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# Preparation, Isomerization, and Aquation of the (*cis*-β-Dichlorotriethylenetetramine)chromium(III) Cation

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The reaction of $[Cr(N)_4ox]^+$ complexes ($(N)_4$ = $(en)_2$ or trien)[1] with HCl in anhydrous solution is shown to be a general synthetic route to the *cis*-$[Cr(N)_4Cl_2]^+$ series and is used to prepare previously unreported *cis*-β-$[Cr(trien)Cl_2]^+$. This ion is characterized through electronic and infrared spectroscopy. Chloride aquation of *cis*-β-$[Cr(trien)Cl_2]^+$ is extremely rapid and is shown to occur via two simultaneous pseudo-first-order reactions ($k_{fast} = 3.0 \times 10^{-2}$ s$^{-1}$ and $k_{slow} = 5.0 \times 10^{-3}$ s$^{-1}$ at 0 °C). The different aquation rates are pH independent (between pH 1 and pH 3) and result from the presence of two geometric isomers (*SS*(*RR*) and *SR*(*RS*)) of *cis*-β-$[Cr(trien)Cl_2]^+$. Facile isomerization between the cis-β and cis-α forms is observed in the presence of water, and the intermediacy of the aquochloro ions is proposed. The rapid rate of chloride aquation is discussed, and an explanation, based on trans attack of water, is proposed.

## Introduction

As part of a study of the photochemistry of transition metal–amine complexes, our attention was drawn to the ions of the series *cis*-$[Cr(N)_4Cl_2]^+$ ($(N)_4$ = $(NH_3)_4$, $(en)_2$, or trien).[1] Despite the recent interest in the stereochemical consequences of transition metal photolysis, especially about the characteristically photoreactive Cr(III) center, only two members of this series, *cis*-$[Cr(en)_2Cl_2]^+$ [2] and *cis*-α-$[Cr(trien)Cl_2]^+$,[3] have been well characterized. Despite several reports of its existence,[4] the parent ion, *cis*-$[Cr(NH_3)_4Cl_2]^+$, is not well characterized, and while Garner[3,5] and co-workers have thoroughly studied *cis*-α-$[Cr(trien)Cl_2]^+$, there have been no reports of the isomeric cis-β ion. Even the syntheses of the known ions *cis*-$[Cr(en)_2Cl_2]^+$ [2] and *cis*-α-$[Cr(trien)Cl_2]^+$ [3] proved cumbersome and unreliable, so a more general synthetic route was sought.

Before photochemical studies could proceed, a thorough knowledge of the aqueous chemistry of these ions was essential, so the solution behavior of the previously unreported *cis*-β-$[Cr(trien)Cl_2]^+$ ion was studied. The ion displayed a rich and puzzling solution chemistry, substantially different from that of the cis-α isomer, and a kinetic study was undertaken in order to quantify the differences.

## Experimental Section

**Preparation of Complexes. Oxalato Complexes.** Established methods were used to prepare $[Cr(en)_2ox]Br$[6] and α-$[Cr(trien)ox]Br$.[3] The α configuration has been assigned to $[Cr(trien)ox]^+$ on the basis of infrared spectra;[3] the preparative methods and infrared spectra of the complexes used here were similar to those reported[3] and are consistent with the α configuration.

Two general reaction schemes were used. In the first, the appropriate oxalato complex was suspended in freshly distilled, dry methanol. Dry HCl gas was bubbled through the stirred suspension for 4–6 h, and the suspension changed from a deep red to purple. Upon cooling at 0 °C, the chloride salt of the dichloro complex precipitated.

A second technique involved the reaction of the appropriate oxalato complex with HCl generated upon the water-induced decomposition of the thionyl chloride solvent. This proved to be the more convenient method and details are given below. No difference could be detected between the complexes prepared in these two media.

**(*cis*-Dichlorobis(ethylenediamine))chromium(III) Perchlorate.** A solid sample of $[Cr(en)_2ox]ClO_4$ (1.0 g) was added to thionyl chloride (50 mL) in a 100-mL Erlenmeyer flask. The solution was vigorously stirred with a magnetic stirring bar for a few minutes, and about 1 mL of water was added a drop at a time (20–25 drops). Within 10 min the red solution cleared, leaving an immiscible purple oil; stirring was stopped and the solution was allowed to sit for an additional 10 min. The thionyl chloride was decanted from the purple oil, and a cold $HClO_4$ solution (0.1 N, 3–4 mL) was added to dissolve the oil. This solution was quickly filtered into a prechilled solution of $NaClO_4$ (8 N, 5–6 mL at 0 °C). After ca. 20 min at 0 °C the precipitate was collected by filtration, washed with ethanol and ether, and air-dried; yield 0.57 g (ca. 60%).

Anal. Calcd for $C_4H_{16}N_4Cl_2Cr(ClO_4)$: Cr, 15.2; Cl(free), 20.7. Found: Cr, 15.1; Cl, 20.5. The electronic absorption spectrum (maxima at 530 nm (ε 71) and 402 nm (ε 70)) and infrared spectra agreed with published values[7] and with those of an independently prepared sample.[2]

**(*cis*-α-Dichlorotriethylenetetramine)chromium(III) Perchlorate.** Reaction of α-$[Cr(trien)ox]ClO_4$ with $SOCl_2$ and $H_2O$, followed by crystallization from aqueous 8 M $NaClO_4$, with a procedure virtually identical with that used for the preparation of *cis*-$[Cr(en)_2Cl_2]ClO_4$ was used. Yields varied between 70 and 75%.

Anal. Calcd for $C_6H_{18}N_4Cl_2Cr(ClO_4)$: Cr, 14.1; Cl(free), 19.2. Found: Cr, 14.1; Cl, 19.2. The same species can be prepared by recrystallization (from an acidified solution of $NaClO_4$) of either *cis*-α-$[Cr(trien)Cl_2]Cl\cdot H_2O$ or *cis*-β-$[Cr(trien)Cl_2]Cl$.

