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THERMAL REACTIONS OF COORDINATION COMPOUNDS

PART II. CHLOROBROMOBIS(ETHYLENEDIAMINE)- AND DIBROMOBIS(ETHYLENEDIAMINE)-COBALT (III) COMPLEXES*

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ABSTRACT

The thermal solid–solid and gas–solid reactions of *cis*- and *trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$, *cis*- and *trans*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, *cis*-$[Co(en)_2(H_2O)Br]Br_2 \cdot H_2O$, *cis*-$[Co(en)_2(H_2O)Cl]Br_2 \cdot H_2O$, *cis*-$[Co(en)_2ClBr]NO_3$, and *cis*-$[Co(en)_2Br_2]NO_3$ with various ammonium salts and HCl and HNO_3, were investigated by various thermal techniques. All of the reactions yielded the *trans* isomeric products. The various reaction temperatures and reaction intervals were determined for the mixtures. An overall mechanism for the "*trans-preferred*" reactions is described.

INTRODUCTION

In Part I of this series[1], the solid–solid and gas–solid *trans*-preferred reactions of the dichlorobis (ethylenediamine) cobalt (III) complexes, *cis*- and *trans*-$[Co(en)_2Cl_2]X$, with various ammonium salts, hydrogen chloride and hydrogen nitrate were described. It was found that ammonium nitrate and/or hydrogen nitrate were required for the *trans*-preferred reactions of these complexes. For the analogous bromo complexes, the thermal deaquation of *cis*- and *trans*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, *cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$, and *cis*-$[Co(en)_2H_2OBr]Br_2 \cdot H_2O$ have previously been reported[2,3]. It was found that the main products of these reactions were *cis*-$[Co(en)_2Br_2]Br$ or *cis*-$[Co(en)_2BrCl]Br$, although a small amount of *trans* isomer was also present. This was contrary to the fact that only *cis*-$[Co(en)_2Cl_2]Cl$ was obtained in the thermal deaquation of the corresponding aquo or aquo-chloro complexes[2]. The partial formation of the *trans* isomer in the former case is believed to be due to the stereochemical effect of replacement of the bulky bromide ion for coordination water.

The solid–solid or gas–solid reaction of the $[Co(en)_2ClBr]Br$ and $[Co(en)_2Br_2]Br$ complexes, as well as their aquo analogs with ammonium salts, should be similar to those found for the analogous chlorocomplexes. The above reactions are described in detail here as well as a general reaction mechanism for all of the *trans*-preferred reactions.

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* For Part I, see Ref. 1.

