature indicates a large number of glaring anomalies to any simple attempt at understanding trends and controlling factors, and one must await, with impatience, publication of a systematic and detailed investigation. In spite of suggestions that the proton-exchange rates might be a good measure of the  $\text{p}K_a$  for a series of similar compounds,<sup>1</sup> there is no experimental evidence to support this assumption.

The observation in so many cases that the rate of proton exchange is very much faster than the rate of base hydrolysis is in keeping with the  $\text{S}_{\text{N}}1\text{cb}$  mechanism but does not constitute proof. Indeed, it appeared that until recently attention was deliberately focused on such systems to avoid complications in the study of proton exchange that were accompanied by a parallel base hydrolysis.

A comparison of the rates of proton exchange (relatively slow) and base hydrolysis (very fast) of *trans*- $[\text{Co}(\text{cyclam})\text{Cl}_2]^+$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) indicated that they were similar, and a study of the base hydrolysis indicated considerably more exchange in the product than in the substrate.<sup>22,23</sup> It was shown that this extra exchange did not take place subsequent to the act of base hydrolysis and therefore must have been a consequence of the base hydrolysis itself. This reasonably definitive proof of the involvement of the deprotonated conjugate base also indicates that  $k_{-1}$  and  $k_2$  in eq 10 and 11 were of similar magnitude. The observation of general base catalysis was further evidence for this conclusion.

#### Labilizing Power of the Amido and Hydroxo Ligands.

In view of the low acidity of coordinated amines, the lability of amido conjugate bases must be very large in those cases where base hydrolysis is rapid. It is necessary, therefore, to examine those factors which cause the ligands  $\text{NH}_2^-$  (or  $\text{NHR}^-$  or even  $\text{NR}_2^-$ ) and  $\text{OH}^-$  to be so much more labilizing than their conjugate acids  $\text{NH}_3$  ( $\text{NH}_2\text{R}$ ,  $\text{NHR}_2$ ) and  $\text{H}_2\text{O}$ . The two factors to consider are (a) charge and (b) electron

(17) S. C. Chan, *J. Chem. Soc.*, 2103 (1967).

(18) L. E. Erickson, *J. Amer. Chem. Soc.*, **91**, 8284 (1969).

(19) R. K. Nanda and R. N. Nanda, *Inorg. Chem.*, **8**, 104 (1969).

(20) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **8**, 1595 (1969), report unpublished data of I. I. Olsen.

(21) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).

(22) C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).

(23) C. K. Poon, Ph.D. Thesis, University of London, 1967.

**Table I**  
**Comparison of Rate Constants for Aquation of Some Aquo**  
**Complexes with Those of Their Hydroxo Conjugate Bases**

|  | $k_{25}$ , sec <sup>-1</sup>      | $k_{\text{hyd}}/k_{\text{aq}}$ | Ref |
|--|-----------------------------------|--------------------------------|-----|
| <i>cis</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>               | $1.6 \times 10^{-6}$              | $7.5 \times 10^3$              | 16  |
| <i>cis</i> -[Co(en) <sub>2</sub> (OH)Cl] <sup>+</sup>                              | $1.2 \times 10^{-2}$              |                                | a   |
| <i>cis</i> -[Cr(en) <sub>2</sub> (H <sub>2</sub> O)Cl] <sup>2+</sup>               | $3 \times 10^{-5}$ <sup>e</sup>   | $10^2$                         | b   |
| <i>cis</i> -[Cr(en) <sub>2</sub> (OH)Cl] <sup>+</sup>                              | $3.3 \times 10^{-3}$              |                                | c   |
| <i>cis</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup>   | $3.8 \times 10^{-6}$ <sup>f</sup> | $2.5 \times 10^2$              | d   |
| <i>cis</i> -[Co(en) <sub>2</sub> (OH)H <sub>2</sub> O] <sup>2+</sup>               | $9.3 \times 10^{-4}$              |                                | d   |
| <i>trans</i> -[Co(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>3+</sup> | $5.5 \times 10^{-6}$ <sup>f</sup> | $2.0 \times 10^2$              | d   |
| <i>trans</i> -[Co(en) <sub>2</sub> (OH)H <sub>2</sub> O] <sup>2+</sup>             | $1.2 \times 10^{-3}$              |                                | d   |

<sup>a</sup> M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961). <sup>b</sup> D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962). <sup>c</sup> D. C. Olsen and C. S. Garner, *ibid.*, **2**, 558 (1963). <sup>d</sup> W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1280 (1961). <sup>e</sup> Extrapolated data at 35°. <sup>f</sup> Divided by two for the statistical effect.

displacement, and factor b can to some extent be divided into inductive ( $\sigma$  bonding) and conjugative ( $\pi$  bonding) effects.

**Charge Effect.** Insofar as one can adopt an electrostatic argument, the conjugate base, having one positive charge less than the conjugate acid, will hold its ligands less tightly and be more labile in a dissociative reaction. However, it is not possible to change the charge on a complex without changing other factors such as the nature of the ligands, the nature of the central atom, and the oxidation state of the central atom, and so an independent assessment of the effect of charge is not possible.

Direct comparison of an aquo complex with its hydroxo conjugate base can be made in many cases, and a factor of  $10^2$  (Table I) seems usual. However, rate differences of this magnitude or even greater are commonly found within a series of complexes of the same charge type simply as a result of changing one of the ligands. Therefore electronic displacement effects may be as important, if not more important, than the effect of charge.