The chloride monohydrate salt reported by Garner[3] could be prepared by a similar procedure; after decantation of the thionyl chloride, the remaining oil was dissolved in concentrated HCl (10 mL) and poured into dry methanol (100 mL). After 18 h at −10 °C, the flat purple crystals were collected by filtration, washed with ethanol and ether, and air-dried; yield ca. 30%. The electronic (see Table I) and infrared spectra agreed with the reported spectra.[7]

**(*cis*-β-Dichlorotriethylenetetramine)chromium(III) Chloride.** The starting material, α-$[Cr(trien)ox]Br$ (0.50 g), was reacted in thionyl chloride as described above; after decantation of the thionyl chloride the purple oil was dissolved in ca. 75 mL of dry methanol which had previously been saturated with gaseous HCl. After 1 h at −10 °C, the purple powder which precipitated was collected by filtration, washed with ethanol and ether, and air-dried; yield 0.27 g (ca. 70%).

Anal. Calcd for $C_6H_{18}N_4Cl_3Cr$: Cr, 17.1; Cl, 34.9. Found: Cr, 16.9; Cl, 34.6.

The same product formed when finely ground α-$[Cr(trien)ox]Br$ was added to freshly dried methanol, and dry HCl gas was bubbled through the suspension for 4 h at room temperature; the purple solid which separated upon cooling (yield ca. 80%) was indistinguishable from that prepared in thionyl chloride.

**Kinetics.** Rates of decomposition of *cis*-β-$[Cr(trien)Cl_2]^+$ at 0 °C were followed spectrophotometrically by monitoring the decrease in absorption at 590 nm, using a Cary 118 recording spectrophotometer. The cell block and solvents were cooled in a $H_2O/MeOH$ bath held at 0 °C (±0.5 °C) with a Lauda K-2/R cooler. Reliable spectra could be recorded within 15 s of dissolution of the complex, and spectra were recorded for 5–7 half-lives. Chloride release was monitored directly using a PHM64 pH-mV meter (Radiometer) and a F1012Cl chloride-sensitive electrode. Reliable measurements could be made within 30 s of dissolution. Adjustments in ionic strengths were made with $NaClO_4$, and pH was adjusted with $HClO_4$.

Each reported rate constant is the average of at least three separate experiments, with more than three experiments necessary when individual rate constant values differed by more than 15%. The initial aquation occurred quickly, so rapid attainment of a homogeneous solution of *cis*-β-$[Cr(trien)Cl_2]^+$ was an experimental problem

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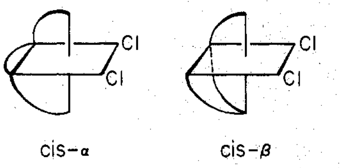


**Figure 1.** *cis*-α- and *cis*-β-$[Cr(trien)Cl_2]^+$.

throughout the kinetic studies, and the solubility properties of the ion prevented the study of a broader range of pH and ionic strength solutions.

**Reagents.** Reagent grade thionyl chloride (Erba RP or Fisher Scientific) was used without purification. Methanol was dried by the method described by Vogel[8] and used immediately after distillation. Gaseous HCl was generated by the addition of concentrated HCl to concentrated $H_2SO_4$.[8] Commercial triethylenetetramine (Eastman) was precipitated as the tetrahydrochloride salt, which served to separate the trien from the common contaminant β,β′,β″-triaminotriethylamine (tren).[9]

Electronic absorption spectra were recorded on a Beckman DB or Cary 118 recording spectrophotometer, while optical densities (elemental analyses) were measured with a Beckman DB. Reflectance spectra, in the visible region, were obtained with a Beckman DK-1A recording spectrophotometer, with MgO used as a reference. Infrared spectra were taken as Nujol mulls between KBr plates on a Perkin-Elmer 257 grating spectrophotometer, calibrated against polystyrene.

**Analyses. Chloride Ion.** The complex salts were decomposed in NaOH solution. The acidified samples were potentiometrically titrated with $AgNO_3$ solution, using a silver electrode and a Radiometer TTT 1c automatic titrator.

**Chromium.** Chromium analyses were performed by alkaline/$H_2O_2$ oxidation of the complexes to $CrO_4^{2-}$, which was determined by the intensity of its absorption at 372 nm ($\epsilon$ 4750 $M^{-1}$ $cm^{-1}$).

## Results

**Preparation of Complexes.** The reaction of oxalato complexes with HCl (eq 1) proceeds smoothly in methanol or

$$[Cr(N)_4ox]^+ + 2HCl \xrightarrow[SOCl_2]{MeOH\ or} cis\text{-}[Cr(N)_4Cl_2]^+ + H_2ox \qquad (1)$$

thionyl chloride and provides a convenient pathway into the *cis*-$[Cr(N)_4ox]^+$ series (see Experimental Section). The reaction in methanol is an example of a well-established route to *cis*-dichlorotetramine compounds which takes advantage of the cis configuration of the starting oxalato complexes.[10] Anhydrous media must be used to prevent formation of the aquochloro ion, and $SOCl_2$ is an especially convenient solvent, for it is widely used as a dehydrating agent both in organic reactions and in the preparation of anhydrous metal chlorides from the hydrated forms.[11] Thionyl chloride offers the following advantages: (a) it dissolves the oxalatotetramine starting materials, while the dichloro products separate as an immiscible oil, (b) its rapid reaction with water makes it an exceedingly anhydrous solvent, preventing aquochloro ion contamination, and (c) the reaction of thionyl chloride with water (eq 2) provides a homogeneous source of the HCl re-

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl \qquad (2)$$

quired for the formation of *cis*-dichloro complexes.