TABLE 1

SOLID–SOLID *trans*-PREFERRED REACTIONS OF COMPLEXES

Type of reaction	*Reaction mixtures*	*Reaction temperatures (°C)*	*Reaction period (min)*			*Product*
			110°C	120°C	130°C	
S-I	*cis*-$[Co(en)_2(H_2O)_2](NO_3)_3 + NH_4Br$	80–95	35	20	10	*trans*-$[Co(en)_2Br_2]^+$
S-I	*trans*-$[Co(en)_2(H_2O)_2](NO_3)_3 + NH_4Br$	80–95	40	25	15	*trans*-$[Co(en)_2Br_2]^+$
S-I	$[Co(en)_2(NO_3)_2]NO_3 + NH_4Br$	120–140	[c]	30–150	25–100	*trans*-$[Co(en)_2Br_2]^+$
S-II	*cis*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O + NH_4NO_3$	70–100	45	25	10	*trans*-$[Co(en)_2Br_2]NO_3$
S-II	*trans*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O + NH_4NO_3$	85–105	50	35	20	*trans*-$[Co(en)_2Br_2]NO_3$
S-III	*cis*-$[Co(en)_2(H_2O)Br]Br_2 \cdot H_2O + NH_4NO_3$	105–125	55	35	15	*trans*-$[Co(en)_2Br_2]NO_3$
S-III	*cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O + NH_4NO_3$	105–125	55	35	15	*trans*-$[Co(en)_2ClBr]NO_3$
S-IV	*cis*-$[Co(en)_2Br_2]Br \cdot H_2O + NH_4NO_3$	150–160	300	145	35	*trans*-$[Co(en)_2Br_2]NO_3$
S-IV	*cis*-$[Co(en)_2ClBr]Br \cdot H_2O + NH_4NO_3$	150–160	300	150	40	[f] *trans*-$[Co(en)_2ClBr]NO_3$ *trans*-$[Co(en)_2Br_2]NO_3$
S-V	*cis*-$[Co(en)_2Br_2]NO_3 + NH_4NO_3$	melting[a]	[c]	435	200	*trans*-$[Co(en)_2Br_2]NO_3$
S-V	*cis*-$[Co(en)_2ClBr]NO_3 + NH_4NO_3$	melting[a]	[c]	450	210	*trans*-$[Co(en)_2ClBr]NO_3$
S-VI	*cis*-$[Co(en)_2Br_2]NO_3 + NH_4Cl$	160–180	[c]	[c]	[c]	[f] *trans*-$[Co(en)_2ClBr]^+$ + *trans*-$[Co(en)_2Br_2]^+$
S-VI	*cis*-$[Co(en)_2Br_2]NO_3 + NH_4Br$	~195[b]	[d]	[d]	[d]	[e]*trans*-$[Co(en)_2Br_2]^+$
S-VI	*cis*-$[Co(en)_2ClBr]NO_3 + NH_4Cl$	165–185	[c]	[c]	[c]	[f] *trans*-$[Co(en)_2Cl_2]^+$ + *trans*-$[Co(en)_2ClBr]^+$
S-VI	*cis*-$[Co(en)_2ClBr]NO_3 + NH_4Br$	~195[b]	[d]	[d]	[d]	[e] *trans*-$[Co(en)_2ClBr]^+$ *trans*-$[Co(en)_2Br_2]^+$
S-VI	*cis*-$[Co(en)_2Cl_2]NO_3 + NH_4Br$	~195[b]	[d]	[d]	[d]	[e] *trans*-$[Co(en)_2Cl_2]^+$ *trans*-$[Co(en)_2ClBr]^+$

[a] Mixture melted before changing to green or yellowish green. [b] Only partial yellowish product. [c] No appreciable reaction to 500 min; the reactions can proceed at 150°C. [d] No appreciable reaction to 500 min even up to temperatures of 160°C; the reaction was never complete. [e] Expected product but never obtained experimentally. [f] The top compound is the major product.

EXPERIMENTAL

Preparation of compounds. The compounds, *cis-* and *trans-*$[Co(en)_2(H_2O)_2](NO_3)_3$, *cis-* and *trans-*$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$, *cis-*$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$, *cis-*$[Co(en)_2H_2OBr]Br_2 \cdot H_2O$, *cis-*$[Co(en)_2ClBr]Br \cdot H_2O$, *cis-*$[Co(en)_2Br_2]Br \cdot H_2O$, and $[Co(en)_2(NO_3)_2]NO_3$, were prepared as previously described[2,3]. Also prepared by previously described procedures were *cis-*$[Co(en)_2ClBr]NO_3$[6], *trans-*$[Co(en)_2ClBr]NO_3$[7] *cis-*$[Co(en)_2Br_2]NO_3$[8], and *trans-*$[Co(en)_2Br_2]Br$[9].

Thermal solid–solid reactions. The mixture of solids was prepared as previously described[1] using a weight ratio of complex–ammonium salt of 1:3 (for NH_4NO_3) or 1:10 (for NH_4Cl or NH_4Br). The reaction temperatures were determined either by a capillary tube method using a Thomas–Hoover melting point apparatus or by high temperature reflectance spectroscopy (HTRS)[10]. Isothermal studies were also carried out by visually observing the color changes of the reaction mixtures contained in 5-mm diameter aluminum cups which were placed in a temperature controlled oven.

Thermal gas–solid reactions. The procedure used was the same as previously described[1].

Reflectance measurements. — A Beckman Model DK-2A spectroreflectometer was used to obtain the reflectance spectra of the mixtures. Freshly prepared MgO was used as the reflectance reference.

RESULTS AND DISCUSSION

Solid–solid trans-preferred reactions

The reaction mixtures studied, the approximate reaction temperature range, reaction intervals at constant temperature, and the composition of the main reaction products are given in Table I. For the convenience of this discussion, the *trans*-preferred reactions are classified into six types each of which are elucidated in Table II.

