

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007**Photochemistry of Coordination Compounds. XIV. Triethylenetetramine and β, β', β'' -Triaminotriethylamine Complexes of Cobalt(III)**

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The photochemistry of $cis-\alpha$ -[Co(tren)ClX] $^{n+}$, $cis-\beta$ -[Co(tren)ClX] $^{n+}$, and [Co(tren)ClX] $^{n+}$ (X = Cl or H₂O) has been studied in acidic solution using a laser-microcell technique. Upon 0° photolysis of the first ligand field bands, using either 488- or 514.5-nm irradiations, the observed photosensitivity is variable. The $cis-\beta$ -tren complexes undergo photoaquation or photoisomerization with quantum yields in the range of 10⁻²-10⁻³, while the $cis-\alpha$ -tren complexes have yields less than 10⁻⁵. [Co(tren)Cl₂] $^{2+}$ photoaquates at 514.5 nm with a yield of 0.015, while [Co(tren)(H₂O)Cl] $^{2+}$ is photoinert. Quantum yields for redox decomposition are less than 10⁻⁶. The relative yields for photosubstitution or photoisomerization as well as the stereochemistries, which generally differ from those of the ground-state reactions, may be explained in terms of the photolysis rules developed for chromium(III) amines.

Introduction

We have been interested in the photochemistry of cobalt(III)-amine complexes in the wavelength region of the first or second ligand field (L_1, L_2) bands. Complexes previously reported on include those of the type [Co(NH₃)₅-X] $^{n+}$ where X = NH₃, H₂O, F, or Cl, $trans$ -[Co(en)₂Cl₂] $^{2+}$ and $trans$ -[Co(cyclam)Cl₂] $^{2+}$,^{1,2} and cis -[Co(en)₂Cl₂] $^{2+}$ and cis -[Co(en)₂(H₂O)Cl] $^{2+}$.³ Photoredox decomposition is negligible (in this wavelength region) for these species and the photochemistry consists of stereospecific and often anti-thermal substitution processes and isomerizations. Quantum yields are low, possibly due to effective competition from radiationless deactivation of the excited state(s) involved. Because of the unknown and probably variable effect of this competition, quantum yields, even relative ones for a related series of compounds, are merely suggestive of the reactivity of the excited state involved and of its reaction mechanism. The nature of the preferred substitutional reaction mode is informative, however, especially in relation to the thermally preferred mode; this is particularly true if both stereochemistries are known.

Our previous results are consistent with the photolysis rules which developed out of the photochemistry of chromium(III) amines:⁴ (1) the octahedral axis having the weakest average crystal field will be the one labilized; (2) if the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. In explaining the excited-state stereochemistry for cobalt(III) amines it was supposed that stereoretentive expulsion or aquation of the labilized ligand occurred. If labilization of one end of an ethylenediamine was predicted, a further assumption was that recoordination would occur to one or another adjacent octahedral position rather than complete dissociation of the ethylenediamine. The above sequence could, of course, be virtual, the entire process being concerted. This rules-based mechanism has the characteristic that while water enters at the labilized position the departing ligand may be from an adjacent one. If the rules approach was abandoned, the results could be explained as due to heterolytic bond fission of the ligand actually lost, followed by suitable rearrangement of the five-coordinated intermediate and

coordination of solvent to give the observed product.

The present study was undertaken to see if some basis could be developed to give preference to one over the other of the two generic types of mechanism. An approach that has been effective in the study of the mechanism of thermal substitution reactions has been to increase the amount of stereochemical information carried by a complex through the use of multidentate ligands. Two which seemed potentially useful are the tren and tren ligands.⁵ The coordination and ligand conformation isomers of interest here are shown in Figures 1 and 2. There are three geometric isomers of [Co(tren)Cl₂] $^{2+}$: $cis-\alpha$, $cis-\beta$, and $trans$ (Figure 1a-c). Not counting optical isomers, there are two ligand conformational isomers of both the $cis-\beta$ (Figure 1d and 1e) and the $trans$ (Figure 1f and 1g) dichloro complexes. For the chloroaquo ion [Co(tren)(H₂O)Cl] $^{2+}$, four possible geometric isomers can occur (Figure 1h-k) since there are now two possible $cis-\beta$ isomers (Figure 1i and 1j); to simplify later discussions, we have labeled these the β' and β'' isomers, respectively. As shown in Figure 2, there is only one possible geometric isomer of [Co(tren)Cl₂] $^{2+}$, while two isomers, previously labeled α and β , exist for [Co(tren)(H₂O)Cl] $^{2+}$.

The thermal reactions and stereochemical rearrangements of the [Co(tren)ClX] $^{n+}$ complexes, X = Cl or H₂O, have been studied in some detail by Sargeson and coworkers.⁶⁻¹⁰ The general finding was that the cis isomers aquate with complete retention of geometric configuration, while $trans$ -[Co(tren)Cl₂] $^{2+}$ aquates stereospecifically to $cis-\beta'$ -[Co(tren)(H₂O)Cl] $^{2+}$. Madan and coworkers^{11,12} have reported on the aquation kinetics of [Co(tren)ClX] $^{n+}$ (X = Cl or H₂O); they noted an anomalously fast aquation rate for the dichloro complex and a normal one for the chloroaquo species, relative to the analogous bis(ethylenediamine) complexes. Steric crowding in models, as well as a series of hydrolysis rate ratios,¹³ suggests that the labile chloride in the dichloro complex is the

(5) Abbreviations used in this paper: en, ethylenediamine; tren, triethylenetetramine; tren, β, β', β'' -triaminotriethylamine.

(6) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(7) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

(8) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

(9) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).

(10) G. H. Searle and A. M. Sargeson, *Inorg. Chem.*, **12**, 1014 (1973).

(11) S. K. Madan, W. M. Reiff, and J. C. Bailar, *Inorg. Chem.*, **4**, 1366 (1965).

(12) W. V. Miller and S. K. Madan, *Inorg. Chem.*, **10**, 1250 (1971).

(13) S. Yuan, W. V. Miller, and S. K. Madan, *Inorg. Chim. Acta*, **7**, 134 (1973).

(1) A. W. Adamson, *Proc. Int. Conf. Coord. Chem.*, **14**, 240 (1972).

(2) R. Pribush, C. K. Poon, C. Bruce, and A. W. Adamson, *J. Amer. Chem. Soc.*, **96**, 3027 (1974).

(3) P. S. Sheridan and A. W. Adamson, *J. Amer. Chem. Soc.*, **96**, 3032 (1974).

(4) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

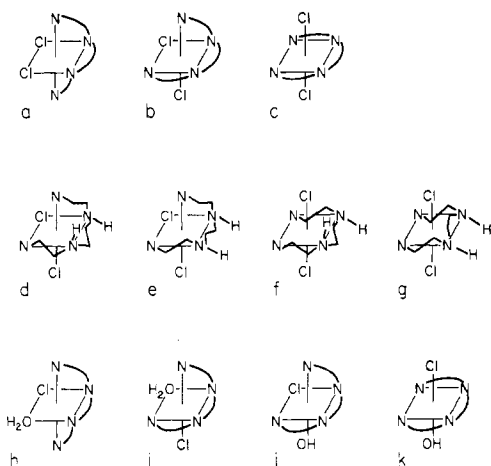


Figure 1. Geometric isomers for $[\text{Co}(\text{trien})\text{Cl}_2]^+$: (a) *cis*- α , (b) *cis*- β , (c) *trans*. Conformational isomers for *cis*- β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$: (d) *SS*, (e) *SR* (see ref 8). Conformational isomers for *trans*- $[\text{Co}(\text{trien})\text{Cl}_2]^+$: (f) *SS*, (g) *SR*. Geometric isomers for $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$: (h) *cis*- α , (i) *cis*- β' , (j) *cis*- β'' , (k) *trans*.