Attempts to dehydrate $[Cr(NH_3)_5H_2O](NO_3)_3$ by refluxing it in thionyl chloride (60 min) were unsuccessful, presumably due to the inability of the electrophilic thionyl chloride to attack the oxygen of the coordinated water molecule. There is no apparent reaction of pure thionyl chloride with coordinated oxalate in complexes of the form $[Cr(N)_4ox]^+$. Addition of water causes immediate reaction, however, suggesting that the hydrochloric acid, generated in the decomposition of the thionyl chloride, is the reactive species.

**Identification of Compounds.** While a unique cis configuration exists for $[Cr(en)_2Cl_2]^+$, there are two obvious geometric isomers possible for a complex with the quadridentate amine trien (Figure 1). The cis-β and cis-α isomers of $[Cr(trien)Cl_2]^+$ can be distinguished by their electronic and infrared spectra, and by their solution chemistry.

**Table I.** Features in the Visible Absorption Spectra of Some Cis-Disubstituted Chromium(III)-Amine Complexes

| Complex | λ, nm (ε) λmax | λmin | λmax | Ref |
|---|---|---|---|---|
| *cis*-α-$[Cr(trien)Cl_2]^+$ [b] | 535 (97.2) | 455 (28.8) | 396 (90.5) | *a* |
| | 534 (95.5) | 455 (28.5) | 396 (86.7) | 3 |
| *cis*-β-$[Cr(trien)Cl_2]^+$ [c] | 542 (100) | 461 (35) | 403 (85) | *a* |
| *cis*-β-$[Cr(trien)Cl_2]Cl$ [d] | 538 | 458 | 402 | *a* |
| *cis*-α-$[Cr(trien)Cl(H_2O)]^{2+}$ [b] | 515 (83.5) | 440 (25.7) | 385 (56.2) | 5 |
| *cis*-$[Cr(trien)Cl(H_2O)]^{2+}$ [b] | 518 (105) | 442 (38) | 391 (70) | *a*, *e* |

[a] This work. [b] Chloride salt in 0.1 N HCl. [c] Methanol solution. [d] Reflectance spectrum of powdered sample. [e] Spectrum obtained within 5 min of the dissolution of *cis*-β-$[Cr(trien)Cl_2]^+$ in 0.1 N HCl at room temperature.

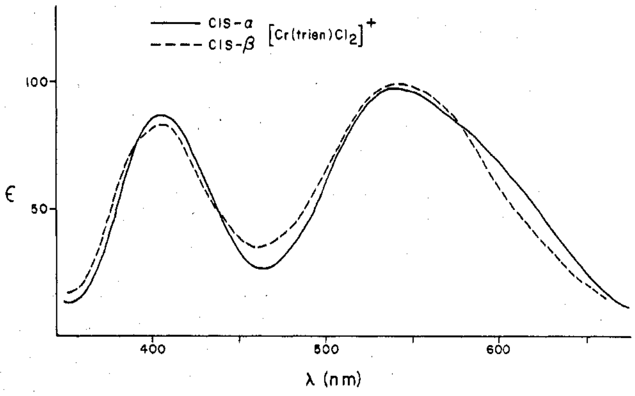


**Figure 2.** Visible absorption spectra of *cis*-α- (in aqueous solution) and *cis*-β-$[Cr(trien)Cl_2]^+$ (in methanol).

**Electronic Spectra.** The principal features of the electronic spectra of *cis*-$[Cr(N)_4Cl_2]^+$ ions are given in Table I and are compared to previously reported values for similar compounds. Assignment of the cis configuration is qualitatively straightforward, for the purple cis complexes ($\lambda_{max}$ ca. 535 nm) are easily distinguished from the green ($\lambda_{max}$ ca. 610 nm) trans isomers. The lowest energy ligand field band ($^4T_{2g} \leftarrow {}^4A_{2g}$ in an $O_h$ field) should be split upon descent to quadrate symmetry, due to the splitting of the $^4T_2$ state into the $^4E$ and $^4B_2$ states. While this splitting is large and observable for trans-disubstituted complexes, it is expected to be about half as large for cis complexes.[12] For the simplest ion, *cis*-$[Cr(NH_3)_4Cl_2]^+$, the two lowest energy ligand field transitions have been predicted to occur at 575 and 514 nm.[12] These bands may not be resolved in solution, however, and should appear as one broad band near 540 nm. Just such a visible spectrum is observed for *cis*-β-$[Cr(trien)Cl_2]^+$, consistent with the proposed *cis*-$[Cr(N)_4Cl_2]^+$ chromophore.

The electronic absorption spectra of *cis*-β- and *cis*-α-$[Cr(trien)Cl_2]^+$ are shown in Figure 2. Increased asymmetry generally leads to increased oscillator strengths for such ligand field bands, and the molar absorptivity coefficients for these cis complexes are larger than those for the more symmetric trans isomers. The additional asymmetry and stereochemical strain induced by the quadridentate trien ligand is reflected in the relatively large $\epsilon$ values for the *cis*-$[Cr(trien)Cl_2]^+$ ions, compared with that of the ethylenediamine analogue.[7] The shoulder on the long-wavelength side of the first ligand field band for *cis*-α-$[Cr(trien)Cl_2]^+$, presumably due to the splitting of the lowest energy, spin-allowed excited states in $O_h$ sym-

