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THERMAL REACTIONS OF COORDINATION COMPOUNDS

PART III. DIAQUOTETRAMMINE-, ANIONOAQUOTETRAMMINE-, AND DIANIONOTETRAMMINECOBALT (III) COMPLEXES

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ABSTRACT

The *solid–solid* and *gas–solid* reactions of $[Co(NH_3)_4X_2]Y_{3-n}$ ($n = 1, 2$) complexes with NH_4X and HX were studied by various thermoanalytical techniques. The *trans*-preferred products were formed in most cases provided that NH_4^+ (H^+) and NO_3^- were both present in the reaction mixtures. With an excess of NO_3^- ion present, such as HNO_3, the completely nitrated product was obtained, according to the equation:

$$cis\text{-}[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O \xrightarrow{HNO_3} trans\text{-}[Co(NH_3)_4Cl_2]NO_3 \xrightarrow{HNO_3}$$

$$(trans\text{-}[Co(NH_3)_4ClNO_3]NO_3) \xrightarrow{HNO_3} trans\text{-}[Co(NH_3)_4(NO_3)_2]NO_3.$$

INTRODUCTION

In Parts I[1] and II[2] of this series, the solid–solid and gas–solid *trans*-preferred reactions of some diaquoammine-, aquohaloammine-, and dihalobis(ethylenediamine)-cobalt(III) complexes with various ammonium salts (NH_4X) and gases (HCl and HNO_3) were described. The subject of this investigation is to extend this series by the examination of the thermal *trans*-preferred reactions of the tetramminecobalt(III) complexes of the general formula, $[CoA_4X_2]^{n+}$, where A is ammonia and X may be an anion or water.

The dihalotetramminecobalt(III) complexes, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_4Br_2]Br$, have been reported[3,4] to be the thermal degradation products from both the diaquo or aquohalo-complexes, $[Co(NH_3)_4(H_2O)_2]X_3$ and $[Co(NH_3)_4(H_2O)X]X_2$ ($X = Cl$, Br). According to Mori *et al.*[5], the products were the *cis*-isomers. However, Lemay and Bailar[6] found that the product, *cis*-$[Co(NH_3)_4Cl_2]Cl$, obtained from the deaquation of the diaquo- or aquohalo-complexes was actually contaminated with other decomposition compounds. The reflectance spectrum of the product contained a strong absorption band in the 600–700 nm region which was due to the presence of the $[CoCl_4]^{2-}$ ion. The *cis*-$[Co(NH_3)_4Br_2]Br$ complex is even more difficult to obtain by the analogous thermal deaquation reaction because the two bromide ions in the *cis*-position put an even greater steric strain on the structure than do the chloride ions. Chang and Wendlandt[7,8] found that in most cases, *cis*-dihalobis(ethylenediamine)cobalt(III) complexes were the main products in the thermal deaquation of the diaquo- or aquohalo-complexes.

Several *cis*→*trans* thermal isomerization reactions have been reported for *cis*-$[Co(NH_3)_4Cl_2]Cl$[4,9]. The reverse reaction, *trans*→*cis*, has been reported for *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$[6,10], and was interpreted in terms of an aquation–anation reaction sequence. For the chromium(III) complex, *trans*-$[Cr(NH_3)_4(H_2O)Br]Br$, the *cis*-isomer was formed by heating it at 153°C[11].

The subject of this investigation is two-fold: (1) the thermal properties of some diaquo- and aquohalotetramminecobalt(III) complexes; and (2) the thermal solid–solid and gas–solid *trans*-preferred reactions of these complexes with ammonium salts and various gases. In the former investigation, *cis*-$[Co(NH_3)_4(H_2O)X]X_2$ ($X = Cl$, Br) was the deaquation product from the diaquo- complexes, as previously reported[4]. Efforts to obtain the pure *cis*-dichloro-, chlorobromo-, and dibromotetrammine-complexes were unsuccessful. For the latter investigation, the reaction of $[Co(NH_3)_4(H_2O)_2](NO_3)_3$ with NH_4Cl and NH_4Br, gave *trans*-$[Co(NH_3)_4Cl_2]Cl$ and *trans*-$[Co(NH_3)_4Br_2]Br$, respectively. Likewise, analogous thermal reactions of $[Co(NH_3)_4(H_2O)_2]X_3$, *cis*-$[Co(NH_3)_4(H_2O)X]X_2$ ($X = Cl$, Br), and *cis*-$[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O$, with NH_4NO_3 all resulted in the formation of the *trans*-$[Co(NH_3)_4X_2]NO_3$ complexes. Gas–solid reactions of the above complexes all gave *trans*-$[Co(NH_3)_4Cl_2]NO_3$ as the intermediate followed by the formation of the dinitrato-complex, *trans*-$[Co(NH_3)_4(NO_3)_2]NO_3$, as the final product.