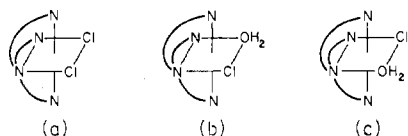


Figure 2. Geometric isomers of $\text{Co}(\text{trien})$ complexes: (a) $[\text{Co}(\text{trien})\text{Cl}_2]^+$, (b) α - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$, (c) β - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$.

one *cis* to the tertiary nitrogen; the aquation product is therefore expected to be the β isomer (Figure 2c).

We felt that the photochemistry of these two series of complexes might be revealing as to the type of excited-state reaction mechanism that was present. The rules mechanism approach predicts certain of the complexes to be relatively inert, while the direct heterolytic bond-breaking mechanism would predict normal photoactivity.

Experimental Section

Preparation of Compounds. *cis*- α - $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ (Figure 1a). This complex was prepared by the chloride anation of *cis*- α - $[\text{Co}(\text{trien})(\text{NO}_2)_2]^+$ as described by Sargeson and Searle.⁷ It was found that at least three recrystallizations from dilute hydrochloric acid solution were necessary, for both *cis*- α - and *cis*- β - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (Figure 1h and probably the β' form, Figure 1i) were found to be impurities. The visible spectra of solutions of our product agreed closely with that reported;⁷ extinction coefficient values throughout the visible-wavelength region and in particular at the band maxima were the same as for the published spectra, within the reading error of the latter.

cis- α - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (Figure 1h). *cis*- α - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ was allowed to aquate in 0.2 *N* hydrochloric acid solution, giving essentially pure product after 8–10 hr at room temperature.⁹ Again, spectra of solutions of the product agreed closely with the published one.⁷

cis- β - $[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ (Figure 1b). This complex was prepared by passing gaseous hydrochloric acid through an ethanolic suspension of β - $[\text{Co}(\text{trien})\text{CO}_3]\text{Cl}\cdot 5\text{H}_2\text{O}$, as described by Sargeson and Searle.⁷ At least two recrystallizations were necessary to separate the chloro-aquo species present as impurity. The visible spectrum of a solution of the final product agreed closely with that of Sargeson and Searle.⁷

cis- β' - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (Figure 1i). A solution of pure *cis*- β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ (Figure 1b) in 0.2 *N* hydrochloric acid aquates to give the desired product in 2 hr at room temperature. Upon aquation of *cis*- β - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ in HClO_4 , the major product (96%) was proposed to be the β' (Figure 1i) isomer,⁹ and this assignment was later confirmed by a single-crystal X-ray structure determination.¹⁴

The *cis*- β' - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ used in the photolyses was prepared in a similar manner (but in an HCl and not an HClO_4 solution), so we also assume the β' structure (Figure 1i) for this species.

$[\text{Co}(\text{trien})\text{Cl}_2]\text{Cl}$ (Figure 2a). The method of Liu, as described by Madan,¹² was used to prepare this complex. It was recrystallized twice from 6 *N* hydrochloric acid before use. The visible absorption spectrum of a solution agreed well with that reported.¹¹

β - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (Figure 2c). A solution of the pure dichloro complex (Figure 2a) in 0.2 *N* hydrochloric acid aquated to give the desired product in 1 hr at room temperature. While not unequivocally established, it is believed (see Introduction) that it is the β isomer which is the predominant product in the above procedure.¹³

Triethylenetetramine. The trien was purchased from the Aldrich Chemical Co. (technical grade) and was purified by isolation of the hydrochloric acid salt. This salt was recrystallized from cold water before use.

β, β', β'' -Triaminotriethylamine. The tren was separated as the hydrochloric acid salt from technical grade triethylenetetramine obtained from the Aldrich Chemical Co., using the method of Sacconi, *et al.*¹⁵ The trihydrochloride salt was recrystallized twice from cold water before use.

Preparation of Samples for Use. The various complexes are quite susceptible to aquation and it was desirable to purify them chromatographically just before use. A solution of the complex in ice cold 0.2 *N* hydrochloric acid was passed through a cationic exchange column (Sephadex SP-C-25) which had been prechilled by means of an ice water containing jacket. Elution was with ice-cold 0.2 *N* hydrochloric acid and the appropriate band was collected in a prechilled flask held in an ice bath. These precautions were necessary to inhibit thermal aquation reactions. Further, in the case of $[\text{Co}(\text{trien})\text{Cl}_2]^+$ (Figure 2a) it was necessary to photolyze the solution within a few minutes of its chromatographic separation, since the thermal aquation is significant even at 0° ($k = 3 \times 10^{-3} \text{ sec}^{-1}$ at 25°^{11,12}).

Photolyses. Photolyses were performed in much the same manner as described earlier.^{2,3} A jacketed 10-cm micropolarimeter cell of 5.0-cm³ volume was used, and the contents were held to near 0° by circulation of an ice-water slush. After irradiation, the cell was transferred directly to a recording spectrophotometer (Cary Model 14R) for spectral analysis. The irradiation source was a CW argon laser (Coherent Radiation Model 52G) with an output of about 1 W at either 488 or 514.5 nm. Absorbed light intensities were measured by the output meter reading as calibrated by reineckate actinometry.² Because of the speed of many of the thermal aquation reactions, it is doubtful whether this work could have been done without the use of the high intensity, small cross section beam of a laser source. The maximum continuous output of the laser used was 1.3 W, which corresponds to an incident light intensity of about $5.3 \times 10^{-6} \text{ einstein sec}^{-1}$. When impinged upon our cell window of 0.5-cm² area and completely absorbed in a 10-cm cell, this corresponds, after correction for intensity loss due to reflection, to an absorbed flux of about $1.0 \times 10^{-3} \text{ einstein l}^{-1} \text{ sec}^{-1}$.

Photolyses during quantum yield determinations were kept to a maximum of 10–15% total reaction, to reduce interference from secondary photolysis and inner filter effects. Standard spectrophotometric techniques were employed, with eq 5 of ref 3 used to allow for the changing absorbed light intensity during such runs.

Analytical Procedures. All analyses for product complexes were made by monitoring changes in the visible absorption spectra. An independent method for Co(II) determination has been described previously.^{1,16} It was not feasible to analyze for released chloride because of the 0.2 *N* HCl solvent used during all irradiations. Such an acidic medium was necessary to inhibit the rapid base-catalyzed aquation of these complexes, and hydrochloric acid was chosen for its convenience in the chromatographic purification which preceded each photolysis.

