

radii, namely,  $C(1)\cdots O(3) = 2.911$  (8) Å. The distances between the different hydrogen-bonded chains are all somewhat larger than this sum.

**Acknowledgment.**—The authors are indebted to Mr. H. Karlsson for his skilful assistance in the prepara-

tion of the crystals and in the X-ray work and to Mrs. M. Hillberg for excellent technical assistance. This work has been supported by grants from the Malmfonden—Swedish Foundation for Scientific Research and Industrial Development, which are hereby gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF ROCHESTER, ROCHESTER, NEW YORK 14627

## The Stereochemistry of Base Hydrolysis of $Co(NH_3)_5X^{2+}$ and $Co(en)_2LX^{n+}$ Ions

By FRANCIS R. NORDMEYER

Received February 17, 1969

The stereochemistry of base hydrolysis of  $Co(NH_3)_5X^{2+}$  and  $Co(en)_2LX^{n+}$  complexes is examined in terms of the  $SN1CB$  mechanism. Stereochemical results reported for the  $[Co(NH_3)_4(^{15}NH_3)X]^{2+}$  complexes support the conclusion that the leaving group,  $X^-$ , leaves from a position *cis* to an amido group to form a trigonal-bipyramidal intermediate and that  $H_2O$  enters the intermediate by the microscopic reverse of this process. It is argued that for the base hydrolysis reactions of  $Co(en)_2LX^{n+}$  complexes only two of a possible four (or three of a possible five where  $L = NH_3$ ) trigonal-bipyramidal intermediates will be important. Assuming that only these two intermediates are important, the retention of optical activity in the base hydrolysis of active *cis*- $Co(en)_2LX^{n+}$  can be predicted from the yield of *trans* product from *cis*- and from *trans*- $Co(en)_2LX^{n+}$ .

A wealth of evidence has been put forward recently to support the conclusion that cobalt(III) complexes of the type  $Co(NH_3)_5X^{2+}$  and  $Co(en)_2LX^{n+}$  undergo base hydrolysis by way of an  $SN1CB$  mechanism involving a five-coordinate intermediate.<sup>1-7</sup> A portion of this evidence involves the observation that the products of base hydrolysis reactions generally possess stereochemistry which is independent of the leaving group,  $X^-$ .<sup>3,5,7</sup> This observation supports the conclusion that the reactions of complexes differing only in their leaving group proceed through a common intermediate or set of intermediates.

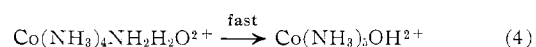
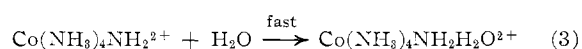
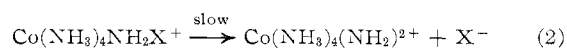
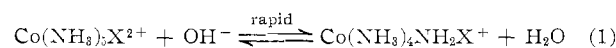
It has been recognized previously that several intermediates may be important for the base hydrolysis of *cis*- $Co(en)_2LX^{n+}$  complexes.<sup>8,9</sup> For reactions in which more than one intermediate is possible, an  $SN1CB$  mechanism does not demand that the stereochemistry of products be independent of leaving group since the leaving group may influence the relative rates of formation of the intermediates which in turn will affect the product distribution. Thus, the observation that the stereochemistry of products is independent of leaving group indicates that not only is the decomposition of the intermediate independent of the leaving group but also its formation is independent of the leaving group. This

being the case, it seems worthwhile to investigate the principles which govern the formation and the decomposition of the five-coordinate intermediate.

The stereochemistry of base hydrolysis of  $Co(en)_2LX^{n+}$  complexes has been found to be compatible with a proposed reaction scheme in which the five-coordinate intermediate has a trigonal-bipyramidal structure.<sup>9</sup> The purpose of this paper is to show that the results of a recent stereochemical investigation of the base hydrolysis of  $Co(NH_3)_4(^{15}NH_3)X^{2+}$  complexes<sup>5</sup> suggest a specific steric course for the formation and decomposition of a trigonal-bipyramidal intermediate. An examination of the reported stereochemistry for reactions of  $Co(en)_2LX^{n+}$  complexes suggests that the same principles apply to these complexes also.