It is not possible to make an analogous direct comparison of the rates of corresponding pairs of amine and amido complexes but, by setting an upper limit for  $K_a$ , it is possible to calculate a minimum value for the ratio. Thus, for Co(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup> at 25°,  $\mu = 1.0$ ,  $k_{\text{aq}} = 1.7 \times 10^{-6}$  sec<sup>-1</sup>,  $k_{\text{base hydrolysis}} = 0.26$  M<sup>-1</sup> sec<sup>-1</sup>,<sup>11</sup> and  $K_a/K_w < 0.05$  (since there is no departure from second-order behavior at [OH<sup>-</sup>] = 1.0 M),<sup>11</sup> and so the ratio of the rates of aquation of [Co(NH<sub>3</sub>)<sub>4</sub>-NH<sub>2</sub>Cl] and [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> ( $k_{\text{amido}}/k_{\text{amine}}$ ) must be greater than  $10^6$ . Such an effect is quite common in the reactions of the cobalt(III)-amine complexes and is far too large to be accounted for by charge differences alone.

**Electron Displacement Effects.** The sensitivity of the rate of reaction of octahedral complexes to the nature of the "nonparticipating" ligands is often quite marked,

either as a "trans effect" or often as an effect that does not greatly depend upon the relative positions of the ligands concerned. The effect has been documented most systematically for the aquation reactions of cobalt(III) complexes. In 1956 both Ingold and Ašperger<sup>24</sup> and Basolo and Pearson<sup>25</sup> separately attempted to rationalize the effects in terms of the electron displacement properties of these ligands and in particular invoked conjugative or  $\pi$ -bonding effects. Indeed it was specifically assumed that, in order to assign a direction to the electron displacement, a conjugative effect was more important than an inductive effect. Ligands which could be formulated as potential  $\pi$  donors were said to labilize by a combination of electron repulsion in the ground state and  $\pi$ -bonded stabilization of the five-coordinate intermediate. This type of labilizing effect was associated with stereochemical change when Co(III) complexes were involved. It was therefore suggested that the labilizing power of the amido group in the conjugate base was a consequence of its  $\pi$ -bonding ability<sup>25,26</sup> and that the labilizing sequence should be NH<sub>2</sub> > OH > Cl.

The observation that base hydrolysis of cobalt(III)-amines generally occurs with considerable stereochemical change was considered to be in accord with this proposal since the  $\pi$ -bonding stabilization would be most effective when the amido group occupied an equatorial position in a trigonal-bipyramidal five-coordinate species. (See Figure 1.) However, the importance of this type of interaction has been questioned recently. An essentially dissociative mechanism has been assigned to the aquation of complexes of the type [M(N<sub>4</sub>)ACl]<sup>n+</sup> where M is a trivalent metal (Cr, Co, Rh) and N<sub>4</sub> represents four nitrogen donors which may come from four monodentate, two bidentate, or one quadridentate ligand.<sup>27</sup> It has been suggested that, in the trans complexes, the trigonal-bipyramidal intermediate is characterized by a much higher entropy of activation ( $\Delta S^\ddagger = +5 \rightarrow +15$  cal deg<sup>-1</sup> mol<sup>-1</sup>) than the square-pyramidal form ( $\Delta S^\ddagger = -10 \rightarrow -5$  cal deg<sup>-1</sup> mol<sup>-1</sup>). It was also observed that stereoretentive multidentate nitrogen donors readily prevent stereochemical change in complexes where it would otherwise exist and the entropy of activation decreases accordingly. However, the prevention of steric change does not unduly affect the labilizing power of ligands such as OH or Cl, and so it was concluded that the  $\pi$ -bonding effect was not the major cause of the trans labilizing power of these ligands, although it might make a contribution. It is noteworthy that these stereoretentive ligands can cause their Co(III) complexes to undergo base hydrolysis with retention of configuration without decreasing reactivity (see below).

Buckingham, *et al.*,<sup>20</sup> have examined the problem of  $\pi$ -bonding stabilization with a very elegantly chosen

(24) S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

(25) R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 4878 (1956).

(26) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature (London)*, **187**, 477 (1960).

(27) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

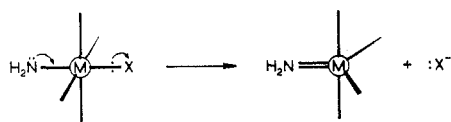


Figure 1.

ligand system. The complex  $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$  (trenen = 1,8-diamino-3-(2-ethylamino)-3,6-diazaoctane) possesses an asymmetric nitrogen trans to the chlorine (in the isomer examined; Figure 2), and it was resolved into optically active enantiomers.  $^1\text{H}$  nmr studies indicated that the proton on this nitrogen exchanged far more rapidly than the others in the complex, and it was suggested (but not proved) that this proton was lost in forming the conjugate base. A study of the optical activity changes associated with base hydrolysis indicated unambiguously that, once background racemization in the chloro substrate and hydroxo product had been accounted for, *no racemization could be detected as a direct consequence of the act of base hydrolysis*. The inference therefore is that the amido nitrogen atom does not adopt a planar configuration at any stage during base hydrolysis and that  $\pi$  bonding is therefore unimportant. It is suggested that the labilizing effect operates through the N-Co  $\sigma$  bond. However, although the protons on the asymmetric nitrogen are exchanged most readily, it is not necessarily this one that produced the labilizing effect. Indeed it has been strongly suggested (see below) that a *cis*-amido group is necessary for effective hydrolysis.<sup>27a</sup>