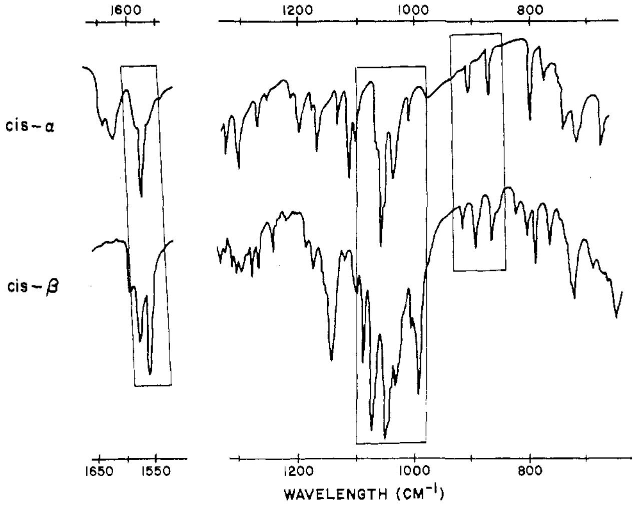


**Figure 3.** Infrared spectra of *cis*-α- and *cis*-β-[Cr(trien)Cl$_2$]Cl.

**Table II.** Diagnostic Infrared Spectral Regions for Distinguishing the α and β Isomers of *cis*-[Cr(trien)Cl$_2$]Cl

| Wavelength, cm$^{-1}$ | Assignment | Cis-α | Cis-β |
|---|---|---|---|
| 1560–1600 | Asym NH$_2$ band | 1 (s) | 2 (s-med, sp) |
| 980–1100 | CH$_2$ or NH$_2$ twist | 2–3 (s) | 4–5 (s-med) |
| 860–940 | CH$_2$ rock | 2 (med) | 4- (med) |

[a] Abbreviations: s, strong; med, medium; sp, splitting.

metry, is characteristic of *cis*-α-[M(trien)Cl$_2$]$^+$ (M = Co,[13] Rh,[14] Cr[3]) complexes. No such shoulder is observed for *cis*-β-[Cr(trien)Cl$_2$]$^+$, again consistent with the electronic spectra of the analogous Co(III) and Rh(III) complexes.

**Infrared Spectra.** Infrared spectra provide strong support for these assignments, and the spectra of *cis*-α- and *cis*-β-[Cr(trien)Cl$_2$]Cl are shown in Figure 3. The diagnostic regions, as summarized by Garner,[3] for distinguishing between the cis-α and cis-β complexes are outlined in Table II. The differences in these spectra occur in precisely the diagnostic regions, and unambiguously support the assignment of the cis-α and cis-β configurations.

**Rate of Aquation.** The most dramatic difference which distinguishes *cis*-β-[Cr(trien)Cl$_2$]$^+$ from the cis-α isomer is the rate of chloride aquation. A kinetic study of the first aquation step of cis-β-[Cr(trien)Cl$_2$]$^+$ (vide infra) shows that this species aquates several orders of magnitude more rapidly than the cis-α isomer. At room temperature, an initially purple solution of cis-β-[Cr(trien)Cl$_2$]$^+$ becomes pink (aquochloro ion) within 30 s, even in very acidic solutions. A corresponding solution of *cis*-α-[Cr(trien)Cl$_2$]$^+$ remains purple for at least 1 h under the same conditions.

**Isomerization of *cis*-β-[Cr(trien)Cl$_2$]$^+$.** The [Cr(trien)ox]$^+$ used as the starting materials throughout has been assigned the α configuration[3] (see Experimental Section), yet after reaction with HCl (generated in thionyl chloride) the resulting purple oil contains *cis*-β-[Cr(trien)Cl$_2$]$^+$; a methanol solution of the oil has an electronic spectrum indistinguishable from that of the isolated cis-β complex, and when the oil is dissolved in acidic aqueous solution, its electronic spectrum is that of *cis*-[Cr(trien)Cl(H$_2$O)]$^{2+}$ within 30 s. Such rapid aquation is uniquely characteristic of the cis-β isomer, so if the assignment of the α configuration for [Cr(trien)ox]$^+$ is correct,[3] then isomerization about the Cr center must occur during its reaction with HCl.

The presence of water in the solvent medium has a marked effect on the configuration of the dichloro complex eventually isolated from the purple oil. If dry methanol, saturated with dry HCl gas, is added to the purple oil, *cis*-β-[Cr(trien)Cl$_2$]Cl precipitates. If even small amounts of water are present (4 mL of 37% HCl solution (concentrated HCl) and 100 mL of dry methanol), *cis*-α-[Cr(trien)Cl$_2$]Cl·H$_2$O separates from the solution. In the latter case, the electronic spectrum of the mother liquor shows it to contain *cis*-β-[Cr(trien)Cl]$^+$, and the addition of water causes rapid aquation of the complex. This confirms that the cis-β isomer remains the predominant species in the methanolic solution, even though cis-α-[Cr(trien)Cl$_2$]Cl·H$_2$O had precipitated from that solution. With perchlorate as the precipitating anion, similar results were observed; *cis*-α-[Cr(trien)Cl$_2$]ClO$_4$ separates from aqueous solution, but *cis*-β-[Cr(trien)Cl$_2$]ClO$_4$ precipitates from a dry methanol solution. These results are summarized in reactions 3–7.

$$\alpha\text{-}[Cr(trien)ox]^+ \xrightarrow[\text{MeOH or } SOCl_2]{HCl\ (dry)} cis\text{-}\beta\text{-}[Cr(trien)Cl_2]^+ \qquad (3)$$

$$cis\text{-}\beta\text{-}[Cr(trien)Cl_2]^+ \begin{cases} \xrightarrow[MeOH]{HCl_{(g)}} cis\text{-}\beta\text{-}[Cr(trien)Cl_2]Cl & (4) \\ \xrightarrow[MeOH]{LiClO_4} cis\text{-}\beta\text{-}[Cr(trien)Cl_2]ClO_4 & (5) \\ \xrightarrow[MeOH]{HCl_{(aq)}} cis\text{-}\alpha\text{-}[Cr(trien)Cl_2]Cl\cdot H_2O & (6) \\ \xrightarrow[H_3O^+]{NaClO_4} cis\text{-}\alpha\text{-}[Cr(trien)Cl_2]ClO_4 & (7) \end{cases}$$

Attempts to recrystallize *cis*-β-[Cr(trien)Cl$_2$]Cl from aqueous solution as the perchlorate salt were unsuccessful, for when *cis*-β-[Cr(trien)Cl$_2$]Cl is dissolved in 0.1 N H$_2$SO$_4$ and quickly (within 20 s) filtered into an iced, acidic solution of NaClO$_4$, the crystalline product which forms within minutes is cis-α-[Cr(trien)Cl$_2$]ClO$_4$. This is consistent with reaction 7 and shows that interconversion between the cis-α and cis-β configurations occurs in the nonaqueous solvents methanol and thionyl chloride (reactions 3–5), while isomerization to the cis-α form occurs only in the presence of water (reactions 6 and 7).