**$Co(NH_3)_5X^{2+}$  Complexes.**—It has recently been reported that base hydrolysis of *trans*- $Co(NH_3)_4(^{15}NH_3)Cl^{2+}$  gives 50% *cis*- and 50% *trans*- $Co(NH_3)_4(^{15}NH_3)OH^{2+}$ .<sup>5</sup> The same distribution of products also results from the base hydrolysis of the bromo- and nitratopentaammine complexes.<sup>5</sup> This result can be explained in terms of a detailed mechanism.

According to the  $SN1CB$  mechanism the following sequence of steps occurs for  $Co(NH_3)_5X^{2+}$



We are concerned with the stereochemistry of the formation (step 2) and decomposition (step 3) of the five-coordinated intermediate.

(1) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Son, Inc., New York, N. Y., 1967, pp 177-193.

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

(3) R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

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

(5) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **89**, 5129 (1967).

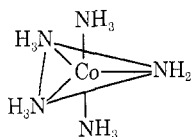
(6) C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).

(7) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).

(8) R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).

(9) R. G. Pearson and F. Basolo, *Inorg. Chem.*, **4**, 1522 (1965).

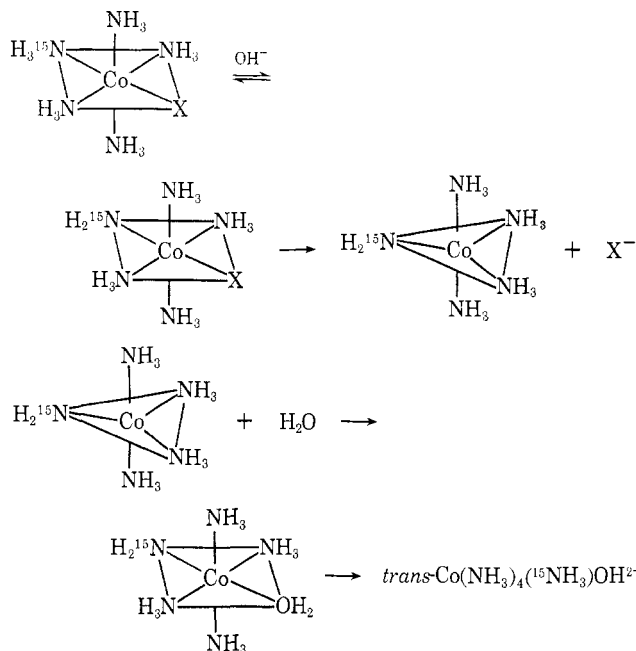
In agreement with previous workers,<sup>9</sup> the structure of the intermediate will be initially taken to be



In this configuration the amido group can stabilize the trigonal bipyramid by donating  $\pi$ -electron density to the Co  $d_{x^2-y^2}$  orbital in the trigonal plane.<sup>8</sup> This intermediate may decompose to an octahedral complex by attack of  $H_2O$  at an edge of the trigonal plane. There are two possibilities for this attack; it may come either adjacent to the amido group or opposed to the amido group. Also, the intermediate was formed from an octahedral complex by a reverse of this process. Thus the ligand  $X^-$  may have left the incipient trigonal plane either from a position adjacent to the amido group or from a position opposed to it. There are two ways in which step 2 can occur and there are two ways in which step 3 can occur. In total then, there are four possible paths for this reaction.

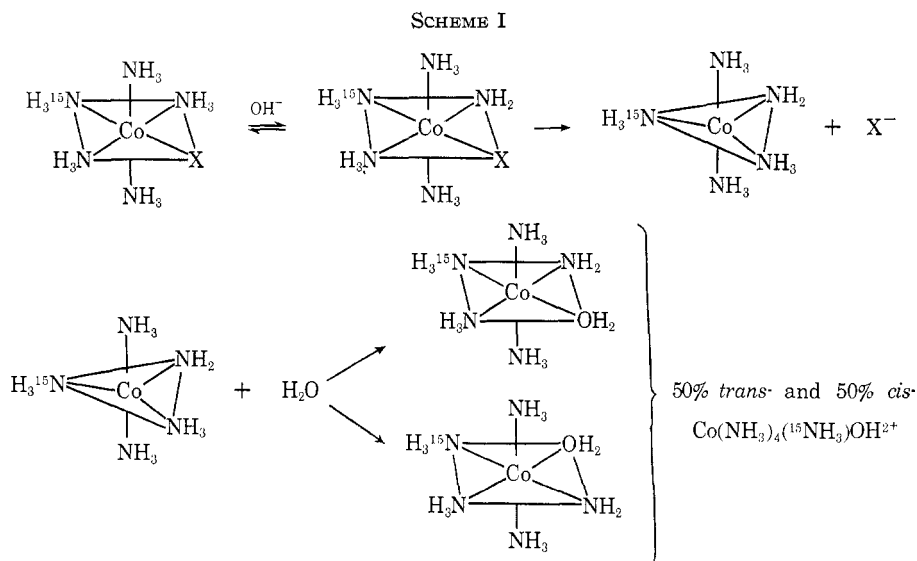
At this point we will make the following assumption: the entering water molecule approaches the intermediate at the same position, relative to the amido group, from which the leaving group has departed. This assumption appears to be reasonable in that the activated complex leading to formation of the intermediate should resemble that leading to its decomposition. In the case that the leaving group and the entering group are identical, this assumption is demanded by the principle of microscopic reversibility.