A far less complete and definitive study of the base hydrolysis of  $[\text{Co}(2,3,2\text{-tet})\text{Cl}_2]^+$  (2,3,2-tet = 1,9-diamino-3,7-diazanonane) indicates that the  $\beta$ -*RR,SS*<sup>28</sup> isomer is converted to *trans*-(*RS*)- $[\text{Co}(2,3,2\text{-tet})\text{-(OH)}_2]^+$ ,<sup>30</sup> the nitrogen inversion and stereochemical change taking place synchronously with the first act of base hydrolysis. A planar amido nitrogen in a trigonal-bipyramidal intermediate is indicated in this case (Figure 3). This differs from the case above in that the nitrogen undergoing inversion could be *cis* to the leaving group. It is clear that a great deal more information is required before the role of  $\pi$  bonding can be correctly assessed.

**Evidence for Reactive Five-Coordination Intermediate.** *Trapping of Intermediate.* In assigning a dissociative mechanism to the aquation of the conjugate base it is necessary to demonstrate a reactive intermediate of lower coordination number which may, if its lifetime is adequate, discriminate between the various

(27a) NOTE ADDED IN PROOF.  $[\text{Co}(\text{N-CH}_3\text{-trenen})\text{Cl}]^{2+}$  (N-CH<sub>3</sub>-trenen = 1,8-diamino-3-(2-ethylamino)-6-methyl-3,6-diazaoctane), which has no amine protons trans to the leaving group, undergoes base hydrolysis some 16 times slower than the trenen analog: A. D. Buckingham and A. M. Sargeson, private communication, 1970.

(28) The *R,S* designation describes the configurations of the coordinated secondary nitrogens and is based on the sequence rules of Cahn, Ingold, and Prelog.<sup>29</sup> *RR,SS* indicates an unresolved (racemic) mixture of the *RR* and *SS* forms.

(29) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

(30) R. Nithyananthan, Ph.D. Thesis, University of London, 1970.

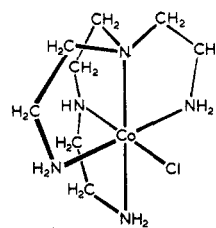
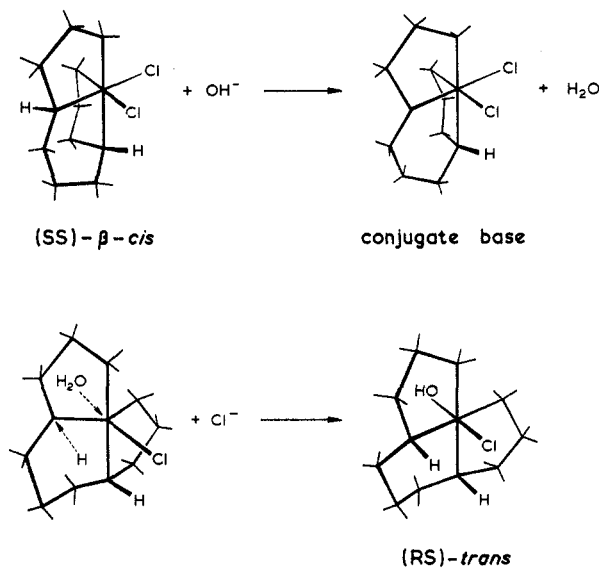
Figure 2. *sym*- $[\text{Co}(\text{trenen})\text{Cl}]^{2+}$ .

Figure 3. A scheme for the conversion of (*SS*)- $\beta$ -*cis*- $[\text{Co}(2,3,2\text{-tet})\text{Cl}_2]^+$  to (*RS*)-*trans*- $[\text{Co}(2,3,2\text{-tet})\text{OHCl}]^+$  by way of a conjugate base with a planar amido nitrogen.

reagents available. Furthermore, this discrimination should be independent of the way in which the intermediate was generated. At first, when it was believed that water was far more efficient than other nucleophiles for trapping the intermediate, two approaches were adopted. Pearson, *et al.*,<sup>31</sup> by using a less voracious solvent, dimethyl sulfoxide, showed that the replacement of Cl in *cis*- $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]^+$  by  $\text{NO}_2^-$ ,  $\text{N}_3^-$ , or NCS was base catalyzed at a rate that was independent of the nature and concentration of the anionic reagent. Similar behavior has been demonstrated for the analogous Rh(III) complexes.<sup>32</sup> In these cases, competition by the solvent for the five-coordinate intermediate was negligible, and in the latter case some direct competition between  $\text{H}_2\text{O}$  and anionic ligands was also observed in aqueous solution. Taube and Green<sup>33</sup> examined the discrimination of the intermediate for  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  and showed that, in the base hydrolysis of  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ , the  $^{18}\text{O}$  enrichment factor in the  $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$  product was independent of the nature of X (X = Cl, Br, I) and equal to 1.006, suggesting that  $\text{H}_2\text{O}$  was the entering species and there was no discrimination. It did not reflect the isotopic enrichment in the hydroxide ion (1.04), an effect that might be expected if  $\text{OH}^-$  were the entering group,

(31) R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Amer. Chem. Soc.*, **82**, 4434 (1960).

(32) A. Panunzi and F. Basolo, *Inorg. Chim. Acta*, **1**, 223 (1967).