EXPERIMENTAL PART

Preparation of compounds

The diaquo-complexes, $[Co(NH_3)_4(H_2O)_2]X_3$ ($X = NO_3$, Br), were prepared by the addition of HNO_3 or HBr to $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$. The reddish colored compounds precipitated immediately upon the addition of the acid and were filtered off, washed with 95% ethanol, diethyl ether, and dried at room temperature in air. The chloride complex, $[Co(NH_3)_4(H_2O)_2]Cl_3$, was prepared in a similar manner except that $[Co(NH_3)_4CO_3]Cl$ was employed as the starting material. The compounds, $[Co(NH_3)_4CO_3]NO_3 \cdot 0.5H_2O$ and $[Co(NH_3)_4CO_3)Cl$, were prepared by the method described by Schlessinger[12].

The haloaquo-complexes, *cis*-$(Co(NH_3)_4H_2OX]X_2$ ($X = Cl$, Br), were prepared by the thermal deaquation of the corresponding diaquo-complexes. Maximum temperatures of heating were 70 and 45°C, for the chloride and bromide complexes, respectively. The mixed halo-complexes, *cis*-$[Co(NH_3)_4H_2O\,Cl]Br_2$ and *cis*-$[Co(NH_3)_4H_2OBr]Cl_2 \cdot 0.5H_2O$, were prepared by the addition of ice-cold concentrated HBr or HCl to saturated solutions of *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$ and *cis*-$[Co(NH_3)_4H_2OBr]Br_2$, respectively. The compounds, *cis*-$[Co(NH_3)_4H_2OX](NO_3)_2$ ($X = Cl$, Br), were prepared by a similar method except that dilute HNO_3 was employed. Several hours were taken for the violet colored precipitates to separate from solution. The nitrato-complexes, $[Co(NH_3)_4H_2ONO_3](NO_3)_2$[13] and $[Co(NH_3)_4(NO_3)_2]NO_3$[14], were prepared as previously described.

Trans-$[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ was prepared by the method described by Schlessinger[12]; the anhydrous product was obtained by heating this compound at 100°C for several hours. *Cis*-$[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O$ was prepared by the method of Werner[15], as was the complex, *cis*-$[Co(NH_3)_4Cl_2]_2S_2O_6$. The compound, *trans*-$[Co(NH_3)_4Br_2]Br$, was prepared as previously described[16].

Analyses of the complexes are shown in Table I.

TABLE I

ANALYSES OF COMPLEXES

Compound	*Co(%)*		*NH₃(%)*	
	Theor.	*Found*	*Theor.*	*Found*
$[Co(NH_3)_4(H_2O)_2](NO_3)_3$	16.88	17.4	19.51	19.6
$[Co(NH_3)_4(H_2O)_2]Br_3$	14.63	14.5	16.91	16.1
$[Co(NH_3)_4(H_2O)_2]Cl_3$	21.87	22.0	25.28	24.7
$[Co(NH_3)_4H_2OCl]Cl_2$	23.44	23.6	27.09	26.8
$[Co(NH_3)_4H_2OBr]Br_2$	15.32	15.1	17.70	17.4
$[Co(NH_3)_4H_2OCl]Br_2$	17.32	17.2	20.02	20.8
$[Co(NH_3)_4H_2OBr]Cl_2 \cdot 0.5H_2O$	19.33	20.2	22.34	23.1
$[Co(NH_3)_4H_2OCl](NO_3)_2$	19.35	19.7	22.34	22.4
$[Co(NH_3)_4H_2OBr](NO_3)_2$	16.89	16.3	19.52	19.1
$[Co(NH_3)_4H_2ONO_3](NO_3)_2$	17.80	17.7	20.58	20.7
$[Co(NH_3)_4(NO_3)_2]NO_3 \cdot H_2O$	17.80	18.1	20.58	20.8
$[Co(NH_3)_4Cl]Cl_2$	25.25	25.9	29.18	28.9
$[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O$	24.31	23.9	28.10	28.5

Thermal solid–solid reactions

The mixture of solids was prepared as previously described[1] by 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 freshly prepared mixture was placed in an oven at reaction temperature; completion of the reaction was indicated by the color change (for *trans*-$[Co(NH_3)_4Cl_2]^+$ — green; for *trans*-$[Co(NH_3)_4Br_2]^+$ — yellowish green). The resulting mixture was then extracted with ethanol several times. The products were insoluble in ethanol; however, pure compounds were difficult to obtain. The purified products were identified by reflectance spectroscopy and by elemental analysis. The approximate reaction temperatures were determined either by a capillary tube method, using a Thomas–Hoover melting apparatus, or by high temperature reflectance spectroscopy (HTRS)[17].

Thermal gas–solid reactions

The procedure used was the same as that previously described[1].

Reflectance measurements

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

Mass-loss and isothermal vacuum deaquation

Mass-loss studies were performed on the DuPont thermogravimetric analyzer, Model 950. Sample sizes used ranged in mass from 4–5 mg; a heating rate of 5°C/min, and a dynamic nitrogen furnace atmosphere were employed. Low-pressure isothermal deaquation reactions were carried out by placing the weighed aquo-complexes in a vacuum oven at 90–110°C until the weight-loss corresponded to the loss of coordinated water.