(*a*) *Type S-I reactions*

The reaction of *cis-*$[Co(en)_2(H_2O)_2](NO_3)_3$ with NH_4Br, as revealed by the reflectance curves in Fig. 1, shows that the product, *trans-*$[Co(en)_2Br_2]^+$ (anion unknown), is obtained only at temperatures above 75°C. The reflectance curve of the mixture began to change at 50°C but the reaction appeared to be most rapid above 100°C. According to the capillary tube measurements (Table I), the yellowish-green product was obtained at about 95°C. It was also observed that this reaction can proceed at room temperature if permitted to stand two or more days. The color changes observed were: light-red→violet→yellowish-green. Similar results were obtained for the *trans-*$[Co(en)_2(H_2O)_2](NO_3)_3 + NH_4Br$ mixture in which *trans-*$[Co(en)_2Br_2]^+$ was obtained as the product.

The reaction of $[Co(en)_2(NO_3)_2]NO_3$ with NH_4Br required higher reaction temperatures and/or reaction intervals than with the diaquo complex. This is probably due to difficulty involved in breaking the Co^{3+}–ONO_2^- bond in contrast to the easily

TABLE II

THE CLASSIFICATION OF THE *trans*-PREFERRED REACTIONS (WHERE $X = Cl^-$, $Y = Br^-$, $Z = NO_3^-$)

Type S-I Complex-nitrate and ammonium (or hydrogen)halide

$$\begin{matrix}(cis\text{-}, trans\text{-})[Co(en)_2(H_2O)_2]Z_3 \\ [Co(en)_2Z_2]Z\end{matrix} + NH_4\begin{pmatrix}X\\Y\end{pmatrix} \rightarrow trans\text{-}[Co(en)_2\begin{pmatrix}X_2\\Y_2\end{pmatrix}]^+$$

Type S-II Diaquo-halide and ammonium (or hydrogen) nitrate

$$(cis\text{-}, trans\text{-})[Co(en)_2(H_2O)_2]\begin{pmatrix}X_3\\Y_3\end{pmatrix}\cdot 2H_2O + NH_4Z \rightarrow trans\text{-}[Co(en)_2\begin{pmatrix}X_2\\Y_2\end{pmatrix}]^+$$

Type S-III Haloaquo-halide and ammonium (or hydrogen) nitrate

$$cis\text{-}[Co(en)_2H_2O(\underset{Y}{\overset{X}{X}})](\underset{Y}{\overset{X}{Y}})(\underset{H_2O}{H_2O}) + NH_4Z \rightarrow trans\text{-}[Co(en)_2(\underset{Y_2}{\overset{X_2}{XY}})]^+$$

Type S-IV Dihalo-halide and ammonium (or hydrogen) nitrate

$$cis\text{-}[Co(en)_2(\underset{Y_2}{\overset{X_2}{XY}})](\underset{Y}{\overset{X}{Y}})\cdot H_2O + NH_4Z \rightarrow trans\text{-}[Co(en)_2(\underset{Y_2}{\overset{X_2}{XY}})]^+$$

Type S-V Dihalo-nitrate and ammonium (or hydrogen) nitrate

$$cis\text{-}[Co(en)_2(\underset{Y_2}{\overset{X_2}{XY}})]Z + NH_4Z \rightarrow trans\text{-}[Co(en)_2(\underset{Y_2}{\overset{X_2}{XY}})]^+$$

Type S-VI Dihalo-nitrate and ammonium (hydrogen) halide

$$cis\text{-}[Co(en)_2(\underset{\substack{Y_2\\Y_2}}{\overset{\substack{X_2\\XY}}{XY}})]Z + NH_4(\underset{\substack{X\\Y}}{\overset{\substack{X\\X}}{Y}}) \rightarrow trans\text{-}[Co(en)_2(\underset{\substack{XY\\Y_2}}{\overset{\substack{X_2\\X_2}}{XY}})]^+$$