**Reaction of *cis*-β-[Cr(trien)Cl$_2$]$^+$ in Acidic Solution.** Dissolution of *cis*-β-[Cr(trien)Cl$_2$]$^+$ in aqueous solution (pH <4) causes rapid changes in the electronic spectra. There is a blue shift in the lowest energy ligand field band which is consistent with replacement of a chloride ligand by a water molecule. There is no detectable interference from cis–trans isomerization or other secondary processes, and the electronic spectrum of the product ($\lambda_{max}$ ca. 518 nm) is consistent with the formation of *cis*-[Cr(trien)Cl(H$_2$O)]$^{2+}$.

A chloride-sensitive electrode was used to demonstrate that the reaction leads to the release of chloride ions and that one chloride ion is released per initial ion of *cis*-β-[Cr(trien)Cl$_2$]$^+$. No pH changes could be detected during the course of the reaction, so that no substantial amine aquation can be occurring (less than 2% Cr–N bond cleavage). These results demonstrate that the reaction is simply the aquation of a chloride ligand from *cis*-β-[Cr(trien)Cl$_2$]$^+$ (eq 8).

$$cis\text{-}\beta\text{-}[Cr(trien)Cl_2]^+ + H_2O \xrightarrow{H^+} cis\text{-}[Cr(trien)Cl(H_2O)]^{2+} + Cl^- \qquad (8)$$

The electronic spectra showed the aquochloro product to be in the cis configuration, but attempts to isolate it as a solid and to characterize the ligand configuration in the reaction product were unsuccessful.

At room temperature, the aquation of *cis*-β-[Cr(trien)Cl$_2$]$^+$ is complete within minutes, so the kinetics of the reaction were studied near 0 °C. The rate of chloride loss was measured by monitoring changes in the electronic spectra and by using a chloride-sensitive electrode to follow the growth of free chloride ions in solution. Figure 4 shows a semilogarithmic plot of $(A_t - A_\infty)$ vs. time, with $A$ representing the optical density at 590 nm. Such simple aquations usually yield linear

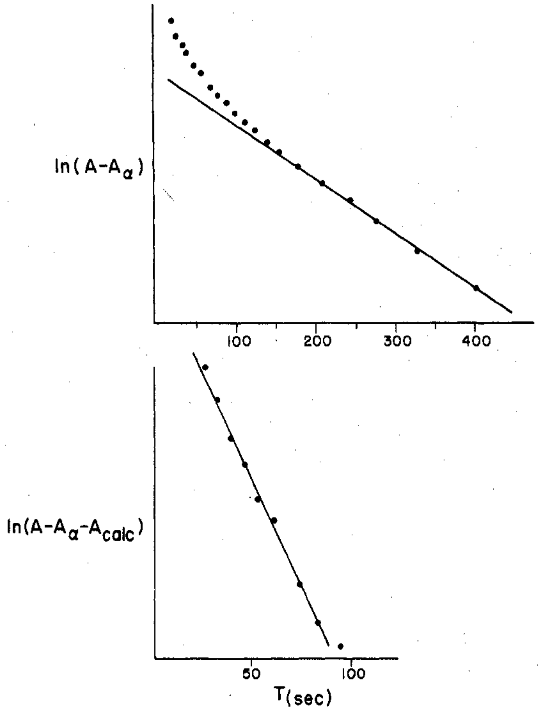


**Figure 4.** Typical kinetic plots for the aquation of *cis*-β-$[Cr(trien)Cl_2]^+$ at 0 °C.

**Table III.** Kinetic Data for the Aquation of *cis*-β-$[Cr(trien)Cl_2]ClO_4$ at 0–1 °C

| $[H^+]$, M | μ, M | $10^3k_{fast}$ | $10^3k_{slow}$ | $k_{fast}/k_{slow}$ | Technique[a] |
|---|---|---|---|---|---|
| 0.001 | 0.1 | 28.3 | 4.73 | 6.6 | S |
| 0.01 | 0.1 | 30.7 | 4.98 | 6.2 | S |
| 0.1 | 0.1 | 32.8 | 5.2 | 6.5 | S |
| 0.001 | 0.1 | 33.4 | 4.91 | 6.8 | Cl |
| 0.01 | 0.1 | 32.6 | 5.13 | 6.4 | Cl |
| 0.1 | 0.1 | 30.1 | 5.29 | 5.7 | Cl |
| 1.0 | 1.0 | 49.5 | 4.75 | 10.4 | Cl |
| 0.01 | 1.0 | 49.2 | 4.68 | 10.5 | Cl |

[a] S = rate determined by Δ*A* at 590 nm; Cl = chloride-sensitive electrode.

plots, indicating pseudo-first-order behavior, but it is clear from Figure 4 that pseudo-first-order behavior is not observed for reaction 8 until after about 100 s has elapsed. The deviations from first order are readily shown to be due to another, faster reaction which occurs during the first 100 s.[15] After subtraction of the spectral changes due to the slower, first-order reaction, the faster reaction also gives linear plots, indicative that it is also a pseudo-first-order process. Similar results were yielded by the measurements with the chloride-sensitive electrode, and the kinetic data are summarized in Table III.