RESULTS AND DISCUSSION

Mass-loss and isothermal deaquation studies

The mass-loss curves of the complexes, *cis*-$[Co(NH_3)_4H_2OCl]Br_2$, *cis*-$[Co(NH_3)_4H_2OBr]Cl_2 \cdot 0.5H_2O$, *cis*-$[Co(NH_3)_4H_2OCl](NO_3)_2$, and *cis*-$[Co(NH_3)_4H_2OBr](NO_3)_2$, are shown in Fig. 1. Under the given experimental conditions, curves A and B do not indicate intermediate mass plateaus due to the deaquation of the coordinated water. In curve C, *cis*-$[Co(NH_3)_4H_2OCl](NO_3)_2$ is found to dissociate slightly before the deaquation is completed. Only the complex in curve C, *cis*-$[Co(NH_3)_4H_2OBr](NO_3)_2$, shows complete mass-loss due to the deaquation reaction. Therefore, the preparation of the new complexes, $[Co(NH_3(_4Cl(NO_3)]NO_3$ and $[Co(NH_3)_4Br(N)_3)]NO_3$, by low pressure isothermal deaquation appears possible.

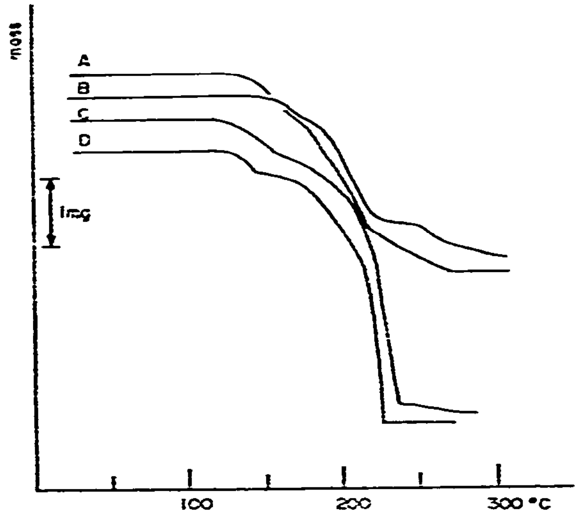


Fig. 1. Mass-loss curves of complexes. (A) *cis*-$[Co(NH_3)_4H_2OBr]Cl_2 \cdot 0.5H_2O$. (B) *cis*-$[Co(NH_3)_4H_2OCl]Br_2$. (C) *cis*-$[Co(NH_3)_4H_2OCl](NO_3)_2$. (D) *cis*-$[Co(NH_3)_4H_2OBr](NO_3)_2$.

At the present time, no attempt was made to prepare and isolate the product which would contain the *cis*- + *trans*-isomers. From curves A and B, the preparation of the dihalotetramminecobalt(III) complexes by thermal deaquation appears to be difficult.

From the low pressure isothermal deaquation reactions, bluish-violet colored deaquation products were obtained from *cis*-$[Co(NH_3)_4H_2OCl]Cl$, *cis*-$[Co(NH_3)_4H_2OCl]Br_2$, and *cis*-$[Co(NH_3)_4H_2OBr]Br_2 \cdot 0.5H_2O$; however, a dull-green colored product was obtained from *cis*-$[Co(NH_3)_4H_2OBr]Br_2$. Although the ammonia contents of all of the above suspected dihalotetramminecobalt(III) complexes were close to the calculated values, the deaquation product from *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$ exhibited the bluishviolet color characteristic of *cis*-$[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O$[12].

The reflectance spectra of all of the dihalotetramminecobalt(III) complexes, as shown in Fig. 2, indicate two common properties: (1) a strong absorption between 600–700 nm; and (2) two reflectance peaks at about 450 and 600 nm, respectively. The reflectance spectrum of *cis*-$[Co(NH_3)_4Cl_2]_2S_2O_6$ shows clearly only one absorption and one reflectance maximum at 535 and 440 nm, respectively. This complex has been shown to have the *cis*-isomeric configuration and the absorption maximum at 535 nm is in agreement with the literature[6]. Apparently, the absorption band at 600–700 nm is due to deaminated and/or a reduced product containing the ion, $[CoCl_4]^{2-}$, or its bromide analog. Neither the *cis*- or *trans*-$[Co(NH_3)_4ClBr]^+$ complexes have been successfully prepared; we can predict, however, that *cis*-$[Co(NH_3)_4ClBr]^+$ should