Results

cis- α - $[\text{Co}(\text{trien})\text{Cl}_2]^+$ (Figure 1a). Relatively prolonged irradiation at either 488 or 514.5 nm of a solution of this complex produced no detectable spectral changes. From the irradiation times, the reproducibility of the spectra, and estimates of the spectra of possible products, we place the maximum quantum yield for any aquation reaction, and in particular for formation of *cis*- α - $[\text{Co}(\text{trien})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (Figure 1h), as about 5×10^{-5} . No detectable Co(II) was produced, and from the limits of the detection method, we place the

(14) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **8**, 1293 (1969).

(15) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

(16) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

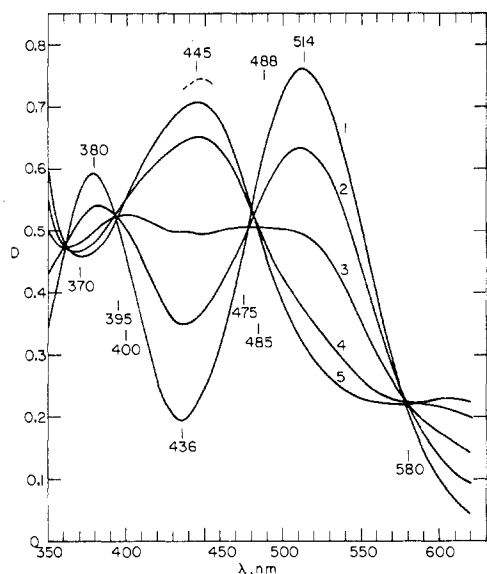


Figure 3. Photolysis of $cis\text{-}\beta'$ -[Co(trien)(H₂O)Cl]²⁺ at 488 nm, 0–1°, 0.2 *N* hydrochloric acid, and $ca. 5 \times 10^{-4}$ *M* complex: curve 1, initial solution; curve 2, 63-sec irradiation; curve 3, 284-sec irradiation; curve 4, 750-sec irradiation; curve 5, 1600-sec irradiation. Numbers give the wavelengths of spectral features and mark isobestic points. Dashed line represents estimated terminus of the photolysis.

maximum yield for redox decomposition as 1×10^{-6} .

$cis\text{-}\alpha$ -[Co(trien)(H₂O)Cl]²⁺ (Figure 1h). Irradiations at either of the two wavelengths of solutions of this complex caused a very slight initial change but then no further change in the absorption spectrum; we attribute this change to the presence of a small amount of impurity, perhaps one of the β isomers (Figure 1b or 1i). No Co(II) formation could be detected. As before, we place the maximum quantum yields for aquation and for redox decomposition as 5×10^{-5} and 1×10^{-6} , respectively.

$cis\text{-}\beta'$ -[Co(trien)(H₂O)Cl]²⁺ (Figure 1i). Figure 3 reproduces a few of the spectral sequences obtained on the 488-nm irradiation of a $ca. 5 \times 10^{-4}$ *M* solution of this complex; entirely analogous sequences were obtained on 514.5-nm irradiations. The changes do not correspond to the formation of any of the possible diaquo isomers but are consistent with the formation of $trans$ -[Co(trien)(H₂O)Cl]²⁺. We can find no published spectrum for this last complex (for good reason—see under “isomerization rate studies” below), but interpolation of those for $trans$ -[Co(trien)Cl₂]⁺ and $trans$ -[Co(trien)(H₂O)₂]³⁺ (see Figure 1f) indicates that the terminal spectrum of Figure 3 is that expected for $trans$ -[Co(trien)(H₂O)Cl]²⁺. This conclusion is supported by the isomerization rate studies described further below. To be somewhat conservative, we have taken the dashed 445-nm maximum in Figure 3 to represent the true terminus of the photolysis and on this basis obtain a quantum yield (for reaction 5 in Figure 4) of 5.7×10^{-3} at 488 nm and 4.5×10^{-3} at 514.5 nm. The decrease with increasing wavelength probably exceeds the experimental uncertainty.

Extensive photolysis of $cis\text{-}\beta'$ -[Co(trien)(H₂O)Cl]²⁺ could produce about 90% conversion to $trans$ -[Co(trien)(H₂O)Cl]²⁺, but further photoisomerization was prevented by the thermal isomerization of the photoproduct (reaction 4, Figure 4). It is not possible to rule out the possibility that $trans$ -[Co(trien)(H₂O)Cl]²⁺ may undergo secondary photolysis to return to the $cis\text{-}\beta$ isomer (that is, that reaction 4 of Figure 4 may be photochemically as well as thermally induced). Based upon the presence of a photostationary state contain-

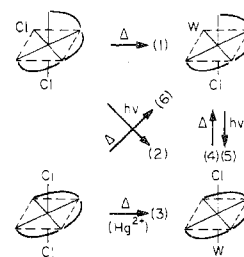


Figure 4. Thermal and photochemical reactions of various Co^{III}-trien complexes.

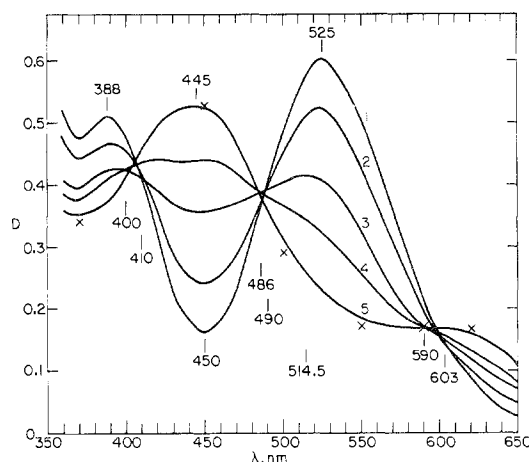


Figure 5. Photolysis of $cis\text{-}\beta$ -[Co(trien)Cl₂]⁺ at 514.5 nm, 0–1°, 0.2 *N* hydrochloric acid, and $ca. 5 \times 10^{-4}$ *M* complex. Photolysis times in sec for curves 1–5, respectively: 0, 65, 250, 750, 1100. X points: curve 5 of Figure 3 fitted at the 445-nm maximum. Numbers give the wavelengths of spectral features and mark isobestic points.

ing about 90% $trans$ -[Co(trien)(H₂O)Cl]²⁺ and the (highly conservative) assumption that thermal isomerization is negligible, a maximum value of 2.5×10^{-3} can be placed on the quantum yield for the photoinduced formation of $cis\text{-}\beta$ -[Co(trien)(H₂O)Cl]²⁺ from the $trans$ isomer. This is a generous upper limit, however, and the true quantum yield must be substantially less, for thermal isomerization from the $trans$ to the $cis\text{-}\beta$ form was demonstrably significant under these conditions.

Note in Figure 3 the shift in isobestic points between the first and last third of the photoreaction. A probable explanation of this shift is considered in the section on isomerization rate studies below.

Finally, no Co(II) could be detected after extensive photolysis at either wavelength, and we conclude that the yield for photoredox decomposition is less than 1×10^{-6} .