(33) H. Taube and M. Green, *Inorg. Chem.*, **2**, 948 (1963).

and this was taken as strong evidence against a simple  $S_N2$  reaction.

With suitable care it is possible to demonstrate competition between water and other anionic reagents for the reactive five-coordinate intermediate, and, in suitably signposted substrates, to determine the relative effectiveness and the steric course of the capture of anionic reagents in a quantitative fashion.<sup>34-36</sup> These and similar studies are extremely important in establishing the dissociative mechanism because, having shown that entry of a ligand that is not solvent cannot take place before or after the act of base hydrolysis, it follows that the ligand can only enter by trapping the reactive species of lower coordination number that is formed in the act of base hydrolysis.

*Shape of the Intermediate.* A common feature of the base hydrolysis of fairly simple cobalt(III)-amine complexes is the extensive amounts of stereochemical change. A selection of reactions of known steric course is collected in Table II. It appears that, once one moves away from  $[\text{Co}(\text{en})_2\text{XY}]^{n+}$  systems, complete retention of configuration becomes much more common.

It has been shown that the steric course of the base hydrolysis of complexes of the type  $[\text{Co}(\text{en})_2\text{AX}]^{n+}$  is independent of the nature of X.<sup>35-37</sup> This would tend to support a dissociative mechanism provided the nature of ligand X did not have an enormous effect upon the distribution of the different possible five-coordinate intermediates.

The steric change has been ascribed to the formation of a trigonal-bipyramidal intermediate, and Basolo and Pearson<sup>38</sup> have attempted to rationalize the observed steric courses for cis and trans isomeric pairs of  $[\text{Co}(\text{en})_2\text{ACl}]^{n+}$  cations in terms of two possible intermediates, each with the amido group in the trigonal plane and one with group A in the trigonal plane as well (see Figure 4). It should be noted that the trans isomer can only generate A and its enantiomer in equal quantities, whereas the cis complex can generate intermediate B and that enantiomer of A that retains the original configuration of the substrate. The three forms of B differ in the location of the amido group, and only one gives an equal chance for the formation of D and L product.

Green<sup>39</sup> has suggested that the factor which determines the ratio in which the A and B intermediates are formed is the donor ability of ligand A. The stronger the donor, the more likely is ligand A to be found in the trigonal plane.

Further insight has been thrown on the problem by the use of  $^{15}\text{NH}_3$  to signpost the simple  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  cation trans to Cl.<sup>35</sup> The product composition (40%

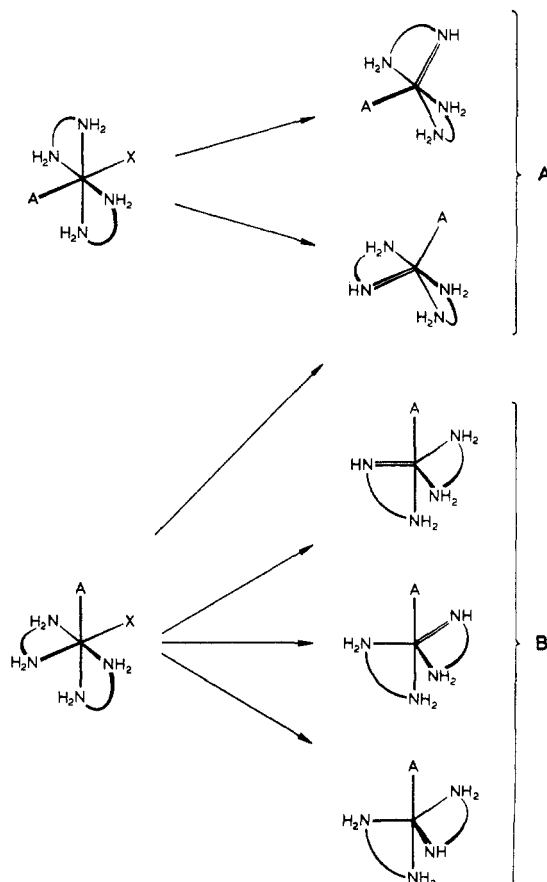


Figure 4. Possible trigonal-bipyramidal intermediates derived from the dissociation of the conjugate bases of *trans*- and *cis*- $[\text{Co}(\text{en})_2\text{AX}]^{2+}$  assuming that the amido linkage must be in the trigonal plane. A-type intermediates also have ligand A in the trigonal plane.

*cis*- and 60% *trans*- $[\text{Co}(\text{NH}_3)_4(^{15}\text{NH}_3)\text{OH}]^{2+}$ ) is far from any statistically determined amount and indicates that the conjugate base neither changes the amido group by proton exchange nor loses it by proton capture before the water enters. It is not easy to explain these results in terms of a trigonal bipyramid with the amido group, derived from the amine trans to the chlorine, in the trigonal plane. Buckingham, Olsen, and Sargeson<sup>35</sup> have attempted to explain the results in terms of a distorted square pyramid (Figure 5), but Nordmeyer<sup>40</sup> has proposed that these and many other steric courses can be explained if it is assumed that the labile conjugate base was the one with the amido group cis to the leaving group, in spite of the fact that the trans amine protons are much more labile. This postulate also allows one to understand why *cis*- $[\text{Co}(\text{en})_2\text{AX}]^{n+}$  complexes, with an amino group trans to X, are never much more reactive than their trans isomers and, on many occasions, are less reactive.