Both reactions are only slightly pH sensitive between pH 1 and 3, and the ratio of rate constants ($k_{fast}/k_{slow}$) averaged ca. 6.4 throughout this pH range (at $\mu = 0.1$). At a higher ionic strength ($\mu = 1.0$) both reactions are still pH insensitive, but the change in ionic strength affects the faster reaction more dramatically than the slower reaction, their ratio increasing to ca. 10.5.

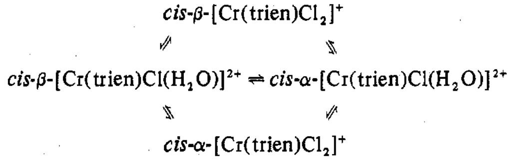
## Discussion

The experimental results reveal two notable exceptions to the current models[7] for the chemistry of chromium(III)–amine complexes, i.e., the facile isomerizations between the cis-α and cis-β forms of $[Cr(trien)Cl_2]^+$ and the unusually rapid aquation of cis-β-$[Cr(trien)Cl_2]^+$.

**Cis-α ⇌ Cis-β Isomerization.** Extensive molecular rearrangements have been noted during substitutions at Cr(III) centers in such nonaqueous media as $Me_2SO$, DMF,[16] and liquid ammonia.[17] The isomerization which accompanies the reaction of *cis*-α-$[Cr(trien)ox]^+$ to *cis*-β-$[Cr(trien)Cl_2]^+$ (reaction 3) represents another example of the stereomobility of Cr(III) complexes in nonaqueous media; such stereomobility contrasts with the well-documented stereorigidity of chromium(III) amines in aqueous solution.[18]

The details of this nonaqueous stereomobility are unknown, for it is not a general phenomenon. Once formed, for example, the $[Cr(trien)Cl_2]^+$ ions are resistant to further isomerization in anhydrous media. No isomerization was observed between the cis-α and cis-β forms of $[Cr(trien)Cl_2]^+$ after methanolic solutions of each isomer were refluxed for 6 h or after solid samples of each isomer were held at 120 °C for 24 h. In the presence of water, however, *cis*-β-$[Cr(trien)Cl_2]^+$ isomerizes rapidly to the cis-α form (reactions 6 and 7).

The lack of isomerization under dry conditions and the facile isomerization in the presence of even low concentrations of water suggest a crucial role for water in the isomerization. One possibility, represented in reaction 9, is that water is needed



$$\begin{tikzcd} & cis\text{-}\beta\text{-}[Cr(trien)Cl_2]^+ \arrow[dl, shift left, harpoon] \arrow[dr, harpoon] & \\ cis\text{-}\beta\text{-}[Cr(trien)Cl(H_2O)]^{2+} \arrow[rr, rightleftharpoons] \arrow[dr, harpoon] & & cis\text{-}\alpha\text{-}[Cr(trien)Cl(H_2O)]^{2+} \arrow[dl, harpoon] \\ & cis\text{-}\alpha\text{-}[Cr(trien)Cl_2]^+ & \end{tikzcd} \qquad (9)$$

to form the more stereomobile aquochloro ions and that rapid isomerization between the aquated species leads to the isomerized dichloro product. The initial step in such a scheme, the aquation of *cis*-β-$[Cr(trien)Cl_2]^+$ is exceptionally rapid. It is one of the most rapid aquations reported for chromium(III)–amine complexes,[7] and it occurs several orders of magnitude more rapidly than the aquation of the cis-α isomer[5] (vide supra). Such facile aquation helps account for the observation that isomerization can occur quickly, even at 0 °C and in the presence of low concentrations of water.

Isomerization between *cis*-α- and *cis*-β-$[Cr(trien)Cl(OH_2)]^{2+}$ has been previously postulated[5] and it is a common observation that aquated trien complexes of Co(III) isomerize more readily than the dihalo complexes. For example, aquation of *cis*-α- and *cis*-β-$[Co(trien)Cl_2]^+$ proceeds with retention of configuration (in aqueous solution),[19] while the diaquo ion readily isomerizes.[20]

As proposed, this scheme does not account for the fact that chloride anation of an aquo–chloro intermediate, especially at low chloride levels (as in reaction 7), is an unlikely step in such a rapid isomerization. General experience with chromium(III) amines suggests that the introduction of two cis chloride ligands in aqueous solution is difficult, even in high chloride concentrations. If the aquated chloride ligand is not lost to the bulk solution but is held in a loosely bonded configuration (perhaps in the complex's solvation shell), then chloride recoordination could more readily occur. The high ionic strength present under conditions suitable for precipitation would hinder escape of the chloride and would promote the formation of $\{[Cr(trien)Cl(H_2O)]\cdot Cl\}^+$ ion pairs; it is noteworthy that under lower ionic strength conditions (acidic aqueous solutions), the primary reaction of *cis*-β-$[Cr(trien)Cl_2]^+$ is aquation, with no interference from β–α isomerization detected.

A further driving force for the isomerization would be the precipitation of insoluble *cis*-α-$[Cr(trien)Cl_2]Cl$, but a quantitative measure of the relative solubilities of the cis-α and cis-β dichloro isomers is prevented by the rapid aquation of the cis-β isomer. Fractional crystallizations of *cis*-α- and *cis*-β-$[M(trien)Cl_2]Cl$ (M = Co,[13] Rh [14]) suggest that the cis-α isomer is the less soluble, but extrapolation of such solubility trends to Cr(III) complexes is questionable.