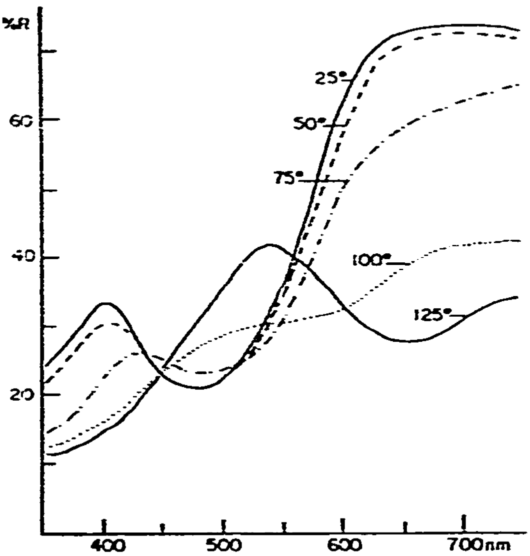


Fig. 1. Reflectance spectra of a mixture of *cis*-$[Co(en)_2(H_2O)_2](NO_3)_3$ + NH_4Br at various temperatures.

broken Co^{3+}–OH_2 bond. For both of the reactions, the presence of both ammonium and nitrate ions are essential for the *trans*-preferred reactions; this is in agreement with the reactions observed [1] for the chloro complexes and NH_4Cl. The equation for the *trans*-preferred reaction can be written as:

$$\textit{cis-, trans-}[Co(en)_2(H_2O)_2](NO_3)_3 + NH_4Br \xrightarrow{\Delta} \textit{trans-}[Co(en)_2Br_2]^+ NO_3^- + 2NH_4NO_3$$

(*b*) *Type S-II reactions*

It has previously been reported[3] that a mixture of *cis-* and *trans-*$[Co(en)_2Br_2]Br$ is obtained in the deaquation of *cis-*$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$. In the *trans*-preferred reaction of *cis-*$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$ with NH_4NO_3, only *trans-*$[Co(en)_2Br_2]^+$ is obtained. This reaction is shown by the high temperature reflectance curves in Fig. 2. The reaction, in this case, began above 50°C and was completed at about 125°C. Similar results were obtained for the reaction of *trans-*$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$. The equation for this reaction can be written as:

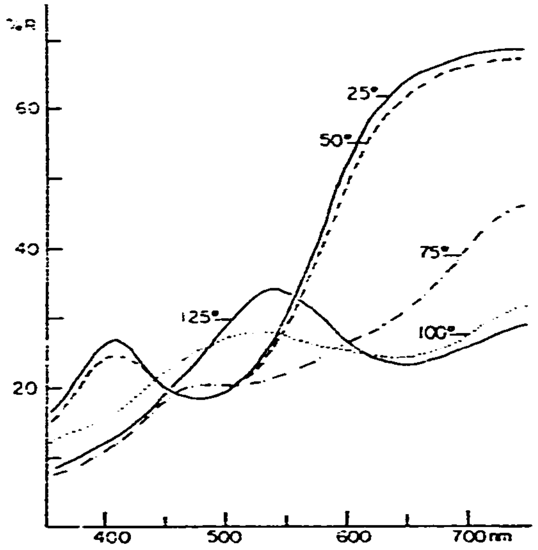


Fig. 2. Reflectance curves of a mixture of *cis-*$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O + NH_4NO_3$ at various temperatures.

$$\textit{cis-, trans-}[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O + NH_4NO_3 \rightarrow \textit{trans-}[Co(en)_2Br_2]NO_3 + NH_4Br + 4H_2O$$

(*c*) *Type S-III reactions*

The *trans*-preferred reaction between *cis-*$[Co(en)_2H_2OBr]Br_2 \cdot H_2O$ and NH_4NO_3 is shown by the high temperature reflectance curves given in Fig. 3. The green colored *trans-*$[Co(en)_2Br_2]^+$ is obtained at 150°C. It is of interest to note that only *trans-*$[Co(en)_2ClBr]^+$ is obtained as the product in the reaction of *cis-*$[Co(en)_2$-$H_2OCl]Br_2 \cdot H_2O$ with NH_4NO_3. This is a promising synthetic procedure for this com-