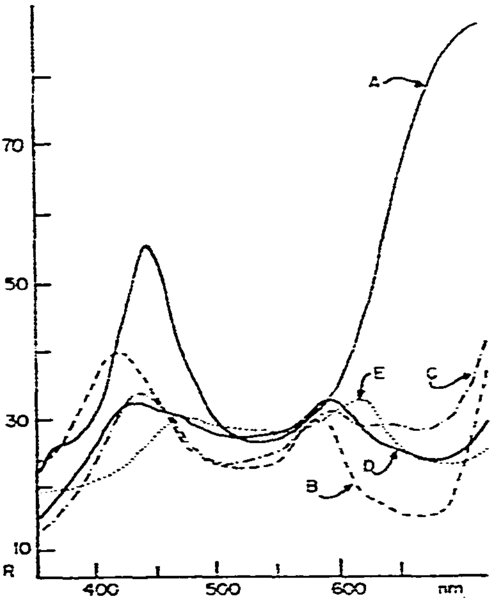


Fig. 2. Reflectance spectra of deaquation products. (A) *cis*-$[Co(NH_3)_4Cl_2]_2S_2O_6$. (B) deaquation product from *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$. (C) deaquation product from *cis*-$[Co(NH_3)_4H_2OCl]Br_2$. (D) deaquation product from *cis*-$[Co(NH_3)_4H_2OBr]Cl_2$. (E) deaquation product from *cis*-$[Co(NH_3)_4H_2OBr]Br_2$.

have a spectrum similar to *cis*-$[Co(NH_3)_4Cl_2]^+$, with a slight shifting to a higher wavelength. Therefore, the suspected *cis*-$[Co(NH_3)_4ClBr]^+$ is probably contaminated with some reduced Co(II) product. Due to the greater steric strain for two coordinated bromide ions in the *cis*-position, the possibility for the formation of *cis*-$[Co(NH_3)_4Br_2]^+$ is even more doubtful.

Solid-state trans-preferred reactions of complex nitrates

The reaction mixtures studied, the approximate reaction temperature range, and the main products are given in Table II.

TABLE II

SOLID-STATE REACTION OF COMPLEX-NITRATES

	Reaction mixture	*Temperature interval (°C)*	*Main product*
II-1	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + NH_4Cl$	90–115	*trans*-$[Co(NH_3)_4Cl_2]Cl$[a]
II-2	$[Co(NH_3)_4H_2O(NO_3)](NO_3)_2 + NH_4Cl$	90–115	*trans*-$[Co(NH_3)_4Cl_2]Cl$[a]
II-3	$[Co(NH_3)_4(NO_3)_2]NO_3 \cdot H_2O + NH_4Cl$	90–115	*trans*-$[Co(NH_3)_4Cl_2]Cl$[a]
II-4	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + NH_4Br$	110–125	*trans*-$[Co(NH_3)_4Br_2]Br$[a]
II-5	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + CH_3NH_3Cl$	75[b]	*cis*- + *trans*-$[Co(NH_3)_4Cl_2]^+$
II-6	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + (CH_3)_2NH_2Cl$	80[b]	*cis*- + *trans*-$[Co(NH_3)_4Cl_2]^+$
II-7	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + (CH_3)_3NHCl$	80[b]	*cis*- + *trans*-$[Co(NH_3)_4Cl_2]^+$
II-8	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + KCl$		no *trans*-product
II-9	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + KBr$		no *trans*-product
II-10	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + (CH_3)_4NCl$		no *trans*-product
II-11	$[Co(NH_3)_4H_2OCl](NO_3)_2 + NH_4Cl$	115–125	[c]*trans*-$[Co(NH_3)_4Cl_2]^+$
II-12	$[Co(NH_3)_4H_2OCl](NO_3)_2 + NH_4Br$	115–125	[c]*trans*-$[Co(NH_3)_4ClBr]^+$
II-13	$[Co(NH_3)_4H_2OBr](NO_3)_2 + NH_4Br$	115–125	[c]*trans*-$[Co(NH_3)_4Br_2]^+$

[a] The product was identified by reflectance and other analytical methods after purification; halide rather than nitrate in the product. [b] The reaction mixture exhibits a color change of from pink-red to almost blue (*cis*-) even at room temperature. [c] The product was identified by its reflectance spectrum

The reaction of $[Co(NH_3)_4(H_2O)_2](NO_3)_3$ with NH_4Cl, as shown by the curves in Fig. 3, indicates that *trans*-$[Co(NH_3)_4Cl_2]^+$ is formed at temperatures between 100–125 °C. The complex, $[Co(NH_3)_4(H_2O)_2]^{3+}$, has been found to undergo a *cis-trans* isomerization in solution with an equilibrium constant of 6.0 ± 0.5 at 20 °C. Apparently, the diaquotetramminecobalt(III) complexes (chloride, bromide, and nitrate) prepared here are in the *cis*- form because a precipitate is formed immediately before any isomerization occurs.