At this time, it is dangerous to become too deeply involved in discussion of the relative merits of the various intermediates that have been proposed because there are probably no more independent facts than there are variables. It is also abundantly clear that when the central metal is not Co(III) there is no

(34) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88**, 5443 (1966).

(35) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **90**, 6539 (1968).

(36) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **90**, 6654 (1968).

(37) R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, **4**, 433 (1965).

(38) F. Basolo and R. G. Pearson, *ibid.*, **4**, 1522 (1965).

(39) M. Green, *J. Chem. Soc. A*, 762 (1967).

(40) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).

**Table II**  
Steric Course of Some Base Hydrolysis Reactions of Tervalent Metal Complexes

| M  | N <sub>4</sub>     | A  | % trans   | % cis                             | Ref    |       |
|----|--------------------|--|---|-----------------------------------|--------|-------|
|    |                    |  | (a) [Co(NH <sub>3</sub> ) <sub>4</sub> ACl] <sup>2+</sup> |                                   |        |       |
|    |                    | <i>trans</i> - <sup>16</sup> NH <sub>3</sub> | 60  | 40                                | 39     |       |
|    |                    |  | (b) [M(en) <sub>2</sub> ACl] <sup>n+</sup>                |                                   |        |       |
| Co |                    | <i>cis</i> -OH                               | <3  | 61 ± 3                            | 36 ± 3 | 8     |
|    |                    | <i>trans</i> -OH                             | 6 ± 2   | 94 ± 2                            |        | 8     |
|    |                    | <i>cis</i> -Cl                               | 63 ± 2  | 21 ± 2                            | 16 ± 2 | 8     |
|    |                    | <i>trans</i> -Cl                             | >95   | <5                                |        | 8     |
|    |                    | <i>cis</i> -Br                               | 60 ± 5  | 40 ± 5                            |        | 8     |
|    |                    | <i>trans</i> -Br                             | >95   | <5                                |        | 8     |
|    |                    | <i>cis</i> -NCS                              | 20 ± 2  | 56 ± 4                            | 24 ± 4 | 7a, c |
|    |                    | <i>trans</i> -NCS                            | 24 ± 2  | 76 ± 2                            |        | 7a    |
|    |                    | <i>cis</i> -N <sub>3</sub>                   | 55 ± 2  | 45 ± 2                            |        | d     |
|    |                    | <i>trans</i> -N <sub>3</sub>                 | 90 ± 2  | 10 ± 2                            |        | d     |
|    |                    | <i>cis</i> -NH <sub>3</sub>                  | 22 ± 2  | 63 ± 2                            | 15 ± 2 | 36    |
|    |                    | <i>trans</i> -NH <sub>3</sub>                | 36 ± 2  | 64 ± 2                            |        | 36    |
|    |                    | <i>cis</i> -NO <sub>2</sub>                  | 33 ± 2  | 46 ± 2                            | 23 ± 2 | 24    |
|    |                    | <i>trans</i> -NO <sub>2</sub>                | 94 ± 2  | 6 ± 2                             |        | 24    |
|    |                    | <i>trans</i> -CN                             | 100   | 0                                 |        | e     |
| Ru |                    | <i>cis</i> -Cl                               | 0   | 100                               | 0      | f     |
|    |                    | <i>cis</i> -OH                               | 0   | 100                               | 0      | f     |
| Rh |                    | <i>cis</i> -Cl                               | 0   | 100                               | 0      | g     |
| M  | N <sub>4</sub>     | A  | % trans   | % cis                             | Ref    |       |
|    |                    |  | (c) [M(N <sub>4</sub> )ACl] <sup>n+</sup>                 |                                   |        |       |
| Co | trien <sup>b</sup> | <i>D-α-cis</i> -Cl                           | Not reported  | mainly <i>D-α</i>                 | h      |       |
|    | trien              | <i>D-α-cis</i> -OH                           | Not reported  | some <i>D-α</i> mainly <i>L-β</i> | h      |       |
|    | trien              | <i>L-β-cis</i> -Cl                           | Not reported  | mainly <i>L-β</i>                 | i      |       |
|    | trien              | <i>L-β-cis</i> -OH                           | Not reported  | mainly <i>L-β</i>                 | i      |       |
|    | 2,3,2-tet          | <i>trans</i> -Cl ( <i>RS</i> )               | 100 ( <i>RS</i> )   | 0                                 | 30     |       |
|    | 2,3,2-tet          | <i>trans</i> -Cl ( <i>RR,SS</i> )            | 100 ( <i>RS</i> )   | 0                                 | 30     |       |
|    | 2,3,2-tet          | <i>β-cis</i> -Cl ( <i>RR,SS</i> )            | 100 ( <i>RS</i> )   | 0                                 | 30     |       |
|    | 2,3,2-tet          | <i>β-cis</i> -OH ( <i>RR,SS</i> )            | 0   | 100 <i>β-cis</i> ( <i>RR,SS</i> ) | 30     |       |
|    | cyclam             | <i>cis</i> -Cl                               | 0   | 100                               | 23     |       |
|    | cyclam             | <i>trans</i> -Cl                             | 100   | 0                                 | 23     |       |
|    | cyclam             | <i>cis</i> -OH                               | 0   | 100                               | 23     |       |
|    | cyclam             | <i>trans</i> -OH                             | 100   | 0                                 | 23     |       |
| Cr | cyclam             | <i>cis</i> -Cl                               | 0   | 100                               | j      |       |
|    | cyclam             | <i>trans</i> -Cl                             | 100   | 0                                 | j      |       |
|    | cyclam             | <i>cis</i> -OH                               | 0   | 100                               | j      |       |
|    | cyclam             | <i>trans</i> -OH                             | 100   | 0                                 | j      |       |
| Rh | cyclam             | <i>cis</i> -Cl                               | 0   | 100                               | k      |       |
|    | cyclam             | <i>trans</i> -Cl                             | 100   | 0                                 | k      |       |
|    | cyclam             | <i>cis</i> -OH                               | 0   | 100                               | k      |       |
|    | cyclam             | <i>trans</i> -OH                             | 100   | 0                                 | k      |       |