reactions. Deprotonation of the *trans* ammonia followed by collapse to the intermediate would correspond to leaving and entering from an opposed position.



Such a steric path would lead to 100% *trans*-Co(NH<sub>3</sub>)<sub>4</sub>-(<sup>15</sup>NH<sub>3</sub>)OH<sup>2+</sup> which is not in accord with the observations.

Deprotonation of a *cis* ammonia followed by collapse to the intermediate would correspond to leaving and entering from an adjacent position (see Scheme I).



Only two of the possible four paths are consistent with this assumption: either  $X^-$  leaves from the position opposed to the amido group in step 2 and  $H_2O$  enters at a position opposed to the amido group in step 3 or  $X^-$  leaves from an adjacent position in step 2 and  $H_2O$  enters at an adjacent position in step 3.

The predictions of these two paths may be compared to the experimental results for the  $Co(NH_3)_4(^{15}NH_3)X^{2+}$

This steric path is consistent with the experimental observations. Thus, the stereochemical results support the conclusion that formation of an amido group *cis* rather than *trans* to the leaving group leads to the formation of the trigonal-bipyramidal intermediate.<sup>10</sup> This result is readily understood in terms of the stabilization of the incipient trigonal bipyramid by the  $\pi$ -donating group.

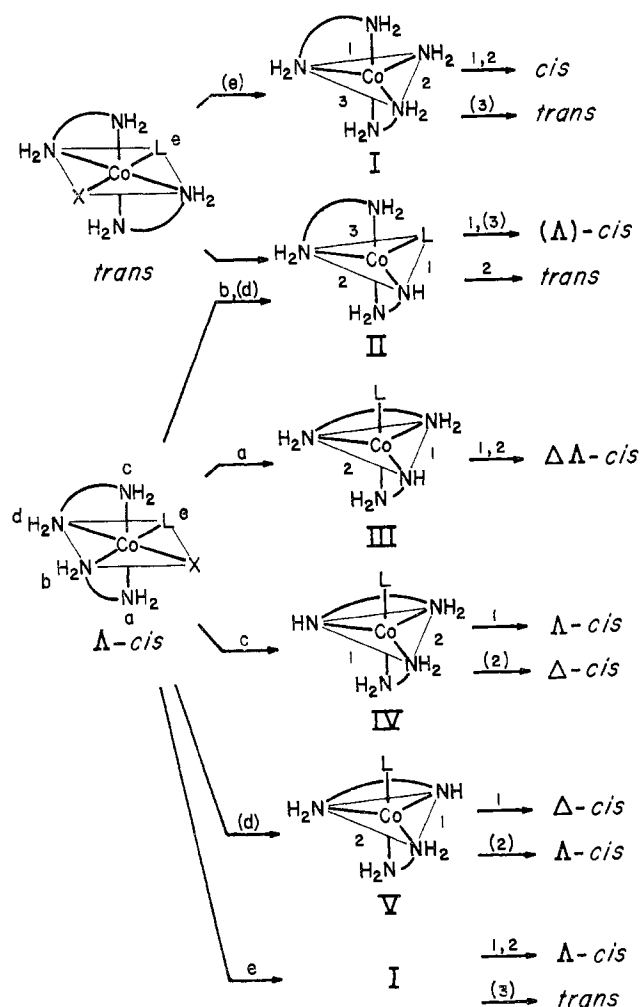
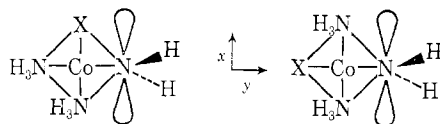


Figure 1.—Reaction paths for the base hydrolysis of  $\text{Co}(\text{en})_2\text{LX}^n+$ .