The formation of *trans*-$[Co(NH_3)_4Cl_2]^+$ from the reactions, $[Co(NH_3)_4H_2O(NO_3)](NO_3)_2 + NH_4Cl$ (II-2) and $[Co(NH_3)_4(NO_3)_2]NO_3 \cdot H_2O + NH_4Cl$ (II-3), occurs in about the same temperature ranges as the diaquo-nitrate (II-1). A slightly higher temperature is found for the reaction, $[Co(NH_3)_4(H_2O)_2](NO_3)_3 + NH_4Br$ (II-4); the green colored *trans*-$[Co(NH_3)_4Br_2]^+$ is obtained between 110–125 °C. Reaction temperatures are lower for the reactions between $[Co(NH_3)_4(H_2O)_2](NO_3)_3$

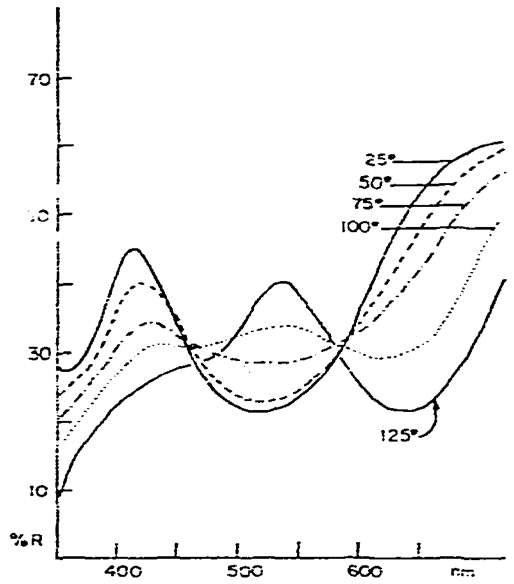


Fig. 3. Reflectance curves of $[Co(NH_3)_4(H_2O)_2](NO_3)_3+NH_4Cl$ at various temperatures.

and various onium chlorides (II-5, II-6, II-7), but these mixtures evolve liquid water so that the final mixture contains both *cis*- and *trans*-$[Co(NH_3)_4Cl_2]^+$ products. There is no *trans*-$[Co(NH_3)_4Cl_2]^+$ product from the reactions of $[Co(NH_3)_4(H_2O)_2]$-$(NO_3)_3$ with KCl or $(CH_3)_4NCl$ (II-8 and II-10); the lack of NH_4^+ ion or nitrogen bonded hydrogen is responsible for these negative results. The reactions, *cis*-$[Co(NH_3)_4H_2OCl](NO_3)_2+NH_4Cl$ (II-11), show the *trans*-preferred reaction as predicted. However, the percentage yield of the *trans*-product is lower than that for the diaquo-nitrate (II-1) reaction and higher temperatures and longer reaction times are necessary. Apparently, *cis*-$[Co(NH_3)_4H_2OCl](NO_3)_2$ is not the intermediate product from *cis*-$[Co(NH_3)_4(H_2O)_2](NO_3)_3+NH_4Cl$ (II-1) as expected. The product, *trans*-$[Co(NH_3)_4ClBr]Br$, was qualitatively identified in the reaction mixture, $[Co(NH_3)_4(H_2O)Cl](NO_3)_2+NH_4Br$ (II-13).

The reflectance maxima for *trans*-$[Co(NH_3)_4Cl_2]^+$ and *trans*-$[Co(NH_3)_4Br_2]^+$ are 535 and 563 nm, respectively. The product from (II-12) after purification showed a broad reflectance band with a maximum at 550 nm. It was not possible to obtain pure *trans*-$[Co(NH_3)_4ClBr]^+$ from the reaction (II-12) because of the rapid hydrolysis which made recrystallization impossible.

Solid-state trans-preferred reactions of complex-halides

The solid-state *trans*-preferred reactions of the complex halides are summarized in Table III. The reflectance curves of a mixture of $[Co(NH_3)_4(H_2O)_2]Cl_3+NH_4NO_3$ at various temperatures are illustrated in Fig. 4.

For the reaction illustrated in Fig. 4, the product, *trans*-$[Co(NH_3)_4Cl_2]NO_3$, is seen to be obtained between 75–100°C (85–95°C, color change observed). The reaction temperature range for the mixture, cis-$[Co(NH_3)_4H_2OCl]Cl_2+NH_4NO_3$ (III-2), was higher than that for the diaquo-chloride, namely, 100–120°C. For the

TABLE III

SOLID-STATE *trans*-PREFERRED REACTIONS OF SOME COMPLEX-HALIDES

	Reaction mixture	*Reaction temperature (°C)*	*Main product*
III-1	$[Co(NH_3)_4(H_2O)_2]Cl_3+NH_4NO_3$	85–95	*trans*-$[Co(NH_3)_4Cl_2]NO_3$[a]
III-2	*cis*-$[Co(NH_3)_4H_2OCl]Cl_2+NH_4NO_3$	100–120	*trans*-$[Co(NH_3)_4Cl_2]NO_3$[a]
III-3	*cis*-$[Co(NH_3)_4Cl_2]Cl\cdot 0.5H_2O+NH_4NO_3$	100–115	*trans*-$[Co(NH_3)_4Cl_2]NO_3$[a]
III-4	$[Co(NH_3)_4(H_2O)_2]Cl_3+KNO_2$		never changed to green
III-5	$[Co(NH_3)_4(H_2O)_2]Br_3+NH_4NO_3$	75–95	*trans*-$[Co(NH_3)_4Br_2]NO_3$[b]
III-6	*cis*-$[Co(NH_3)_4H_2OBr]Br_2+NH_4NO_3$	90–125	*trans*-$[Co(NH_3)_4Br_2]NO_3$[b]
III-7	$[Co(NH_3)_4H_2OBr]Br_2+NH_4Br$		never changed to green
III-8	$[Co(NH_3)_4(H_2O)_2]Cl_3+NaNO_3+NH_4Cl$	80–120	[c]*trans*-$[Co(NH_3)_4Cl_2]^+$
III-9	*cis*-$[Co(NH_3)_4H_2OCl]Br_2+NH_4NO_3$	~125	[c]*trans*-$[Co(NH_3)_4ClBr]^+$
III-10	*cis*-$[Co(NH_3)_4H_2OBr]Cl_2\cdot 0.5H_2O+NH_4NO_3$	~125	[d]*trans*-$[Co(NH_3)_4Cl_2]^+$ +(*trans*-$[Co(NH_3)_4ClBr]^+$)