<sup>a</sup> O = same configuration as starting material, I = inverted configuration. <sup>b</sup> trien = 1,8-diamino-3,6-diazaoctane (triethylenetetramine). <sup>c</sup> M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960). <sup>d</sup> V. Ricevuto, unpublished results. Previous work has been repeated in view of errors in the original spectra. <sup>e</sup> S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 514 (1963). <sup>f</sup> J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **8**, 2124 (1969). <sup>g</sup> S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 1741 (1963). <sup>h</sup> E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *ibid.*, **87**, 4458 (1965). <sup>i</sup> E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120 (1966). <sup>j</sup> J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta.*, **4**, 109 (1970). <sup>k</sup> W. R. Fitzgerald, unpublished results.

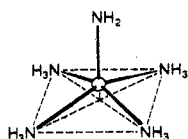


Figure 5. A square-pyramidal five-coordinate intermediate with axial =NH<sub>2</sub>. It has been suggested that the incoming group might attack from either side of the basal plane.

stereochemical change and the reactivity is controlled by the nature of the *trans* ligand. A square-pyramidal intermediate, if indeed the reaction is dissociative, is indicated here.

The steric course of entry of anions is quite different from that of the entry of water. Inadequate data are available for a comprehensive discussion. However, it is likely that, as in substitution in nonaqueous solvents, ion association plays a very important part in determining competition effects and the steric course.

#### Rates and Activation Parameters of Base Hydrolysis

A selection of second-order rate constants and activation parameters for base-catalyzed metal-ligand bond fission is given in Table III. The data for the Co(III) complexes are extensive and are only given in part.

Table III  
Rates and Activation Parameters for the Base Hydrolysis of  $[M(N_4)ACl]^{n+}$

| M  | N <sub>4</sub>  | A   | K <sub>2</sub> (0°), M <sup>-1</sup> sec <sup>-1</sup> | ΔH <sup>‡</sup> , kcal mol <sup>-1</sup> | ΔS <sup>‡</sup> , cal deg <sup>-1</sup> mol <sup>-1</sup> | Ref |
|----|-----------------|---|--|--|---|-----|
| Co | en <sub>2</sub> | trans-OH  | 0.017  | 22                                       | +17   | 8   |
| Co | en <sub>2</sub> | trans-Cl  | 85   | 23                                       | +35   | 8   |
| Co | en <sub>2</sub> | trans-Br  | 110  | 24                                       | +42   | 8   |
| Co | en <sub>2</sub> | trans-NCS   | 0.35   | 23                                       | +27   | 7a  |
| Co | en <sub>2</sub> | trans-NH <sub>3</sub>                             | 1.25   |  |   | 7c  |
| Co | en <sub>2</sub> | trans-N <sub>3</sub>                              | 0.41   |  |   | a   |
| Co | en <sub>2</sub> | trans-NO <sub>2</sub>                             | 0.080  | 24                                       | +26   | 24  |
| Co | en <sub>2</sub> | trans-OH  | 0.13   | 23                                       | +22   | b   |
| Co | en <sub>2</sub> | cis-OH  | 0.37   | 22                                       | +21   | 8   |
| Co | en <sub>2</sub> | cis-Cl  | 15.1   | 24                                       | +37   | 8   |
| Co | en <sub>2</sub> | cis-Br  | 23   | 22                                       | +31   | 8   |
| Co | en <sub>2</sub> | cis-NCS   | 1.40   |  |   | 7a  |
| Co | en <sub>2</sub> | cis-NH <sub>3</sub>                               | 0.50   |  |   | 7c  |
| Co | en <sub>2</sub> | cis-NH <sub>2</sub> CH <sub>3</sub>               | 0.17   | 23                                       | +26   | c   |
| Co | en <sub>2</sub> | cis-NH <sub>2</sub> C <sub>2</sub> H <sub>5</sub> | 0.16   | 23                                       | +26   | c   |
| Co | en <sub>2</sub> | cis-py  | 1600 <sup>k</sup>                                      |  |   | d   |
| Co | en <sub>2</sub> | cis-(4-CH <sub>3</sub> -py)                       | 1300 <sup>k</sup>                                      |  |   | d   |
| Co | en <sub>2</sub> | cis-(3-CH <sub>3</sub> -py)                       | 1300 <sup>k</sup>                                      |  |   | d   |
| Co | en <sub>2</sub> | cis-(4-CH <sub>3</sub> O-py)                      | 1200 <sup>k</sup>                                      |  |   | d   |
| Co | en <sub>3</sub> | cis-N <sub>3</sub>                                | 0.17   |  |   | a   |
| Co | en <sub>2</sub> | cis-NO <sub>2</sub>                               | 0.32   | 23                                       | +19   | 24  |
| Cr | en <sub>2</sub> | trans-Cl  | 0.037 <sup>k</sup>                                     |  |   | e   |
| Cr | en <sub>2</sub> | cis-Cl  | 0.027 <sup>k</sup>                                     |  |   | e   |
| Cr | en <sub>2</sub> | cis-OH  | 2.2 <sup>k</sup>                                       |  |   | f   |
| Cr | en <sub>2</sub> | trans-OH  | 0.3 <sup>k</sup>                                       |  |   | f   |
| Ru | en <sub>2</sub> | cis-OH  | 0.5 <sup>l</sup>                                       |  |   | g   |
| Rh | en <sub>2</sub> | cis-Cl  | 0.002 <sup>k</sup>                                     |  |   | h   |
| Cr | cyclam          | trans-Cl  | 1.6 <sup>m</sup>                                       |  |   | i   |
| Cr | cyclam          | cis-Cl  | 8.2 <sup>m</sup>                                       |  |   | i   |
| Cr | cyclam          | trans-OH  | 0.011 <sup>m</sup>                                     |  |   | i   |
| Cr | cyclam          | cis-OH  | 0.064 <sup>n</sup>                                     |  |   | i   |
| Rh | cyclam          | trans-Cl  | 2 × 10 <sup>-9</sup>                                   | 30                                       | +10   | j   |
| Rh | cyclam          | cis-Cl  | 7.2 × 10 <sup>-4</sup>                                 | 24                                       | +15   | j   |
| Rh | cyclam          | trans-OH  | 6 × 10 <sup>-12</sup>                                  | 38                                       | +28   | j   |