In the amido complexes shown below (the  $\text{NH}_3$  groups above and below the plane have been omitted



for clarity) only the cobalt  $d_{xy}$  and  $p_x$  orbitals are properly oriented to overlap with the amido  $p$  orbital. The  $d_{xy}$  orbital is filled and the cobalt  $p$  orbitals are shared between opposed pairs of groups in  $\sigma$  bonding. In the complex of  $cis$  geometry, the filled amido  $p$  orbital may stabilize the loss of  $\text{X}^-$  by  $\pi$  donation of electron density into the  $p_x$  orbital. This stabilization is not possible for the  $trans$  complex. The strength of the  $\pi$  interaction will, of course, be greater for both the  $cis$  and the  $trans$  complexes after rearrangement to a trigonal bipyramid

(10) (a) It is assumed in this paper that the rate of proton exchange among amido and ammonia groups is slow compared to the rate of decomposition of the intermediate. The absence of proton exchange is indicated by the arguments and results given by Buckingham, Olsen, and Sargeson.<sup>6</sup> (b) It has been suggested<sup>6</sup> that the amido group is formed  $trans$  to the leaving group because the  $trans$  ammonia is more acidic than the  $cis$ . However, the relative amounts of material reacting *via* the  $cis$  and the  $trans$  conjugate bases are not determined by their relative stabilities but by the relative stabilities of the corresponding activated complexes leading to the five-coordinate intermediate. Thus it is possible for the  $cis$  conjugate base to predominate in reactivity even though it is present at lower concentrations.

is complete, but for the  $cis$  complex the  $\pi$  interaction is possible even in the early stages of rearrangement. Thus, it appears that an opposed amido group is not as effective as an adjacent amido group in stabilizing the formation (or decomposition) of the trigonal bipyramid.

It is of interest now to examine the stereochemistry for  $\text{Co}(\text{en})_2\text{LX}^n+$  hydrolyses since the same principles should apply to ethylenediamine systems as well.

**$\text{Co}(\text{en})_2\text{LX}^n+$  Complexes.**—The reaction scheme of Figure 1 describes the possible trigonal-bipyramidal intermediates and steric consequences of each for the base hydrolysis of the  $cis$ - and  $trans$ - $\text{Co}(\text{en})_2\text{LX}^n+$  complexes. The letters over the arrows indicate the position of deprotonation which leads to formation of the intermediate. The numerals indicate the position at which the entering group, usually water, enters. These characters are enclosed in parentheses when they represent leaving or entering from a position opposite the amido group; no parentheses are used with characters when they represent leaving or entering from a position adjacent to the amido group. Reaction paths e and (e) are available only to complexes with  $\text{L} = \text{NH}_3$ . No assumptions have been made other than that proton exchange is not sufficiently rapid to permit the interconversion of these intermediates.<sup>11</sup> Reaction paths involving intermediates II and V have been discussed previously by Pearson and Basolo.<sup>9</sup>

The amido groups of intermediates IV and V are part of an ethylenediamine chain that lies roughly in the trigonal plane. As a result, the filled  $p$  orbital of the amido group is constrained to lie nearly perpendicular to the trigonal plane.<sup>12</sup> In such an orientation the amido group would be ineffective in stabilizing the loss of  $\text{X}^-$ . It follows that reaction paths involving intermediates IV and V may be unimportant compared with other reaction paths.