[a] Product was identified by reflectance data and analysis for NH_3 and Cl^- after purification. [b] Product was identified by reflectance spectroscopy; pure compound was difficult to obtain. [c] Identified by reflectance. [d] Reflectance data showed *trans*-$[Co(NH_3)_4Cl_2]^+$ in final product, but *trans*-$[Co(NH_3)_4ClBr]^+$ is also believed to be present.

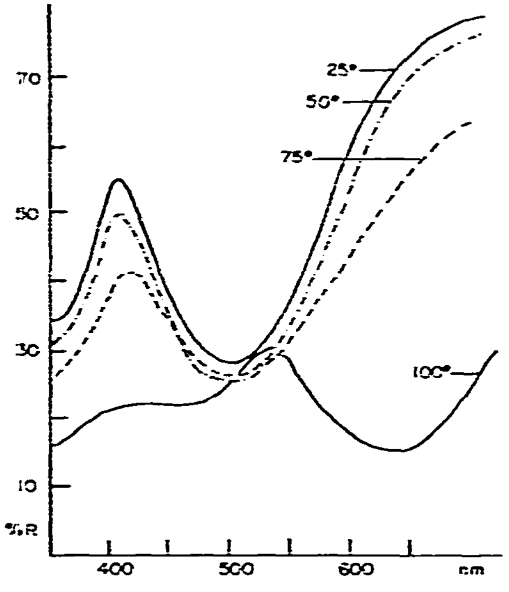


Fig. 4. Reflectance curves of a mixture of $[Co(NH_3)_4(H_2O)_2]Cl_3+NH_4NO_3$ at various temperatures.

mixture, *cis*-$[Co(NH_3)_4Cl_2]Cl\cdot 0.5H_2O+NH_4NO_3$ (III-3), the *trans*-preferred or *cis–trans* isomerization took place between 110–115°C, or slightly lower than that of reaction (III-2). By comparison with previously studied $[Co(en)_2X_2]^{n+}$ systems, the reverse order found for reactions (III-2) and (III-3) is interpreted in terms of the strong bonding of Co–OH_2 in *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$, as indicated by the evidence that higher temperatures are required for deaquation (170–200 °C). As previously mentioned[1], the bond breaking is important to obtain the trigonal bipyramid intermediate which is necessary for the *trans*-preferred reaction.

No *trans*-product was found in the products from reaction mixtures (III-4) and (III-7), because the *trans*-preferred conditions[1] were not met in those mixtures. The complex, *trans*-$[Co(NH_3)_4ClBr]NO_3$, is the product from the reaction mixtures of *cis*-$[Co(NH_3)_4H_2OCl]Br_2 + NH_4NO_3$ (III-9). From the reflectance spectra, *trans*-$[Co(NH_3)_4Cl_2]^+$ rather than *trans*-$[Co(NH_3)_4ClBr]^+$, was the final product in the mixture, *cis*-$[Co(NH_3)_4H_2OBr]Cl_2 \cdot 0.5H_2O + NH_4NO_3$ (III-10).

Gas–solid trans-preferred reactions

The reaction temperatures and products for the gas–solid reactions of the complexes are given in Table IV.

TABLE IV

GAS–SOLID *trans*-PREFERRED REACTIONS

	Reaction mixture	*Experimental temperature (°C)*[a]	*Main product*
IV-1	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + HCl(g)$	85	*trans*-$[Co(NH_3)_4Cl_2]Cl(NO_3)$[b]
IV-2	$[Co(NH_3)_4H_2ONO_3](NO_3)_2 + HCl(g)$	85	*trans*-$[Co(NH_3)_4Cl_2]Cl(NO_3)$[b]
IV-3	$[Co(NH_3)_4(NO_3)_2]NO_3 \cdot H_2O + HCl(g)$	85	*trans*-$[Co(NH_3)_4Cl_2)Cl(NO_3)$[b]
IV-4	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + HBr(g)$	85	*trans*-$[Co(NH_3)_4Br_2]Br(NO_3)$
IV-5	$[Co(NH_3)_4(H_2O)_2](NO_3)_3 + CH_3Cl(g)$	150	no effect
IV-6	$[Co(NH_3)_4(H_2O)_2]Cl_3 + HNO_3(g)$	115	*trans*-$[Co(NH_3)_4Cl_2]NO_3$[c] ↓ prolonged time *trans*-$[Co(NH_3)_4(NO_3)_2]NO_3$
IV-7	*cis*-$[Co(NH_3)_4H_2OCl]Cl_2 + HNO_3(g)$		
IV-8	*cis*-$[Co(NH_3)_4Cl_2]Cl \cdot 0.5H_2O + HNO_3(g)$		
IV-9	$[Co(NH_3)_4(H_2O)_2]Cl_3 + HCl(g)$	150	no effect
IV-10	all complexes + $NH_3(g)$	150	no effect