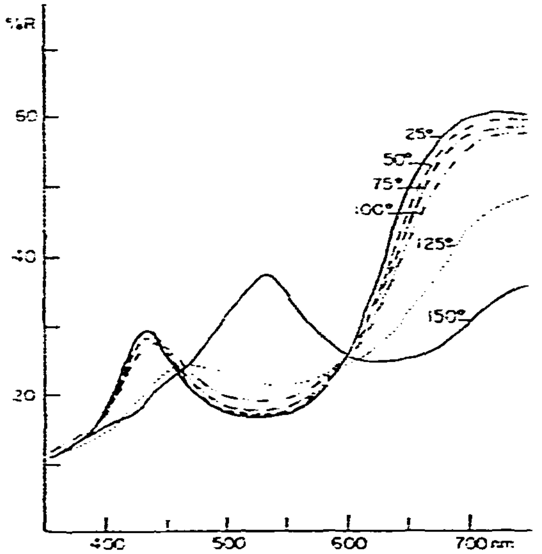


Fig. 3. Reflectance curves of a mixture of cis-$[Co(en)_2H_2OBr]Br_2 \cdot H_2O + NH_4NO_3$ at various temperatures.

pound since the present method for the preparation of cis- and trans-$[Co(en)_2ClBr]^+$ complexes is by the thermal deaquation of cis-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$[7]. This latter method yields a mixture containing 20% of the trans isomer and 80% cis isomer.

(d) Type S-IV reactions

This type of reaction is essentially that of a cis → trans isomerization involving the chlorobromo or dibromo complexes. This isomerization is shown by the reaction

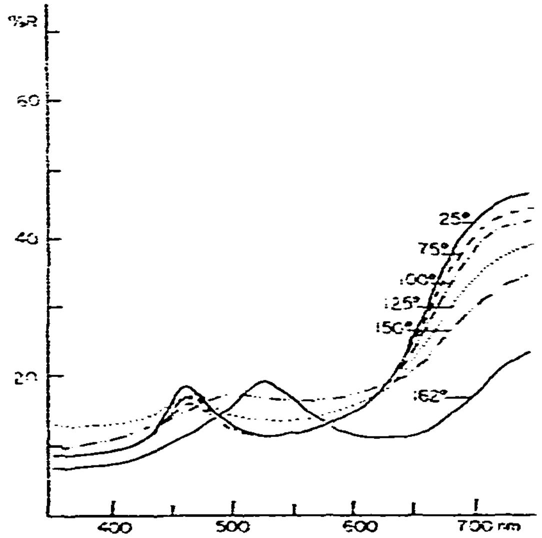


Fig. 4. Reflectance curves of a mixture of cis-$[Co(en)_2ClBr]Br \cdot H_2O + NH_4NO_3$ at various temperatures.

of cis-$[Co(en)_2ClBr]Br \cdot H_2O$ with NH_4NO_3 in Fig. 4. As can be seen, the green colored trans-$[Co(en)_2ClBr]^+$ is present at 162°C. Kinetically speaking, reactions of this type are relatively slower than Type S-II or S-III reactions. The *trans*-preferred reaction of cis-$[Co(en)_2Br_2]Br \cdot H_2O$ had about the same reaction rate as the above compound.

(*e*) *Type S-V reactions*

These reactions are similar to those previously described for the Type S-IV series. It is a *cis* → *trans* isomerization involving the equation:

$$cis\text{-}[Co(en)_2XY]NO_3 \xrightarrow{NH_4NO_3} trans\text{-}[Co(en)_2XY]NO_3$$

where X and Y are Cl^- or Br^-. Again, it is a rather slow reaction kinetically, even slower than the Type S-IV reactions. The reaction mixtures required long periods of heating at elevated temperatures. For example, the *trans* products from the mixtures, cis-$[Co(en)_2ClBr]NO_3 + NH_4NO_3$ and cis-$[Co(en)_2Br_2]NO_3 + NH_4NO_3$, were obtained by heating them at 130°C for about 3 h. Any additional heating of the mixture usually resulted in decomposition of the product.