According to this scheme complexes of  $trans$ - $\text{Co}(\text{en})_2\text{LX}^n+$  undergo base hydrolysis entirely through intermediate II which gives a  $cis$ - and  $trans$ - $\text{Co}(\text{en})_2\text{LOH}^n+$  mixture. The  $\Delta$ - $cis$  complexes react by way of intermediates II and III (and I where  $\text{L} = \text{NH}_3$ ). Since II is the only source of  $trans$ - $\text{Co}(\text{en})_2\text{LOH}^n+$  and since the ratio of  $cis$  to  $trans$  products arising from II must be independent of the geometry of the reactant, we may calculate the fraction of the  $cis$  reaction which proceeds through II

$$\text{fraction II} = \frac{\% \text{ trans from cis}}{\% \text{ trans from trans}}$$

(11) (a) It has been observed in numerous cases that the stereochemistry of base hydrolysis products remains constant as the leaving group,  $\text{X}^-$ , is varied.<sup>3-7</sup> In the above scheme, this can only result if the relative concentrations and reactivities of the deprotonated forms of the reactant remain constant as  $\text{X}^-$  is varied or if concentration and reactivity differences cancel.<sup>11b</sup> The former possibility does not seem unreasonable for forms arising from deprotonation at  $cis$  positions since all should be affected in a similar way by a change in  $\text{X}^-$ . (b) The author is indebted to a reviewer for this observation.

(12) The C-N bonds in  $\text{Co}(\text{en})_2^{3+}$  make an angle of  $12^\circ$  with their respective N-Co-N planes. As the trigonal-bipyramidal structure is being formed, the N-Co-N bond angle will widen and tend to bring the ethylenediamine ring into a flatter conformation. Thus the filled  $p$  orbital of nitrogen will be within less than  $12^\circ$  from perpendicular to the trigonal plane. The  $12^\circ$  angle for  $\text{Co}(\text{en})_2^{3+}$  was calculated from atomic coordinates given by E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

The balance of the reaction, for  $L \neq \text{NH}_3$ , goes through intermediate III to give racemic *cis*-Co(en)<sub>2</sub>-LOH<sup>n+</sup>. The yields of *trans* product from both the *cis* and *trans* reactions allow one to predict the optical purity of the *cis* product from the reaction of the  $\Delta$ -*cis* reactant. This provides a convenient check of the mechanism of these reactions. For reactants in which  $L = \text{NH}_3$ , one must allow for the path through I which may yield additional  $\Delta$ -*cis* product.

Available experimental data are compared with the predicted net retention of optical purity for base hydrolysis of the *cis*-Co(en)<sub>2</sub>LX<sup>n+</sup> complexes in Table I. The predicted optical purity is calculated as the fraction of the reaction that proceeds *via* intermediate II by attack at position 1

$$\% \text{ II}_1 = \frac{\% \text{ trans from cis}}{\% \text{ trans from trans}} \times \% \text{ cis from trans}$$

For  $L = \text{NO}_2^-$  and  $\text{NCS}^-$  the discrepancies between per cent II and per cent  $\Delta$ -*cis* appear to be outside experimental error and seem to call for a reinvestigation of these systems.

The difference  $\% \Delta - \% \text{ II}$  for the Co(en)<sub>2</sub>NH<sub>3</sub>X<sup>2+</sup> reactions is the contribution made by intermediate I. Intermediate II accounts for about 63% of the reaction for most complexes and greatly predominates over I. This indicates that the RNH<sup>-</sup> amido group gives a more stable activated complex than NH<sub>2</sub><sup>-</sup>. This is somewhat surprising because it is known that coordinated NH<sub>3</sub> loses a proton more rapidly<sup>13</sup> and one would expect NH<sub>3</sub> to be more acidic than RNH<sub>2</sub>. However, additional stability arises for RNH<sup>-</sup> because it is fixed in nearly the proper orientation by the ethylenediamine ring and undergoes little entropy loss in forming the activated complex.

Further experiments will be required to establish whether or not *trans*-amido stabilization of the formation and decomposition of the five-coordinate intermediates is important for Co(en)<sub>2</sub>LX<sup>n+</sup> complexes.

(13) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

TABLE I  
STEREOCHEMISTRY OF THE PRODUCTS OF THE BASE HYDROLYSIS OF  
Co(en)<sub>2</sub>LX<sup>n+</sup> COMPLEXES<sup>a</sup>