$cis\text{-}\beta$ -[Co(trien)Cl₂]⁺ (Figure 1b). Figure 5 reproduces a selection of the spectral sequences obtained on the 514.5-nm irradiation of a $ca. 5 \times 10^{-4}$ *M* solution of this complex; entirely analogous sequences were obtained in 488-nm irradiations. The spectra again correspond to $trans$ -[Co(trien)(H₂O)Cl]²⁺ (Figure 1k) as the principal product. The terminal spectrum has the same shape as that in Figure 3, as indicated by the points X, and we again take the terminal spectrum to represent about 90% photolysis (reaction 2 in Figure 4). We obtain, on this basis, the quantum yields 1.1×10^{-2} at 488 nm and 8.0×10^{-3} at 514.5 nm; again, we believe the increase with decreasing wavelength to be real. No Co(II) could be found, and we set the quantum yield for photoredox decomposition at less than 1×10^{-6} .

Since $cis\text{-}\beta'$ -[Co(trien)(H₂O)Cl]²⁺ was a conceivable photo-

product (reaction 1, Figure 4), these quantum yields were calculated at a wavelength where the *cis*- β -dichloro and -chloroaquo ions have an isosbestic point, and they thus represent the quantum yields for the formation of only the *trans* isomer. Such direct photoproduction of *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ may occur (note lack of an isosbestic in Figure 5 near 600 nm), but the extent of *cis*- β' -chloroaquo formation is difficult to measure, for its electronic spectrum is similar to that of the starting material, and, if generated, it would not accumulate but would undergo secondary photolysis to yield the observed *trans*-[Co(trien)(H₂O)Cl]²⁺ (reaction 5, Figure 4). The triangular-plotting technique used to analyze the products of *cis*-[Co(en)₂Cl₂]⁺ photolysis³ cannot be used here since the spectrum of the photoproduct is not accurately known, nor is it possible to separate and analyze the photoproducts by chromatography, due to the rapid thermal isomerization of the *trans* isomer.

The gross spectral changes clearly indicate that *trans*-[Co(trien)(H₂O)Cl]²⁺ is the major photoproduct, even during the initial stages of the reaction, when secondary photolysis is not an important process. The observation that the quantum yield for the formation of *trans*-[Co(trien)(H₂O)Cl]²⁺ from the *cis*- β -dichloro complex (reaction 2, Figure 4) is almost double that from the chloroaquo complex (reaction 5, Figure 4) effectively eliminates secondary photolysis as a significant reaction under these conditions. Thus, we conclude that *trans*-[Co(trien)(H₂O)Cl]²⁺ is the major primary photoproduct.

Postirradiation Spectral Changes. It was observed that a solution of *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ (Figure 1i) irradiated to about 85–90% conversion to *trans*-[Co(trien)(H₂O)Cl]²⁺ (Figure 1k) returned on standing in the dark (at 25°) to a solution whose spectrum was indistinguishable from that of a solution of the starting complex which was allowed to reach aquation equilibrium. That is, the photolyzed solution returned spectrally to *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ (Figure 1i). The immediate import of these observations is that for neither system was photoaquation of the amine ligand or formation of a diaquo complex of importance; either type of product would have been stable in the 0.2 *N* hydrochloric acid medium used, and its presence would have marred the observed spectral return.¹⁷

The thermal return reactions allowed a kinetic identification of the photoproduct. A solution of *cis*- β -[Co(trien)Cl₂]⁺ (Figure 1b) was irradiated to nearly complete conversion, the X points in Figure 6 showing the matching of the spectrum to the final one of Figure 3. The dark reaction was then followed at 0–1°, representative intermediate spectra being shown in Figure 6. The terminal or infinite-time spectrum matches that of the *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ spectrum, as shown by the set of Δ points in the figure. Figure 7 shows the semilogarithmic plot of ($D_t - D_\infty$) vs. time, the D 's being optical densities measured at 520 nm. The plot is not linear, and analyzes to give a major component of slope corresponding to $k_2 = 4.0 \times 10^{-5} \text{ sec}^{-1}$ and a minor component with $k_1 = 3.8 \times 10^{-4} \text{ sec}^{-1}$. The same analysis using the 440-nm

(17) From thermal studies it is known that the equilibrium mixture of *cis*- β' - and *trans*-[Co(trien)(H₂O)Cl]²⁺ is essentially 100% *cis*- β' and that isomerization equilibrium is rapid compared to further chloride aquation. It is also known that the equilibrium between the (*cis*- β') chloroaquo and diaquo species lies far toward the diaquo ion in HClO₄ solution.⁹ Although in the 0.2 *N* HCl solution used for these photolyses it is reasonable that this equilibrium would be shifted toward the aquochloro ion, we find the reactions to be kinetically very slow. The spectrum of a solution of *cis*- β -[Co(trien)(H₂O)₂Cl]³⁺ was not changed after 3 hr at room temperature (or at 0°) in 0.2 *N* HCl.

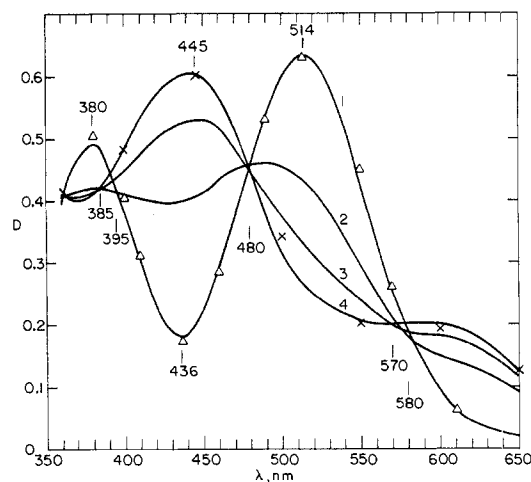


Figure 6. Dark return of photolyzed *cis*- β -[Co(trien)Cl₂]⁺ at 0–1°, 0.2 *N* hydrochloric acid, and *ca.* $5 \times 10^{-4} M$ complex: curve 4, immediately after photolysis; curves 3–1, respectively, at 37 min after photolysis, at 163 min after photolysis, and after no further change. X points: curve 5 of Figure 3 fitted at the 445-nm maximum. Δ points, curve 1 of Figure 3 fitted at the 514-nm maximum. Numbers give the wavelengths of spectral features and mark isosbestic points.

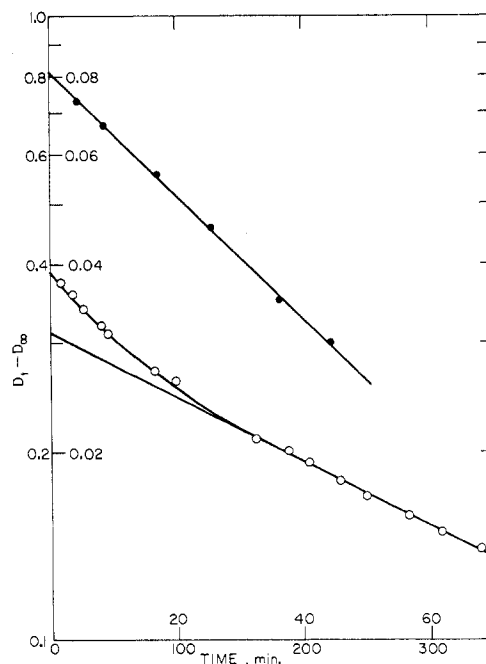


Figure 7. Plot of $D_t - D_\infty$ for the dark reaction following irradiation of *cis*- β -[Co(trien)Cl₂]⁺ at 0–1°, 0.2 *N* hydrochloric acid, and *ca.* $5 \times 10^{-4} M$ complex. Optical densities measured at 520 nm; full circle points are plotted according to the inner scales, to show the fast component.

optical densities gives $k_2 = 4.8 \times 10^{-5} \text{ sec}^{-1}$ and $k_1 = 4.3 \times 10^{-4} \text{ sec}^{-1}$. The two sets are probably within experimental error and average to $k_2 = 4.4 \times 10^{-5} \text{ sec}^{-1}$ and $k_1 = 4.1 \times 10^{-4} \text{ sec}^{-1}$.