(*f*) *Type S-VI reactions*

This type of reaction was perhaps the most difficult to transform into a *trans* product. Very long reaction intervals and higher temperatures were necessary to obtain the pure product. This is no doubt related to the energy requirements involved in the dissociation mechanism to form a trigonal bipyramid intermediate, or

$$cis\text{-}[Co(en)_2XY]^+ \xrightarrow{-Y} [Co(en)_2X]^{2+} \xrightarrow{+X} trans\text{-}[Co(en)_2X_2]^+$$

Experimentally, it was found that it was very difficult to introduce the Br^- anion from the NH_4Br matrix, while the similar reaction involving Cl^- was somewhat less difficult. For example, the reaction between cis-$[Co(en)_2Br_2]NO_3$ and NH_4Cl took place rather easily to form trans-$[Co(en)_2ClBr]^+$. However, it was almost impossible to obtain trans-$[Co(en)_2Br_2]^+$ from a cis-$[Co(en)_2Br_2]NO_3 + NH_4Br$ mixture.

Gas–solid trans-preferred reactions

The reaction of a number of complexes with gaseous HBr and HNO_3 are given in Table III. The results of the solid–gas reactions were similar to those found for the solid–solid reactions. The products, in all cases except with ammonia, were the *trans* complexes. Even the *cis*→ *trans* isomerization reactions occurred. In several cases, the yellowish-green colored dihalo complexes changed to the brown *trans*-dinitrato products (reaction no. 8), on heating in gaseous HNO_3 at elevated temperatures. These are illustrated by the following reactions:

TABLE III

GAS–SOLID THERMAL REACTIONS OF COMPLEXES

Classification	*Reaction mixture*		*Approximate reaction temperature* (°C)	*Product*
G-I	*cis*-$[Co(en)_2(H_2O)_2](NO_3)_3$			
G-I	*trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$	$+HBr(g)$	120	*trans*-$[Co(en)_2Br_2]^+$
	all complexes	$+NH_3(g)$	no reaction	
G-III	*cis*-$[Co(en)_2H_2OCl]Br_2 \cdot H_2O$	$+HNO_3(g)$	125	*trans*-$[Co(en)_2ClBr]NO_3$
G-III	*cis*-$[Co(en)_2H_2OBr]Br_2 \cdot H_2O$	$+HNO_3(g)$	125	[c]*trans*-$[Co(en)_2Br_2]NO_3$
G-IV	*cis*-$[Co(en)_2ClBr]Br \cdot H_2O$	$+HNO_3(g)$	135	[a]*trans*-$[Co(en)_2ClBr]NO_3$
G-IV	*cis*-$[Co(en)_2Br_2]Br \cdot H_2O$	$+HNO_3(g)$	135	*trans*-$[Co(en)_2Br_2]NO_3$
	trans-$[Co(en)_2Br_2]Br$	$+HNO_3(g)$	140–150[d]	[b]*trans*-$[Co(en)_2(NO_3)_2]NO_3$
G-V	*cis*-$[Co(en)_2ClBr]NO_3$			
G-V	*cis*-$[Co(en)_2Br_2]NO_3$	$+HNO_3(g)$	difficult for *cis*→*trans* isomerization	
G-VI	*cis*-$[Co(en)_2ClBr]NO_3$			
G-VI	*cis*-$[Co(en)_2Br_2]NO_3$	$+HBr(g)$	no reaction	

[a] Qualitative identification by reflectance spectrum revealed *trans*-$[Co(en)_2ClBr]NO_3$ as the major product. [b] The brown product gave a negative halide test. Assignment of the *trans* isomer is based on the overall reaction mechanism, *cis*-dihalo→*trans*-dihalo→*trans*-dinitrato, and its spectral similarity to the *trans*-diaquo complex (also brown in color); *cis*-diaquo and *cis*-dinitrato complexes are reddish in color. [c] The yield of *trans* isomer product was about 70% at best. [d] It took 30 min to complete reaction.

$$cis\text{-}[Co(en)_2ClBr]Br\cdot H_2O \xrightarrow[135^\circ]{HNO_3(g)} \left\{\begin{array}{l} trans\text{-}[Co(en)_2ClBr]NO_3\ \text{(major product)} \\ trans\text{-}[Co(en)_2Br_2]NO_3 \\ \quad\Big\downarrow \begin{array}{l} HNO_3(g) \\ 145^\circ \end{array} \\ trans\text{-}[Co(en)_2(NO_3)_2]NO_3 \end{array}\right.$$