Reactant		Co(en) <sub>2</sub> LOH <sup>n+</sup> product			% II <sub>1</sub>	Ref
L	X <sup>-</sup>	% <i>trans</i>	% $\Delta$ - <i>cis</i>	% $\Lambda$ - <i>cis</i>		
<i>trans</i> -NO <sub>2</sub> <sup>-</sup>	Cl <sup>-</sup>	94 ± 1	6			b
$\Delta$ - <i>cis</i> -NO <sub>2</sub> <sup>-</sup>	Cl <sup>-</sup>	34 ± 1	41	25	2.2 ± 0.1	b, c
<i>trans</i> -Cl <sup>-</sup>	Cl <sup>-</sup>	95 ± 2	5			d
$\Delta$ - <i>cis</i> -Cl <sup>-</sup>	Cl <sup>-</sup>	63 ± 2	32	5	3.3 ± 1.4	d
<i>trans</i> -OH <sup>-</sup>	Cl <sup>-</sup>	6 ± 2	94			d
$\Delta$ - <i>cis</i> -OH <sup>-</sup>	Cl <sup>-</sup>	3 ± 2	72	25	47 ± 34	d
$\Lambda$ - <i>cis</i> -OH <sup>-</sup>	Cl <sup>-</sup>	5 ± 1	0	95	78 ± 30	e
<i>trans</i> -NCS <sup>-</sup>	Cl <sup>-</sup>	24 ± 2	76			f
$\Delta$ - <i>cis</i> -NCS <sup>-</sup>	Cl <sup>-</sup>	18 ± 2	50	32	57 ± 8	f, g
<i>trans</i> -NH <sub>3</sub> <sup>h,i</sup>	Cl <sup>-</sup>	36 ± 2	64			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,i</sup>	Cl <sup>-</sup>	22 ± 2	30	48	39 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,i</sup>	NO <sub>2</sub> <sup>-</sup>	37 ± 2	63			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,i</sup>	NO <sub>2</sub> <sup>-</sup>	23 ± 2	30	47	39 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,k</sup>	Cl <sup>-</sup>	27 ± 2	49			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,k</sup>	Cl <sup>-</sup>	17 ± 2	23	36	31 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,k</sup>	NO <sub>2</sub> <sup>-</sup>	27 ± 2	48			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,k</sup>	NO <sub>2</sub> <sup>-</sup>	17 ± 2	22	35	30 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,l</sup>	Cl <sup>-</sup>	32 ± 2	57			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,l</sup>	Cl <sup>-</sup>	20 ± 2	31	38	36 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,l</sup>	NO <sub>2</sub> <sup>-</sup>	32 ± 2	57			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,l</sup>	NO <sub>2</sub> <sup>-</sup>	20 ± 2	29	40	36 ± 4	j
<i>trans</i> -NH <sub>3</sub> <sup>h,m</sup>	Cl <sup>-</sup>	8 ± 2	16			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,m</sup>	Cl <sup>-</sup>	7 ± 2	7	8	14 ± 5	j
<i>trans</i> -NH <sub>3</sub> <sup>h,m</sup>	NO <sub>2</sub> <sup>-</sup>	9 ± 2	16			j
$\Delta$ - <i>cis</i> -NH <sub>3</sub> <sup>h,m</sup>	NO <sub>2</sub> <sup>-</sup>	8 ± 2	9	9	14 ± 5	j

<sup>a</sup> All data at 0° unless specified otherwise. <sup>b</sup> S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956). <sup>c</sup> A. Jensen, F. Basolo, and R. G. Pearson, unpublished results, cited by F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, pp 233, 235. <sup>d</sup> S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962). <sup>e</sup> E. A. Dittmer and R. D. Archer, *J. Am. Chem. Soc.*, **90**, 1468 (1968). <sup>f</sup> C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956). <sup>g</sup> M. E. Baldwin and M. L. Tobe, *ibid.*, 4275 (1960). <sup>h</sup> Measured at 25°. <sup>i</sup> In a 1 M ClO<sub>4</sub><sup>-</sup> medium. <sup>j</sup> Reference 7. <sup>k</sup> In a 1 M N<sub>3</sub><sup>-</sup> medium; Co(en)<sub>2</sub>NH<sub>3</sub>N<sub>3</sub><sup>2+</sup> products are also formed. <sup>l</sup> In a 1 M SCN<sup>-</sup> medium; Co(en)<sub>2</sub>NH<sub>3</sub>NCS<sup>2+</sup> products are also formed. <sup>m</sup> In a 1 M N<sub>3</sub><sup>-</sup> medium. Values are for the Co(en)<sub>2</sub>NH<sub>3</sub>N<sub>3</sub><sup>2+</sup> product.

The reaction scheme is sufficiently involved that data of the type in Table I do not exclude the importance of *trans*-amido stabilization.

**Acknowledgment.**—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.