[a] The temperature shown is the temperature at which the experiment was performed. [b] Gaseous HCl or HBr was passed through the preheated complex, brownish gas (NO_2) and liberation of heat were observed. If HCl passed over the surface of precooled complex (~5 °C), the reaction is slow and the bluish-violet product (*cis*-$[Co(NH_3)_4Cl_2]^+$) rather than green *trans*-isomer is obtained. [c] It is difficult to judge and to stop the reaction to obtain the green *trans*-$[Co(NH_3)_4Cl_2]^+$ product.

The green colored *trans*-$[Co(NH_3)_4Cl_2]Cl$ is the major product when gaseous HCl is passed through the complex nitrates as seen in reactions (IV-1) to (IV-3). Under these conditions, the product is formed almost instantly, and a brown gas (NO_2) is evolved. The results indicate that HNO_3 is probably first formed between the HCl and the complex-nitrate which in turn acts as a catalyst for the *trans*-preferred reaction. The gas–solid reactions between HNO_3 and the complex-chlorides also produced the *trans*-dichloro products. The yellowish-green *trans*-$[Co(NH_3)_4Br_2]^+$ is also found in the product from the reaction, $[Co(NH_3)_4(H_2O)_2](NO_3)_3 + HBr$ (IV-4). There was no reaction between gaseous CH_3Cl and $[Co(NH_3)_4(H_2O)_2](NO_3)_3$; this indicates the role of H^+ ion in the *trans*-preferred reaction. A similar negative result was found in the reaction between $[Co(NH_3)_4(H_2O)_2](NO_3)_3 + (CH_3)_4NCl$ (II-10). The results from Table IV indicate that the reactions between gaseous hydrogen halides (HCl and HBr) and complex-nitrates are related to the solid-state reaction with ammonium halides (NH_4Cl and NH_4Br), reactions (III-1) to (III-4). There is no green *trans*-product formed in the reaction between gaseous HCl and $[Co(NH_3)_4(H_2O)_2]Cl_2$ (or *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$). This result again emphasizes the important role of NO_3^- in the *trans*-preferred reaction. The most interesting reactions are those between gaseous HNO_3 and the complex chlorides, reactions (IV-6) to (IV-8). As the hot gaseous HNO_3 passes over the surface of the complexes at elevated temperature, the green *trans*-dichloro product is first formed. On prolonged reaction, the red dinitrato-nitrate product is obtained. In Fig. 5, curves A and B are the reflectance spectra of $[Co(NH_3)_4(H_2O)_2]Cl_3$ and *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$ before treatment with HNO_3 gas, while curve C is the first intermediate product, *trans*-$[Co(NH_3)_4Cl_2]NO_3$. Curve D is the red colored final product, *trans*-$[Co(NH_3)_4(NO_3)_2]NO_3$, obtained after prolonged HNO_3 (g) contact with the complex. Analysis of the latter product and comparison with an authentic sample of $[Co(NH_3)_4(NO_3)_2]NO_3$ (curve E) confirm its structure and composition.

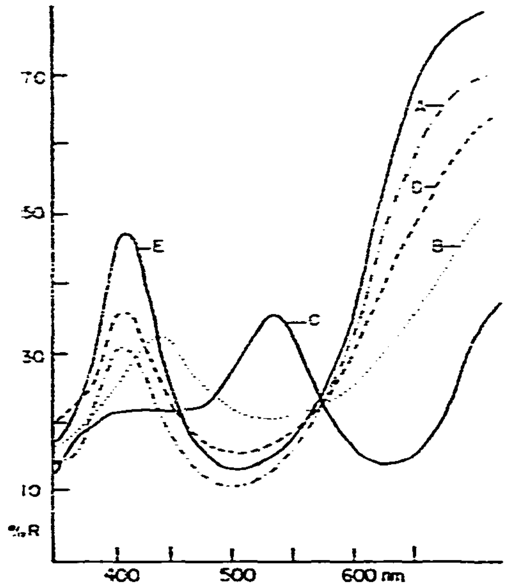
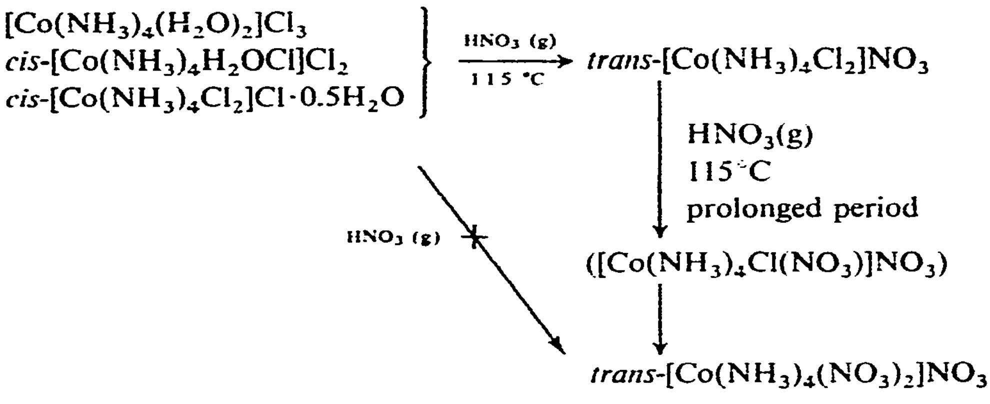