<sup>a</sup> P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960). <sup>b</sup> See Table II, footnote e. <sup>c</sup> S. C. Chan and F. Leh, *J. Chem. Soc. A.* 129 (1966). <sup>d</sup> F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, **78**, 2676 (1956). <sup>e</sup> R. G. Pearson, R. A. Munson, and F. Basolo, *ibid.*, **80**, 504 (1958). <sup>f</sup> See Table I, footnote c. <sup>g</sup> See Table II, footnote f. <sup>h</sup> See Table II, footnote g, <sup>i</sup> E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, **9**, 1781 (1970). <sup>j</sup> See Table II, footnote k. <sup>k</sup> 25°. <sup>l</sup> 24.6°. <sup>m</sup> 26.3°. <sup>n</sup> 25.5°.

As a rule, the rate is sensitive to the nature of the amine but much less sensitive to the nature of other nonparticipating ligands. Some marked exceptions will be discussed separately.

A characteristic feature of the base hydrolysis reaction is the large positive entropy of activation which is found throughout. Indeed, for the  $[Co(en)_2AX]^{n+}$  series, the variation in rate comes largely from differences in the entropy of activation (Table III). The usual lack of dependence on the nature of ligand A (in contrast to acid hydrolysis) is in keeping with the conjugate base mechanism since factors which would increase  $K_a$  (e.g., electron withdrawal) would serve to decrease the ease with which the conjugate base dissociates, and *vice versa*.

Of the cobalt(III) complexes studied, two sorts are unusually reactive. They are (i) the cations of the type  $cis-[Co(en)_2(py)XCl]^{2+}$  (Table III) and (ii) the dichloro and dibromo complexes,  $[Co(N_4)X_2]^+$ , especially the trans isomers (Table IV).

The pyridine complexes present a puzzle because in acid hydrolysis ammonia, primary amines, and hetero-

Table IV  
Rate Constants for the Base Hydrolysis of Some Dichlorotetraamminecobalt(III) Complexes

|   | k <sub>2</sub> (25°) M <sup>-1</sup> sec <sup>-1</sup> | Ref |
|---|--|-----|
| cis-[Co(en) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>                                   | 1,000  | 8   |
| β-cis-[Co(trien)Cl <sub>2</sub> ] <sup>+</sup>  | 200,000  | b   |
| trans-[Co(en) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup>                                 | 3,000  | 8   |
| trans-[Co(N-CH <sub>3</sub> -en) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> <sup>a</sup> | 11,000   | b   |
| trans-[Co(cyclam)Cl <sub>2</sub> ] <sup>+</sup>   | 67,000   | 23  |
| trans-(RS)-[Co(2,3,2-tet)Cl <sub>2</sub> ] <sup>+</sup>                                   | 61,000   | 30  |

<sup>a</sup> N-CH<sub>3</sub>-en = N-methylethylenediamine. <sup>b</sup> R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 709 (1956).

cyclic amines have very similar labilizing effects, but in basic solution the heterocyclic ligands labilize some 10<sup>2</sup> to 10<sup>3</sup> times more effectively than the other amines. It is possible that the heterocyclic nitrogen can function as π-electron pair donor by addition of the hydroxide at the α-carbon atom (Figure 6), but no evidence is available to support or refute this suggestion. A study of the trans isomer would throw light on this problem but so far, in spite of much effort, we have been unable to prepare it.