A set of three experiments was made in which *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ (Figure 1i) was photolyzed to about the same degree as in the experiment of Figure 3 and the dark return reaction observed at 0–1°. A representative set of data for this return is shown in Figure 8. Again, the plots were not linear and analyzed into two components. The average k_2 and k_1 values for the three runs, each measured at 440 and 520 nm, are $k_2 = (4.5 \pm 0.4) \times 10^{-5} \text{ sec}^{-1}$ and $k_1 = (4.6 \pm 0.4) \times 10^{-4} \text{ sec}^{-1}$. We consider these values

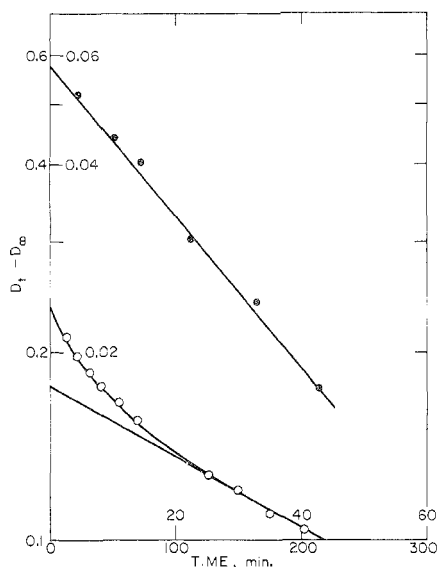


Figure 8. Plot of $D_t - D_\infty$ for the dark reaction following irradiation of $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$ at $0-1^\circ$, $0.2 N$ hydrochloric acid, and $ca. 5 \times 10^{-4} M$ complex. Optical densities measured at 440 nm ; full circle points are plotted according to the inner scales, to show the fast component.

to be the same as those found for the $cis-\beta-[Co(tren)Cl_2]^+$ system, and we have made a kinetic identification of the photoproduct(s) of $cis-\beta-[Co(tren)Cl_2]^+$ and $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$ as being the same.

It seems best to interpret further the above results here rather than in the Discussion. Sargeson and Searle⁹ formed $trans-[Co(tren)(H_2O)Cl]^{2+}$ by the mercuric ion induced aquation of $trans-[Co(tren)Cl_2]^+$ and reported that the former complex then isomerized to $cis-\beta-[Co(tren)(H_2O)Cl]^{2+}$ (presumably the β' isomer) with a rate constant at 15° of $1.7 \times 10^{-3} \text{ sec}^{-1}$. An activation energy of 24 kcal mol^{-1} would make this rate constant 1.7×10^{-4} at 0° or between our k_2 and k_1 values. The comparison further supports our conclusion that the photoproduct is $trans-[Co(tren)(H_2O)Cl]^{2+}$.

It remains to account for the two-component character of our dark return reactions. We cannot find a reasonable explanation in terms of a single species undergoing sequential first-order reactions; the presence of any appreciable amount of diaquo species has been ruled out, for example. We suggest the following. Turning to Figure 1, there are two possible conformational isomers of $cis-\beta-[Co(tren)Cl_2]^+$ (d and e), labeled the *SS* and *SR* isomers after the configurations about the two asymmetric secondary nitrogens. (For this discussion, it is not necessary to consider the *RR* and *RS* isomers, which are merely the optical isomers of the *SS* and *SR* forms.) The same *SS* and *SR* conformational isomers are also possible for $trans-[Co(tren)Cl_2]^+$ (f and g), as well as for the analogous $cis-\beta-$ and $trans-[Co(tren)(H_2O)Cl]^{2+}$ ions. Geometric isomerization between *SS*-*cis*- β and *SS*-*trans* ions (or between *SR* forms) could, in principle, occur without rearrangement about either of the asymmetric nitrogens; interconversion between an *SS* and an *SR* form, however, would require inversion at one of the secondary amine nitrogens and would result in an extensive skeletal rearrangement of the quadridentate amine.

Sargeson and coworkers proposed that their synthesis of $cis-\beta-[Co(tren)Cl_2]Cl$ produced primarily the *SS* isomer, but it is entirely possible that some *SR* isomer formed in our preparations. Aquation would then produce $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$ with the same mixture of conformational isomers. Photolysis of either the dichloro or the chloroaquo

complex would then produce the same mixture of *SS* and *SR* isomers of $trans-[Co(tren)(H_2O)Cl]^{2+}$, assuming that photolysis does not cause inversion of a secondary amine. These, in turn, would undergo parallel dark isomerizations to $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$, with rate constants k_1 and k_2 . Small differences in absorption spectra and in quantum yields would account for the minor shifts in isosbestic points in Figures 3 and 5.

Kinetic analysis of the above scheme shows that the ratio of intercepts of the two straight-line components of Figure 8 is equal to $(\epsilon_B - \epsilon_C)B_0/(\epsilon_A - \epsilon_D)A_0$ where ϵ_A and ϵ_B are the extinction coefficients for the *SS* and *RS* isomers of $trans-[Co(tren)(H_2O)Cl]^{2+}$ and ϵ_C and ϵ_D are the values for the corresponding isomers of $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$. The average of the six values for this ratio is 4.1 ± 0.5 . Since the two pairs of extinction coefficients ϵ_A, ϵ_B and ϵ_C, ϵ_D are probably similar in value, the above ratio should be approximately that of the isomer concentrations. Assuming the *SS* one to be the more stable, $[SS]/[SR] \cong 4$, and the slow rate given by k_2 is assigned to the *SS* series. The corresponding analysis of the run of Figure 7 gives the same meaning to the ratio of intercepts and the average value obtained for the two wavelengths at which the dark return data were analyzed is 3.9 ± 0.1 , or essentially the same as before. This is the expected result according to our suggested explanation.

$trans-[Co(tren)(H_2O)Cl]^{2+}$. The ability to irradiate solutions of $cis-\beta-[Co(tren)Cl]^{2+}$ or of $cis-\beta'-[Co(tren)(H_2O)Cl]^{2+}$ to about 90% conversion to the product $trans-[Co(tren)(H_2O)Cl]^{2+}$ indicates that photolysis of the latter was not of practical importance. Unfortunately, this circumstance is not very informative about the quantitative photochemistry of the *trans* compound. The rather large upper limits given in Table I for any photoreaction reflect the very low estimated extinction coefficients of the compound at the irradiating wavelengths.

$[Co(tren)Cl_2]^+$. Figure 9 shows the spectral changes that occurred on the 514.5-nm irradiation of a $ca. 5 \times 10^{-4} M$ solution of $[Co(tren)Cl_2]^+$ (in $0.2 N$ hydrochloric acid and at $0-1^\circ$). The sequence is indistinguishable from that which occurs on thermal aquation of the complex, and analysis at various wavelengths by the procedure used previously³ indicates that the thermal product $[Co(tren)(H_2O)Cl]^{2+}$ is the only photoproduct. This latter species is not very photosensitive (see below) and relatively short irradiation could produce greater than 95% conversion to the chloroaquo complex.