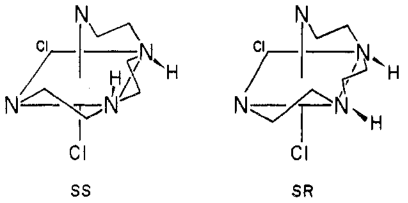


**Figure 5.** Two isomers of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$.

Despite numerous examples, no generally acceptable reason has been presented to account for the ability of a coordinated water molecule to induce changes in the bonding configuration of the trien ligand. Kinetic studies on the isomerization of *cis*-$\alpha$-[Co(trien)$(H_2O)_2$]$^{3+}$ showed that the isomerization rate had an inverse dependence on [$H^+$].[20] Attention has since focused on the secondary amine N–H bonds in the trien backbone, for proton abstraction and inversion at the nitrogen center could lead to isomerization of the complex. The isomerizations of [Cr(trien)$Cl_2$]$^+$ reported here occur in highly acidic media; however, so such proton abstraction seems unlikely. In an effort to determine whether proton abstraction did occur, *cis*-$\alpha$-[Cr(trien)$Cl_2$]$ClO_4$ and *cis*-$\beta$-[Cr(trien)$Cl_2$]$ClO_4$ were isolated after preparation from thionyl chloride solution upon the addition of $D_2O$, rather than $H_2O$ (reactions 5 and 7). Analysis of the N–H region in the infrared spectra of the products showed no evidence for deuterium incorporation in the trien chain. Thus, isomerization must occur without proton abstraction and inversion at a secondary amine nitrogen in the trien ligand.

**Aquation of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$.** Analysis of the kinetic data shows that two different species must be undergoing simultaneous pseudo-first-order aquations during the aquation of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$. Depletion of the more rapidly reacting species occurs within 100 s at 0 °C (see Figure 4), and the linear pseudo-first-order plots which occur from that time on are due to the continuing aquation of the more slowly reacting species. As shown in Figure 5, two geometric isomers are possible for *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$ (the mirror-image *RR* and *RS* isomers are not shown but are energetically degenerate with the *SS* and *SR* isomers, respectively). The difference between the *SS*(*RR*) and *SR*(*RS*) isomers is most easily noted from the positions of the two protons bonded to the secondary amines in the trien chain, but molecular models show that the trien ligand assumes markedly different configurations in the two isomers. The kinetic results suggest that both isomers are present in the initial sample of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$ and that these two isomers aquate at different rates.

Two independent aquations could also result from the presence of an impurity in the *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$, but this seems unlikely. Aquation of *cis*-$\alpha$-[Cr(trien)$Cl_2$]$^+$ is several orders of magnitude too slow to interfere here,[5] and significant contamination of *trans*-[Cr(trien)$Cl_2$]$^+$ can be ruled out on the basis of the electronic spectrum (less than 3% trans complex). (The trans trien configuration is also known to be unstable, due to steric strain on the trien ligand.) The tripodal quadridentate amine $\beta,\beta',\beta''$-triaminotriethylamine (tren) is a common by-product in the preparation of trien, but care was taken to remove tren before formation of the Cr complex. Thus, it is unlikely that contamination by a foreign ion could account for the non-first-order aquation behavior, and the two distinct pseudo-first-order aquation rates must be due to the different aquation rates of the two isomers of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$.

Assuming that the molar absorptivities at 590 nm are similar for the two dichloro isomers, as well as for the aquation products, analysis of the kinetic scheme shows that the *y* intercepts of the two linear plots (Figure 4) correspond to the initial concentrations of the two isomers of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$. Throughout the spectrophotometric and chloride electrode kinetic experiments the ratio $A_{\text{fast}}/A_{\text{slow}}$ (where $A_{\text{fast}}$ represents the *y* intercept of the faster reacting isomer of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$ and $A_{\text{slow}}$ is the *y* intercept of the more slowly reacting isomer) had a constant value of 1.1 (±0.1). Such invariant composition argues against the interference of an impurity and indicates that the preparation of *cis*-$\beta$-[Cr(trien)$Cl_2$]$ClO_4$ reported here leads to an approximately equimolar mixture of the *SS*(*RR*) and *SR*(*RS*) isomers.

In addition to aquation at different rates, both isomers of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$ aquate with puzzling rapidity. The rate of chloride aquation of *cis*-$\alpha$-[Cr(trien)$Cl_2$]$^+$ has been measured at several temperatures,[5] and by using the calculated activation energy (21.2 kcal), a rate constant of $7.3 \times 10^{-6}$ $s^{-1}$ can be estimated for the aquation of *cis*-$\alpha$-[Cr(trien)$Cl_2$]$^+$ at 0 °C under ionic strength and pH conditions analogous to those used for the cis-$\beta$ isomer. Using that estimate, the aquation rate of the more slowly reacting cis-$\beta$ isomer is over 700 times greater than that of the cis-$\alpha$ isomer, while the more rapidly reacting cis-$\beta$ isomer reacts about 4500 times as rapidly as cis-$\alpha$-[Cr(trien)$Cl_2$]$^+$ at 0 °C. In contrast, for the analogous Co(III) complexes, the rate of chloride aquation for the cis-$\beta$ isomer is only 9 times that of the cis-$\alpha$ isomer. The difference between the Co and Cr systems may reflect the different modes of aquation currently proposed for complexes of Co(III) and Cr(III).

Current models for the aquation of Cr(III) amines suggest an associative interchange ($I_A$) pathway[21] with significant Cr–$OH_2$ bond formation necessary before cleavage of the Cr–Cl bond occurs. For Co(III) complexes, a more dissociative (Id or D) process is envisioned, with cleavage of the Co–Cl bond as the rate-determining step.[22] The similar aquation rates for *cis*-$\alpha$- and *cis*-$\beta$-[Co(trien)$Cl_2$]$^+$ and the clean pseudo-first-order aquation of *cis*-$\beta$-[Co(trien)$Cl_2$]$^+$ are consistent with this dissociative model, for changes in trien configuration should have little effect on the rate of Co–Cl bond cleavage. For Cr(III), however, nucleophilic attack by a water molecule is necessary for aquation, so steric hindrance of effective water attack would be reflected in the aquation rate. The observed factor of ca. 6 between the aquation rates of the *SS*(*RR*) and *SR*(*RS*) isomer of *cis*-$\beta$-[Cr(trien)$Cl_2$]$^+$ must result from just such steric changes in the trien backbone.