**Table V**  
**Comparison of the Activation Parameters of**  
**Base Hydrolysis of  $\text{trans-}[\text{Co}(\text{cyclam})\text{Cl}_2]^+$  with**  
**Those for Proton Exchange in Other Systems**

|   | $\Delta H^\ddagger$ ,<br>kcal<br>mol <sup>-1</sup> | $\Delta S^\ddagger$ ,<br>cal deg <sup>-1</sup><br>mol <sup>-1</sup> | Ref |
|---|--|---|-----|
| $\text{trans-}[\text{Co}(\text{cyclam})\text{Cl}_2]^+$ (base hydrolysis)                  | 13.7   | +12   | 23  |
| $\text{trans,trans-}[\text{Co}(\text{N-CH}_3\text{-en})_2(\text{NO}_2)_2]^+$ (D exchange) | 15.9   | +15   | b   |
| $[\text{Co}(\text{NH}_3)_4\text{sarc}]^{2+}$ (H exchange)                                 | 13.5   | +21   | c   |
| $[\text{Co}(\text{NH}_3)_4(\text{N-CH}_3\text{-en})]^{2+}$ (D exchange)                   | 15.4   | +24   | d   |
| $[\text{Co}(\text{NH}_3)_4(\text{N-CH}_3\text{-en})]^{2+}$ (H exchange)                   | 13.5   | +21   | d   |

<sup>a</sup> sarc = *N*-methylaminoacetate (sarcosinate). <sup>b</sup> D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 3428 (1967). <sup>c</sup> B. Halpern, A. M. Sargeson, and K. R. Turnbull, *ibid.*, **88**, 4630 (1966). <sup>d</sup> D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).

The high reactivity of the dichloro complexes is especially marked when they contain secondary amine ligands, but it would appear that the reactivity is due more to an unusually high lability of the conjugate base than to the acidity of the conjugate acid. Thus it has been shown that the conjugate base derived from  $\text{trans-}[\text{Co}(\text{cyclam})\text{Cl}_2]^+$  expels its chloride as fast as, if not faster than, the rate at which it is reprotonated.<sup>22</sup> A point has almost been reached in which deprotonation of the complex is the rate-determining step for base hydrolysis. Significantly, the enthalpy and entropy of activation for the base hydrolysis of this complex are both anomalous but compare very closely with values obtained from a direct study of proton exchange (Table V). It is not clear why such a conjugate base is so labile. It could be simply that this is a nonelectrolyte species with two potentially labile ligands. More research is called for.

When the metal is changed from Co(III), the pattern changes drastically. Cr(III) resembles Co(III) insofar as the rates are not particularly sensitive to the position of the ligands, but the reactivity is considerably reduced. Ru(III) complexes are very sensitive to base hydrolysis but resemble those of Rh(III) (and possibly Pt(IV) were it not for the fact that these undergo reduction or redox-catalyzed substitution<sup>41,42</sup>) in the sense that trans labilization now dominates and the reactions occur with complete retention of configuration. In the case of Rh(III), the absence of a trans amido group makes the trans diacido complex much less reactive than the cis. Often the base hydrolysis contribution cannot

(41) R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 59 (1962).

(42) C. E. Skinner and M. M. Jones, *J. Amer. Chem. Soc.*, **91**, 1984 (1969).

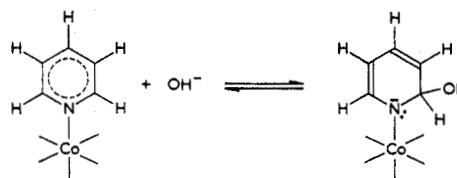


Figure 6. A suggested explanation for the unusual lability of  $[\text{Co}(\text{en})_2(\text{py})\text{Cl}]^{2+}$  toward base hydrolysis.

be observed through the background aquation. Many other examples for Rh(III) and even Pt(IV) have been noted,<sup>43</sup> and the same appears to be true for Ru(III).<sup>44</sup>

### Conclusion

It seems reasonably clear that the normal mechanism for the base hydrolysis of octahedral cobalt(III)-ammine and -amine complexes involves an  $\text{SN}1\text{cb}$  mechanism in which the five-coordinated intermediate takes on trigonal-bipyramidal geometry. This is in keeping with the observation that base hydrolysis is often accompanied by stereochemical change and that cis and trans isomers do not differ enormously in their reactivity. This can be understood if the main labilizing effect occurs in the transition state since in a trigonal bipyramid the symmetry distinction between ligands that were originally trans or cis to the leaving group is lost. Although the sensitivity toward base hydrolysis is less for Cr(III) compounds, the absence of a specific trans effect suggests that Cr(III) too might generate a trigonal-bipyramidal intermediate. In the case of the second- and third-row transition elements the behavior is markedly different. Apart from Ru(III) the sensitivity to base is low, but the dissociative character of base hydrolysis has been demonstrated for Rh(III).<sup>32</sup> Stereochemical change is no longer observed, and the overwhelming influence of the ligand trans to the leaving group suggests strongly that any five-coordinate intermediate is square pyramidal.

This is not necessarily a property of second- and third-row elements because the same behavior can be induced in Co(III) by a suitable choice of ligand. Thus  $\text{trans-}[\text{Co}(\text{NH}_3)_4\text{SO}_3\text{X}]$ ,  $[\text{Co}(\text{CN})_6\text{X}]^{3-}$ , and certain cobaloximes and cobalamines will take on a strong trans-effect behavior, substitute with complete retention of configuration, and lose much of their sensitivity to base hydrolysis. It is clear that, in spite of the large amount of significant work that has been published on the base hydrolysis of octahedral complexes, there are many fundamental questions that remain unanswered, especially in connection with the difference between Co(III) and the other transition elements.

(43) Reference 1, p 187.

(44) See Table II, footnote f.