A kinetic as well as spectral identification of the photoproduct was informative, for there are two possible geometric isomers of the photoproduct (Figure 2b and c). While they have not been separated, these two isomers have been identified by their different rates of thermal chloride aquation.¹² Thermal aquation of $[Co(tren)Cl_2]^+$ gives the slower reacting isomer (β^{13}) as the major product, with only minor, but readily observed, amounts of the more rapidly aquating α isomer being formed. Photoinduced aquation of $[Co(tren)Cl_2]^+$ produced only the β isomer, however, since thermal aquation of the photoproduct (to yield the diaquo ion) displayed clean, first-order behavior, with the same aquation rate as that observed for the major component of the thermally prepared $[Co(tren)(H_2O)Cl]^{2+}$. There is no evidence for any other, more rapidly reacting isomer, so we conclude that photolysis of $[Co(tren)Cl_2]^+$ leads to $\beta-[Co(tren)(H_2O)Cl]^{2+}$ (Figure 2c), with less than 1% of the α isomer (Figure 2b) being formed.

As noted in the Introduction, the thermal aquation rate is anomalously fast for $[Co(tren)Cl_2]^+$, being about 12 times

Table I. Photoreactions and Thermal Reactions of Co^{III} trien, tren, and Related Complexes^a

No.	Complex	Photochemistry			Thermal chemistry ^b	
		Wave length, nm	Quantum yield (0°)	Product	<i>k</i> (25°), sec ⁻¹	Product
1	<i>cis</i> - α -[Co(trien)Cl ₂] ⁺	488	<10 ⁻⁵	No product observed ^c	1.6 × 10 ⁻⁴	<i>cis</i> - α -[Co(trien)(H ₂ O)Cl] ²⁺
		514.5	<10 ⁻⁵	No product observed ^c		
2	<i>cis</i> - α -[Co(trien)(H ₂ O)Cl] ²⁺	488	<10 ⁻⁵	No product observed ^c	5.4 × 10 ⁻⁷	<i>cis</i> - α -[Co(trien)(H ₂ O) ₂] ³⁺
		514.5	<10 ⁻⁵	No product observed ^c		
3	<i>cis</i> - β -[Co(trien)Cl ₂] ⁺	488	0.011	<i>trans</i> -[Co(trien)(H ₂ O)Cl] ²⁺ ^d	1.5 × 10 ⁻³	<i>cis</i> - β '-[Cl(trien)(H ₂ O)Cl] ²⁺
		514.5	0.0080	Same ^d		
4	<i>cis</i> - β '-[Co(trien)(H ₂ O)Cl] ²⁺	488	0.0057	<i>trans</i> -[Co(trien)(H ₂ O)Cl] ²⁺	2.3 × 10 ⁻⁵	<i>cis</i> - β -[Co(trien)(H ₂ O) ₂] ³⁺
		514.5	0.0045	Same		
5	<i>trans</i> -[Co(trien)(H ₂ O)Cl] ²⁺	488	<2.5 × 10 ⁻³	<i>c</i>	1.7 × 10 ⁻³	<i>cis</i> - β '-[Co(trien)(H ₂ O)Cl] ²⁺
		514.5	<2.5 × 10 ⁻³	<i>c</i>		
6	[Co(tren)Cl ₂] ⁺	514.5	0.015	β -[Co(tren)(H ₂ O)Cl] ²⁺	3.0 × 10 ⁻³	β -[Co(tren)(H ₂ O)Cl] ²⁺
7	β -[Co(tren)(H ₂ O)Cl] ²⁺	514.5	<10 ⁻⁵	<i>c, e</i>	2.7 × 10 ⁻⁴ ⁱ	[Co(tren)(H ₂ O) ₂] ³⁺
8	<i>cis</i> -[Co(en) ₂ Cl ₂] ⁺	488	0.0024 ^f	67% <i>trans</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺	2.4 × 10 ⁻⁴	<i>cis</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺
9	<i>cis</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺	488	0.0042 ^f	<i>trans</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺	1.6 × 10 ⁻⁶	<i>cis</i> -[Co(en) ₂ (H ₂ O) ₂] ³⁺
10	<i>trans</i> -[Co(en) ₂ Cl ₂] ⁺	488	4.9 × 10 ⁻⁴ ^g	72% <i>trans</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺	3.5 × 10 ⁻⁵	65% <i>trans</i> -[Co(en) ₂ (H ₂ O)Cl] ²⁺
			0.0011 ^h			
11	<i>trans</i> -[Co(cyclam)Cl ₂] ⁺	488	4.0 × 10 ⁻⁴ ^h	<i>trans</i> -[Co(cyclam)(H ₂ O)Cl] ²⁺	1.1 × 10 ⁻⁶	<i>trans</i> -[Co(cyclam)(H ₂ O)Cl] ²⁺

^a At 0–1° in 0.2 *N* hydrochloric acid. Quantum yields for photoredox decomposition were less than 10⁻⁶. ^b Rate data for trien complexes from ref 9; for tren complexes from ref 12; for ethylenediamine complexes from ref 18. ^c The various possible aquation and isomerization products were considered in setting the maximum yield for any isomerization or net photosubstitution process. ^d We estimate a maximum of 10% *cis*- β '-[Co(trien)(H₂O)Cl]²⁺ formation. ^e Some photoaquation—see Results. ^f From ref 3. ^g From ref 2. ^h At 25°. ⁱ At 65°.

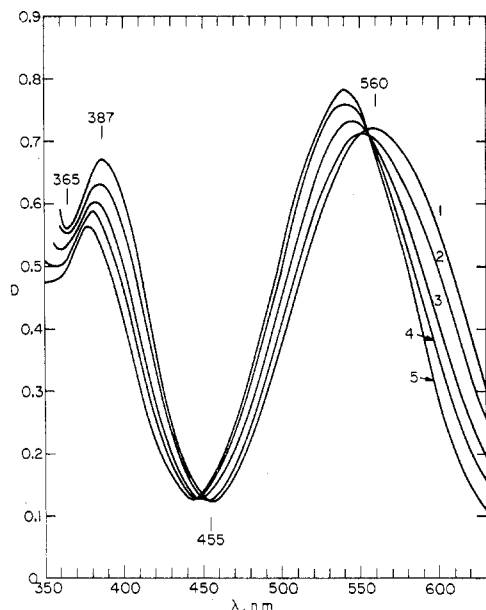


Figure 9. Photolysis of [Co(tren)Cl₂]⁺ at 514.5 nm, 0–1°, 0.2 *N* hydrochloric acid, and ca. 5 × 10⁻⁴ *M* complex: curve 1, initial complex; curves 2–5, 13-, 38-, 80-, and 202-sec irradiations, respectively.

faster than that of *cis*-[Co(en)Cl₂]⁺; *k* at 25° is about 3 × 10⁻³ sec⁻¹. Even though irradiations were started within minutes of the final chromatographic purification some 10–30% correction for concomitant thermal aquation was necessary. Our calculated quantum yield is (1.5 ± 0.4) × 10⁻², the relatively large error limits being due to our estimated uncertainty in the correction.