Fig. 5. Reflectance spectra of various complexes. (A) $[Co(NH_3)_4(H_2O)_2]Cl_3$. (B) *cis*-$[Co(NH_3)_4H_2OCl]Cl_2$. (C) *trans*-$[Co(NH_3)_4Cl_2]NO_3$ from (A) or (B) $+ HNO_3(g)$. (D) *trans*-$[Co(NH_3)_4(NO_3)_2]NO_3$ from (A) or (B) $+ HNO_3(g)$. (E) $[Co(NH_3)_4(NO_3)_2]NO_3$ prepared from literature.

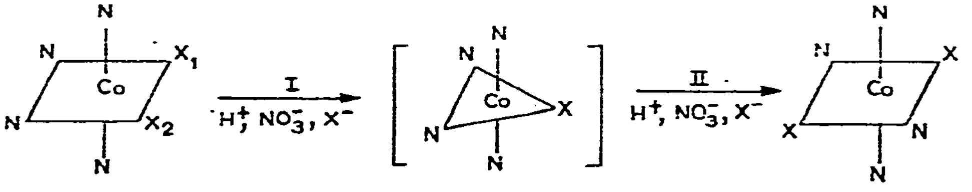
The *trans*-preferred and *cis–trans* isomerization reactions can be summarized as follows:



The other possible intermediate, $[Co(NH_3)_4Cl(NO_3)]NO_3$, was not isolated so its existence is uncertain.

Mechanism of trans-preferred reactions

According to previous reports in this series[1,2], *trans*-dihalo products can be obtained in all cases if both the proton (from HCl, HNO_3, NH_4NO_3, or NH_4Cl) and nitrate ions are present. It has been proposed that dissociation to a trigonal bipyramid transition state probably occurs in all of the *trans*-preferred reactions, according to the reaction:



where X_1, X_2 = H_2O, NO_3^-, Cl^-, or Br^-, *etc.*; X^- = Cl^-, Br.

In this proposed mechanism, $H^+NO_3^-$ (or $NH_4^+NO_3^-$) is necessary for two reasons: (1) to cause the formation of a trigonal bipyramid cobaltium ion, and (2) to induce the entering halide ion to attack the nitrogen–nitrogen (*trans*-effect). The $H^+NO_3^-$ (or $NH_4^+NO_3^-$) obviously plays an important role in the *trans*-preferred reaction, but the actual orientation of H^+ and NO_3^- in the transition state is unknown; it presumably associates to the coordinated chloride through a hydrogen bond. Such a mechanism has frequently been employed to interpret *cis–trans* transformations in octahedral complex reactions. Very few of these mechanisms can satisfactorily explain why the entering group favors the *trans*-addition following the transition state (theoretically only 1/3 enter this edge). A high temperature is usually required for *trans*-preferred reactions which means that enough energy has to be supplied for the formation of trigonal bipyramid transition states.

CONCLUSIONS

The replacement of coordinated chloride ions by nitrate ions in the complexes, *cis*-$[Co(NH_3)_4Cl_2]Cl$ (or *cis*-$[Co(en)_2Cl_2]Cl$), has to be via a *cis–trans* isomerization reaction in gas–solid reactions. The whole problem is simply that the *trans*-preferred or *cis–trans* isomerization reaction is nothing more than an intermediate step to form a suitable orientation of the coordinated chlorides (*cis* → *trans*) for further substitution by nitrate ions. The identification of the products from the solid-state (or gas–solid) heterogeneous reactions are more qualitative than quantitative. However, when chemical reactions occur which involve two solids, the progress of the chemical change is a complex process which depends upon the area and defect structure of contact areas between the reactants. Furthermore, for many solid–solid reactions, the product formed may have different properties from those prepared by other chemical methods due to different concentrations of defects and different crystalline structures[18]. For solid–solid reactions of coordination compounds, the structure of the coordination sphere is easily identified by reflectance spectroscopy; it is much more difficult to identify the ions in the outer sphere by this technique.

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