The factor of ca. $10^3$ between the aquation rates of the cis-$\alpha$ and cis-$\beta$ isomers of [Cr(trien)$Cl_2$]$^+$ is especially distracting. Molecular models do not suggest any unusual steric strain differences in the cis-$\alpha$ and cis-$\beta$ configurations (note the similarities in the intensity of their ligand field absorptions). Nor do molecular models suggest the existence of any "decompression effect"[21] which might be said to induce Id processes in the cis-$\beta$ isomer. Any differences in the solvation energies of either the dichloro or aquochloro ions could not account for the large disparity between the cis-$\alpha$ and cis-$\beta$ aquation rates. Models for Cr(III) aquation currently favor cis attack of the water molecule, but molecular models do not suggest any substantive difference between the cis-$\alpha$ and cis-$\beta$ trien configurations in the area of the two cis chloride ligands. The major fundamental difference between the cis-$\alpha$ and cis-$\beta$ configurations is in the area trans to the two chloride ligands.

In the cis-$\alpha$ configuration, trans attack at the Cr(III) center is hindered by the central link in the trien chain (Figure 6). In addition, the methylene groups of that link would present a hydrophobic surface to the solvation sphere, so "back-side attack" by water would be unlikely for any complex in the cis-$\alpha$ configuration. In contrast, the trans side is not blocked for a complex in the cis-$\beta$ configuration (Figure 6). In addition, hydrophilic amine protons form the molecular surface trans to the chloride ligands, so the solvation sphere would be in intimate contact with the complex in that area. Trans attack

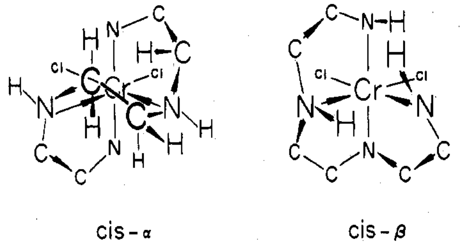

cis-α cis-β

**Figure 6.** Steric blocking of *cis*-α- and *cis*-β-$[Cr(trien)Cl_2]^+$ ions trans to the chloride ligands.

of a solvated water molecule would thus be facilitated in the cis-β complex.

These considerations suggest that the dramatic difference between the rates of chloride aquation of the cis-α and cis-β isomers results from effective trans water attack in the cis-β isomer. The positive end of the ion's dipole must also be in the area trans to the anionic chlorides, so nucleophilic attack from that side is clearly favored. Nucleophilic water attack from the (electron-rich) cis side is usually invoked to account for the stereoretentive nature of most aquations at Cr(III) centers,[22] but the chemistry of *cis*-$[Cr(trien)Cl_2]^+$ is characterized by extensive geometric isomerization, especially in the presence of water (vide infra). Thus, cis attack of water need not be invoked for the aquation of *cis*-β-$[Cr(trien)Cl_2]^+$, and the results are more easily explained with a trans-attack model.

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**Registry No.** *cis*-$[Cr(en)_2Cl_2]ClO_4$, 15654-71-4; *cis*-α-$[Cr(trien)Cl_2]ClO_4$, 15738-64-4; *cis*-β-$[Cr(trien)Cl_2]Cl$, 57793-29-0; *cis*-β-$[Cr(trien)Cl_2]ClO_4$, 61587-73-3; *cis*-$[Cr(trien)Cl(H_2O)]^{2+}$, 16702-00-4; $[Cr(en)_2ox]ClO_4$, 42423-95-0; α-$[Cr(trien)ox]ClO_4$, 20097-09-0; α-$[Cr(trien)ox]Br$, 16060-20-1.

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# Lattice Effects on Electron Resonance of Chromium(III) Complexes. Second-Neighbor Effects

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Zero-field splitting parameters have been measured for $[Cr(NH_3)_5X]^{2+}$ in several $[M(NH_3)_5Y]Z_2$ hosts with X = Cl, Br; Y = Cl, Br; $Z^- = Cl^-, Br^-, I^-, NO_3^-$; and M = Co, Rh, Ir. The guest–host combinations and comparisons were chosen to determine the magnitude and regularities of second-near-neighbor effects in this series of isomorphous orthorhombic hosts. Bound-halogen substitution (Y) in the second shell has about one-tenth the near-neighbor effect on the axial zero-field parameter but gives similar effects to those of the first shell (Z) on the rhombic parameter. Metal ion substitution in the second shell gives smaller effects on both axial and rhombic parameters but temperature variation of these systems reveals new information about temperature-dependent lattice effects. The second-shell effects are correlated with previously proposed models for lattice interactions in this type of host. The $[Rh(NH_3)_5Cl](NO_3)_2$ host system displays a reversible transformation to a lattice with two or more guest sites at low temperatures and undergoes smooth decomposition at high temperatures.

## Introduction

We have studied lattice effects on the electron resonance spectra of molecular ions in crystals by a variety of comparisons albeit inadvertently at times.[1-6] The primary effect appears in the zero-field splitting tensor for $d^3$ and $d^5$ ions with only small **g**-tensor variations.[2,5] An isomorphous series of orthorhombic lattices[5,7,8] with the general formula $[M(NH_3)_5Y]Z_2$ where M = Co, Rh, or Ir, Y = Cl or Br, and $Z^- = Cl^-, Br^-, I^-$, or $NO_3^-$ has been used to study the effect of nearest-neighbor, Z, variations on the paramagnetic $[Cr(NH_3)_5X]^{2+}$ guests (X = Cl or Br) in the analogous cobalt hosts, X = Y. A perspective view of the lattice is shown in Figure 1. Room-temperature lattice comparisons[5] and extensive temperature variation[6] studies in the range from 4 to 570 K have demonstrated the existence of a 20% lattice effect on the axial zero-field splitting parameter, *D*, and large variations of the rhombic parameter, *E*. Both *D* and *E* appear to respond to different lattice mechanisms in the low- and

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