No Co(II) could be detected after extensive photolysis and we place the redox quantum yield as less than 1 × 10⁻⁶. Nor is amine photohydrolysis important since irradiated solutions equilibrated in the dark to give the same spectrum as did nonphotolyzed solutions.

β -[Co(tren)(H₂O)Cl]²⁺ (Figure 2c). Photolysis of this complex at 514.5 nm led to only very minor changes in the visible absorption spectrum of the solution. These changes were consistent with the formation of a little [Co(tren)Cl₂]⁺

but were too small to permit positive identification. The changes quickly terminated in a photostationary state and, assuming the perturbation to be due to the dichloro complex, this state consisted of no less than 95% starting material. We estimate the yield for photoaquation of β -[Co(tren)(H₂O)Cl]²⁺ to be less than about 1 × 10⁻⁵. There was no loss of coordinated amine; irradiated solutions returned to the initial absorption spectrum within 15 min in the dark. No Co(II) could be detected and the yield for photoredox decomposition is set at less than 1 × 10⁻⁶.

Discussion

Our results are summarized in Table I. Included are some data for the related bis(ethylenediamine) complexes as well as the available thermal reaction rate constants.

First, no Co(II) formation was observed; our upper limit for ϕ (redox) is 10⁻⁶ in all cases. This lack of photoredox decomposition now seems to be general for the ligand field photolysis of cobalt(III) amines including mixed-ligand complexes where chloride or water (or fluoride) is the non-ammine group. Photochemistry, where observed, appears always to be one of low quantum yield substitution or isomerization.

Further, the detailed photochemistry of these cobalt(III) amines is clearly not predictable from their thermal reaction chemistry. Photolysis produces molecular structural changes different from those found thermally and, moreover, the striking photoinertness of the *cis*- α trien complexes is not reflected in their thermal behavior. Also, while the various aquochloro species all undergo thermal aquation, no photoaquation of chloride could be detected; the chloroaquo complexes either were photoinert to within our detection limits or underwent a photoisomerization to an isomeric aquochloro species.

A more detailed point is that the photochemistries of the two *cis*- β -trien complexes are similar to those of the structurally analogous *cis*-bis(ethylenediamine) ones. The corresponding *trans*-aquochloro complex is produced as the sole product or, in the case of *cis*-[Co(en)₂Cl₂]⁺, as the principal product. The stereochemistry of these photoreactions must be kinetically controlled since at equilibrium [Co(en)₂(H₂O)Cl]²⁺ exists as about 72% *cis* and 28% *trans* isomers,¹⁸ and

for the corresponding *cis*- β -trien complexes the equilibrium lies at essentially 100% *cis*- β' -[Co(trien)(H₂O)Cl]²⁺. By contrast, the thermal reactions of these four complexes consist of stereoretentive chloride aquations. It thus seems clear that the detailed reaction paths cannot be the same for the photochemical and the thermal reactions (see further below for another aspect, however).

Some mechanistic considerations are the following. First, a heterolytic bond cleavage of the ligand which photoaquates does not account for our results. The principal difference between compounds 1 and 3 (of Table I) as compared to compound 8 lies in the manner in which the two ethylenediamine moieties are bridged (see Figure 1). If in compound 8 the Co-Cl bond is presumed to be directly labilized in the excited state, one would expect the same bond to be about equally labilized in the cases of compounds 1 and 3 since the manner of bridging of the ethylenediamines should not and apparently does not significantly affect the ordering of ligand field excited states. In this sense, the *cis*- α - and *cis*- β -trien complexes are quite similar, with barely distinguishable electronic spectra. From the point of view of ligand field theory, the same chromophore, *cis*-[CoN₄Cl₂]⁺, is present in all three cases. Yet, as noted above, compound 1 is quite photoinert relative to compound 3.

Continuing in the same vein, the photoisomerization observed for the aquochloro species would be treated as due to some reaction sequence following heterolytic cleavage of the Co-OH₂ bond. Compounds 2, 4, and 7 should then be about as photoreactive as is compound 9, again contrary to observation.

A mechanism that is consistent with our results is the rules-based one described in the Introduction. We assume heterolytic (probably solvent assisted) bond cleavage at that octahedral position which is indicated by the rules to be labilized. The immediate product is then a stereoretentive coordination of water at the labilized position. As illustrated by reaction a of Figure 10, this is also the final product if the labilized ligand is monodentate. If this last is part of a multidentate group then, as illustrated by reaction b, recoordination occurs and preferentially at an octahedral site adjacent to the remaining point of attachment of the labilized ligand (an edge displacement¹⁹). Where, as in case c, a secondary nitrogen is labilized, the only recoordination that is sterically permitted is that which annuls the first step, so that no net reaction is observed (see ref 3 for additional discussion of this mechanism).

We thus can account for the relative photoinertness of the α -trien complexes; for these only a secondary nitrogen can be labilized. Reaction d of Figure 10 accounts for the stereospecific photoaquation of *cis*- β -[Co(trien)Cl₂]⁺ and, taking water to be of higher ligand field strength than chloride,²⁰ for the observed photoisomerizations of *cis*- β' -[Co(trien)(H₂O)Cl]²⁺ and for the relative photoinertness of *trans*-[Co(trien)(H₂O)Cl]²⁺.

The mechanism correctly predicts that β -[Co(tren)(H₂O)Cl]²⁺ should be photoinert but incorrectly makes the same prediction for [Co(tren)Cl₂]⁺. While labilization of a primary amine function is predicted in this last case, there is no simple process of recoordination that could lead to the observed photoproduct. There is an alternative to abandoning the

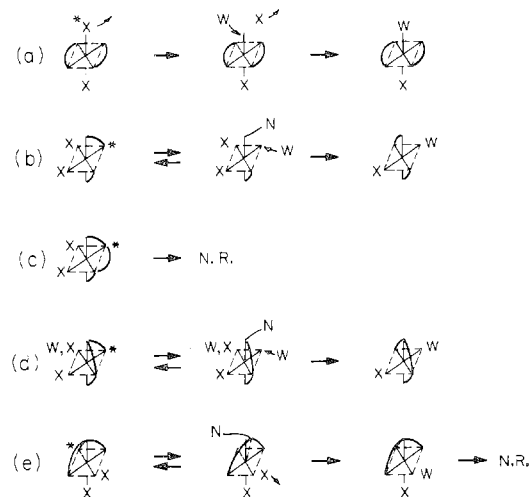


Figure 10. The photolysis rules as applied to (a) *trans*-[Co(en)₂Cl₂]⁺, (b) *cis*-[Co(en)₂Cl₂]⁺, (c) *cis*- α -[Co(trien)Cl₂]⁺, (d) *cis*- β -[Co(trien)Cl₂]⁺ or *cis*- β' -[Co(trien)(H₂O)Cl]²⁺, and (e) [Co(tren)Cl₂]⁺ or β -[Co(tren)(H₂O)Cl]²⁺. The asterisks indicate the ligands that would be labilized upon ligand field photolysis.