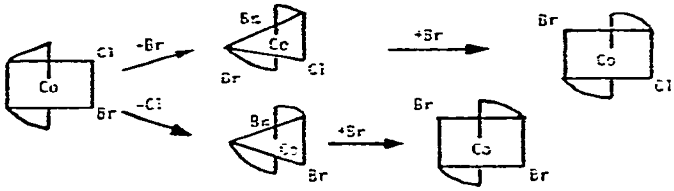
Negative *trans*-preferred reactions were observed between *cis*-$[Co(en)_2ClBr]NO_3$ and *cis*-$[Co(en)_2Br_2]NO_3$ with gaseous HBr, probably for the same reason as discussed with Type S-VI reactions.

Mechanism of trans-preferred reactions

A general survey of the stereochemical changes occurring during octahedral substitution reactions has recently been summarized by Archer[11]. The reactions described, however, all took place in a homogeneous liquid phase. Due to the complexity of the heterogeneous reactions investigated here, quantitative interpretation of the reaction mechanism is impossible at the present time. Only in a few cases have mechanisms for solid-state isomerization reactions been postulated[4,5,12] but only one of these[5] is quantitative in nature.

In Part I of this series[1], the two energy barriers, trigonal bipyramidal reaction mechanism was introduced. Once the mechanism of dissociative intermediates was chosen, it was necessary to consider all of the possible reaction paths and products encountered in the solid–solid *trans*-preferred reactions observed experimentally. The new modified general reaction mechanism of the *trans*-preferred reactions is given in Fig. 5. The dissociation of the ligand X from *cis*-$[Co(en)_2BX]^{n+}$ can yield three possible intermediates: (a) the tetragonal pyramid; (b) the trigonal bipyramid with B in the trigonal plane; and (c) the trigonal bipyramid with B in an axial position. Further rearrangement of the tetragonal pyramid and trigonal bipyramid intermediates can be eliminated because of the lack of data to support these multiple rearrangements, in contrast to the mechanism proposed in homogeneous media[11]. To obtain the *trans* product from *cis*-$[Co(en)_2BX]^{n+}$, the pathway (I-a) and (II-a) must be followed. This is the mechanism that has long been used to explain *cis* → *trans* isomerizations in octahedral complexes. The possible products from the other intermediates lead to inversion or retention of configuration if the backward process is not considered. Hence, the other two pathways are not pertinent to this discussion since the direct (I-a) and (II-a) yields the desired product.

For a S-IV Type reaction, there are two possibilities for the loss of the coordinated halogen ion; it is either the chloride or bromide ion in the compound, *cis*-[Co-$(en)_2ClBr]Br\cdot H_2O$. This mechanism is illustrated as follows:



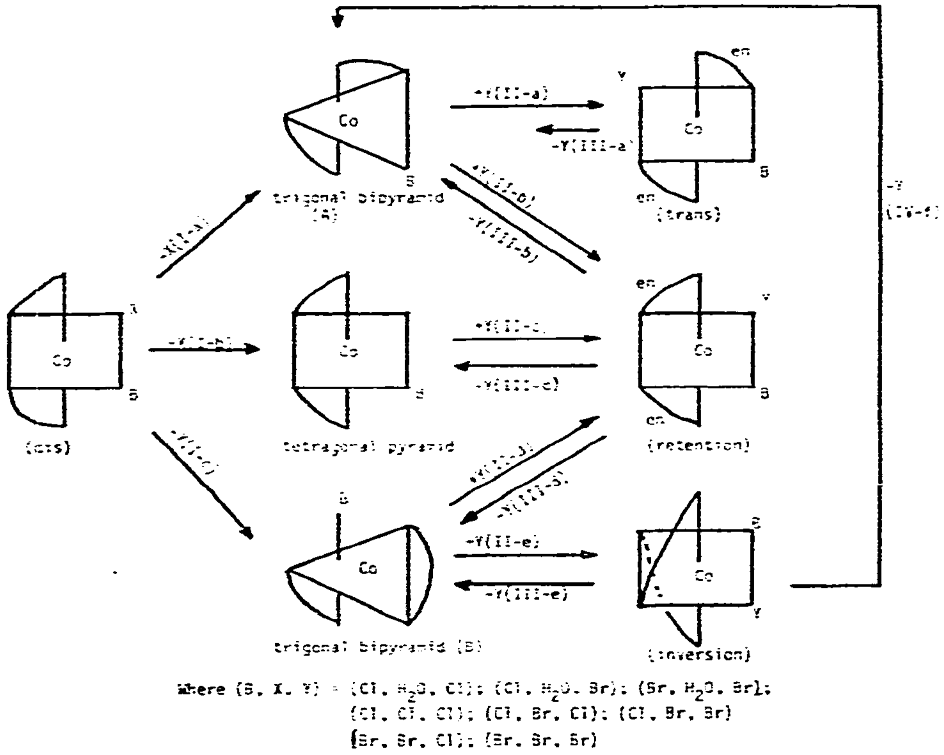
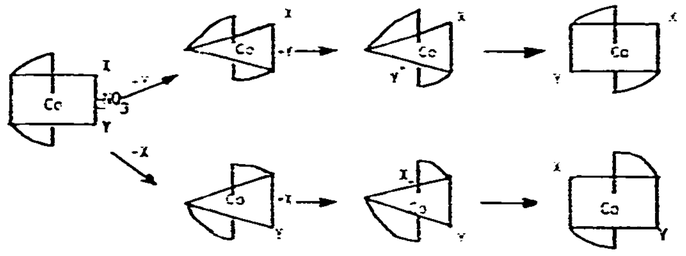


Fig. 5. General mechanism for *trans*-preferred reactions.

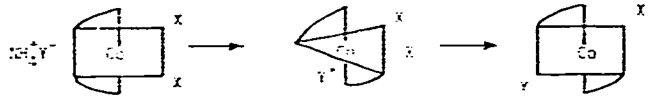
Experimentally, it was found that *trans*-$[Co(en)_2ClBr]NO_3$ was the major product but it was not possible to estimate the amount of *trans*-$[Co(en)_2Br_2]NO_3$ that may have been present in the mixture. It should be realized, however, that the loss of either ligand is a competitive process and that the bromide ligand is easier to lose than the chloride due to the difference in bonding energies between the cobalt (III) ion and the two ligands. In the acid hydrolysis of *cis*-$[Co(en)_2ClBr]^+$, the bromide ligand is replaced by water 3.5 times faster than the chloride ion[11].

For a Type S-V reaction, there are no halogen ions in the ionization sphere because of the use of an NH_4NO_3 matrix. Therefore, the ions involved must come from the coordination sphere of the complex. A reaction of this type can be illustrated by the mechanism:



This reaction is somewhat slower than that for Type S-IV due to the difficulty in orientation of the leaving ligand. The leaving ligand must also attach itself to the trigonal bipyramid.

For a Type S-VI reaction, no appreciable *cis* → *trans* isomerization is observed when NH_4Br is used as the matrix. The product from the reaction, *cis*-$[Co(en)_2Cl_2]NO_3 + NH_4Cl$, is *trans*-$[Co(en)_2Cl_2]NO_3$; however, the *trans*- dihalo product is never obtained from the reaction of *cis*-$[Co(en)_2Cl_2]NO_3 + NH_4Br$. These results indicate that the entering ligand comes probably from the ammonium halide and is intermolecular rather than an intramolecular *cis* → *trans* isomerization. The mechanism for reactions of this type can be represented as:



This type of reaction requires the greatest expenditure of energy to form the trigonal bipyramid intermediate and hence relatively higher temperatures are required (~175°C). From a purely stereochemical consideration, the bulky bromide ion should have more difficulty entering the intermediate than the chloride ion.

In conclusion, the mechanism of the *trans*-preferred reaction proposed here is essentially the same as that previously suggested[1], namely, through the trigonal bipyramid intermediate with the halogen ligand in the trigonal plane. The other mechanisms proposed are useful to explain the experimental results if different initial compounds are employed. The ease of dissociation of the X ligand follows the order: $H_2O > Br \geqslant Cl$ while the ease of entering Y ligand is reversed, or: $Cl > Br$.

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