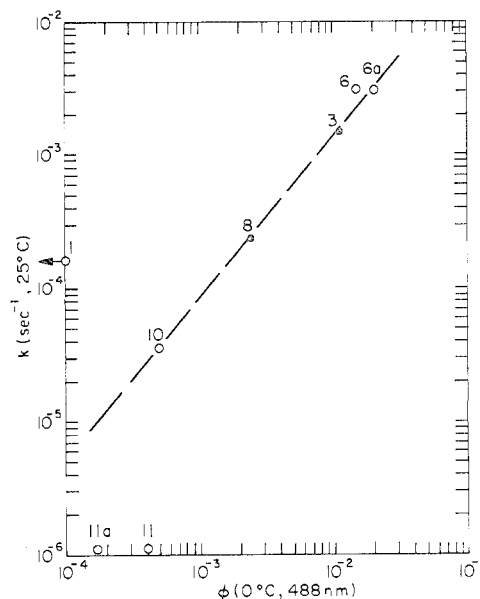


Figure 11. Correlation between ϕ and k . Numbers refer to compounds in Table I. The entry in the table for compound 6 is for 514.5 nm; point 6a corrects to 488 nm assuming the same wavelength dependence as for compounds 3 and 4. Similarly, the datum for compound 11 is for 25° and point 11a corrects to 0° assuming the same temperature dependence as for compound 10. Dark circles mark those compounds for which the photoreactions and thermal reactions are of different stereochemistry.

whole picture at this point. We note that the abnormally large thermal aquation rate constant for [Co(tren)Cl₂]⁺ may be attributed to steric crowding of the chloride *cis* to the tertiary nitrogen.¹³ A possibility, illustrated by sequence e in Figure 10, is that this steric crowding is accentuated following the Co-N bond cleavage at the labilized position (which is *trans* to the chloride which aquates).

The above mechanism is not entirely novel. About the same type of sequence has been postulated for the thermal reaction 6 of Figure 4.⁹ However, we use the "rules" to determine which position is labilized and think it better to write processes such as b and d of Figure 10 as occurring in two steps rather than as a single, concerted one. While it would be sanguine to expect a clearer resolution of excited-

(18) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

(19) D. D. Brown, C. K. Ingold, and R. S. Nyholm, *J. Chem. Soc.*, 2673 (1953).

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

state reaction mechanisms than has been possible for ground states (see ref 20), experiments with optically active chelates might further restrict the range of possibilities.

We have made no attempt in the preceding discussion to assess the spectroscopic description of our reactive excited states. This type of approach has been made, in some detail, by Zink²¹ using conventional ligand field theory to predict σ - and π -bonding changes in various excited states. This approach should be very helpful in the case of cobalt(III) amines where it does appear that the primary act is one of direct heterolytic bond cleavage at a labilized position. We retain a general concern that the thermally equilibrated excited (thexi¹) states which presumably are the chemically reacting species may have a different geometry (and a different spin multiplicity) than the Franck-Condon states used by ligand field theory in treating absorption spectra. A further caution, mentioned in the Introduction, is that mechanistic interpretations of quantum yield variations may be specious; relative photoinertness could, for example, be due

(21) J. I. Zink, *Inorg. Chem.*, **12**, 1018 (1973); *Mol. Photochem.*, **5**, 151 (1973).

to an enhanced rate of radiationless deactivation and not to a mechanistic inability to react.

A final indication that much remains to be explained is illustrated in Figure 11. A near linearity exists in a plot of $\log k$ vs. $\log \phi$ for the various dichloro complexes even though reactions of differing stereochemistry are being compared (and with *cis*- α -[Co(trien)Cl₂]⁺ a clear exception). A similar correlation was noted for a series of chromium(III) amines,²² also unexplained. The thought does emerge, however, that some correspondence may exist between thexi states and the transition states of thermal kinetics.

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Registry No. *cis*- α -[Co(trien)Cl₂]Cl, 14883-58-0; *cis*- α -[Co(trien)(H₂O)Cl]²⁺, 15490-27-4; *cis*- β -[Co(trien)Cl₂]Cl, 51965-59-4; *cis*- β -[Co(trien)(H₂O)Cl]²⁺, 15155-11-0; *cis*- β' -[Co(trien)(H₂O)Cl]²⁺, 52021-54-2; [Co(tren)Cl₂]Cl, 20023-19-2; β -[Co(tren)(H₂O)Cl]²⁺, 33393-52-1; *trans*-[Co(trien)(H₂O)Cl]²⁺, 52021-55-3.

(22) C. Kotal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).

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A Ligand Field Interpretation of the Quantum Yields of Photosolvation of d^6 Complexes

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A method of relating the solvation quantum yields of d^6 complexes having C_{4v} and D_{4h} site symmetries to their spectroscopic properties is developed. The fractional metal d-orbital compositions of photoactive excited states are derived using symmetry wave functions and configuration interactions. It is shown that the fractional metal d_{z^2} orbital character, which may be calculated from the electronic absorption spectrum or approximated using the spectrochemical series, can be directly related to the sum of the quantum yields of solvation of ligands on the z axis. Deviations from the expected correlation lend support to the role of stereochemical hindrance in photosolvation. The derived relationships are discussed in terms of bond weakenings in the excited states and in terms of rates of excited-state deactivation processes including the rates of photochemical reactions and radiationless processes.

Introduction

The photochemistry of a wide variety of d^6 transition metal complexes,^{1,2} particularly that of cobalt(III), has been extensively studied and is still receiving extensive current attention.³ Recently, a ligand field model has been developed to interpret transition metal photoreactions.⁴⁻⁷ According to the ligand field model the differences between the photoreactions in a series of complexes as the metal or the ligands are changed are a consequence of the differences in the photoactive excited state caused by the changes. The differences in the excited states and, hence, the different photo-

reactions can be understood in terms of spectroscopically derived ligand field parameters.

At its current stage of development, the model consists of three interrelated parts.⁷ First, crystal field theory is used to determine the symmetry wave functions, the relative energies of the states, and hence the directionality of the photoreactions. Second, molecular orbital theory is included in the analysis to determine the distribution of the excitation energy along the labilized axis in order to understand which ligand on the axis will be preferentially labilized. Finally, a crystal field determination of the fractional d-orbital composition of the photoactive excited state is used (often in conjunction with the molecular orbital theory) to determine the relative quantum yields of the photoreactions. Of the three parts, the latter one is currently the most primitive. The purpose of this paper is to provide a careful treatment of the problem for the extensively studied group of monosubstituted and trans-disubstituted d^6 complexes.

Our fundamental approach to the problem is based on the idea that the more the excitation energy is concentrated along one molecular axis, the greater will be the quantum yield for loss of ligands on that axis. The distribution of the

(1) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(2) V. Balzani and V. Carassiti, "Photochemistry of Coordination of Compounds," Academic Press, New York, N. Y., 1970.

(3) R. A. Pribush and A. W. Adamson, Abstracts, 29th Southwest Regional Meeting of the American Chemical Society, El Paso, Tex., 1973; R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Amer. Chem. Soc.*, **96**, 3027 (1974).

(4) J. I. Zink, *J. Amer. Chem. Soc.*, **94**, 8039 (1972).

(5) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 164 (1973).

(6) J. I. Zink, *Inorg. Chem.*, **12**, 1018 (1973).

(7) J. I. Zink, *Mol. Photochem.*, **5**, 151 (1973).