(2) G. L. McPherson and L. M. Henling, *Phys. Rev. B*, **16**, 1889 (1977).
(3) L. M. Henling and G. L. McPherson, *Phys. Rev. B*, **16**, 4756 (1977).
(4) G. L. McPherson, W. Heung, and J. J. Barraza, *J. Am. Chem. Soc.*, **100**, 469 (1978).
(5) J. Owen, *J. Appl. Phys.*, **32**, 213S (1961).
(6) J. Owen and E. A. Harris, "Electron Paramagnetic Resonance", S. Geschwind, Ed., Plenum, New York, 1972 pp 427–492.
(7) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
(8) G. L. McPherson, L. J. Sindel, H. F. Quarls, C. B. Frederick, and C. J. Doumit, *Inorg. Chem.*, **14**, 2116 (1975).
(9) R. W. Benê, *Phys. Rev.*, **178**, 497 (1969).
(10) J. C. M. Henning, J. H. denBoef, and G. G. P. vanGorkom, *Phys. Rev. B*, **7**, 1825 (1973).
(11) J. R. Beswick and D. E. Dugdale, *J. Phys. C*, **6**, 3326 (1973).
(12) P. C. Benson and D. E. Dugdale, *J. Phys. C*, **8**, 3872 (1975).
(13) P. H. Davis and R. L. Belford, *ACS Symp. Ser.*, **No. 5**, 51 (1974).
(14) J. S. Griffith, "Theory of Transition Metal Irons", Cambridge University Press, Cambridge, 1961, p 437.
(15) G. L. McPherson, M. H. Nodine, and K. O. Devaney, *Phys. Rev. B*, **18**, 6011 (1978).
(16) A. Edgar, *J. Phys. C*, **11**, L489 (1978).

Contribution from the Department of Chemistry,
State University of New York at Binghamton, Binghamton, New York 13901

Ligand Field Photolysis of Some *cis*-β-1,4,8,11-Tetraazaundecane Complexes of Cobalt(III) and Rhodium(III): Evidence for Stereochemical Control in d^6 Photochemistry

EVON MARTINS, ELLEN B. KAPLAN, and PETER S. SHERIDAN*

Received February 26, 1979

The ligand field photolysis of *cis*-β-$[M(2,3,2\text{-tet})ClX]^{n+}$ (M = Co, Rh; X = Cl, H_2O) and the thermal aquations of *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ and *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ were studied in acidic aqueous solution. Photolysis of *cis*-β-$[Co(2,3,2\text{-tet})Cl_2]^+$ and *cis*-β-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ leads to *trans*-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ as the only photoproduct at efficiences ($\phi_{Cl_2} = 0.0083$, $\phi_{Cl(H_2O)} = 0.0053$) typical for cobalt(III) amine complexes. Photolysis of *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ generates *cis*-β-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ and *trans*-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ with a total chlorine-release efficiency of $\phi = 0.26$ and a trans/cis photoproduct ratio of about 3/1. *cis*-β-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ photoisomerizes to *trans*-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ ($\phi = 0.13$). A kinetic study of the chloride aquation of *cis*-α- and *cis*-β-$[Rh(trien)Cl_2]^+$ and *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ showed that all three ions aquated with retention of the cis configuration and with pH-independent (pH 1–4) pseudo-first-order rate constants (at pH 2, $\phi = 0.15$, and $T = 25$ °C, $k_{Cl^-} = 1.8 \times 10^{-4}$, 16.7×10^{-4} and 3.7×10^{-4} s^{-1}, respectively). The photochemical behavior of *cis*-β-$[M(2,3,2\text{-tet})ClX]^+$ ions is compared to the photochemistry of the analogous trien complexes, and the increased percentage of photoisomerization is justified in terms of a dissociative mechanism.

Introduction

The stereochemical consequences of the ligand field photolysis of Rh(III) and Co(III) complexes have become quite perplexing, as stereoretentive photolyses[1] as well as photoinduced isomerizations[2] have been observed for both metals. Until recently, the only models which dealt with photoinduced stereochemical change in transition-metal complexes were (a) an edge-displacement model,[2d,3] based on the semiempirical photolysis rules,[4] and (b) a mechanism involving distortion of the excited state toward a five-coordinate species with a geometry dependent upon the ligands remaining in the primary coordination sphere.[5] The fundamental difference between these empirical models is the former's retention of at least six-coordinate geometry throughout the reaction, while the latter path assumes the existence of a coordinatively unsaturated species at some point along the reaction coordinate.

A more theoretical analysis of the stereochemical consequences of ligand field excitation of d^6 complexes, recently presented by Vanquickenborne and Ceulemans,[6] also postulated the existence of five-coordinate species during the photolysis. They used an additive point ligand model[7] (APLM) to analyze the orbital energies of the five-coordinate species which would remain following photoinduced ligand labilization. For the d^6 haloammine complexes analyzed, the square-pyramid (SP) structure was calculated to be significantly more stable than the trigonal-bipyramid (TBP) structure, with the photoproduct resulting from stereospecific water attack at the vacant coordination site (trans to the axial ligand) in the SP structure. The stereochemical path of a photochemical reaction can thus be predicted by the calculation of the specific SP species which would predominate.

A tacit assumption in the Vanquickenborne analysis is that the photogenerated five-coordinate species would have a sufficient lifetime to allow intramolecular rearrangement to the lowest energy configuration. For cationic complexes in a tenaciously solvating and highly nucleophilic medium such as water, the existence of coordinatively unsaturated di- and trivalent cations for a finite period is open to question.

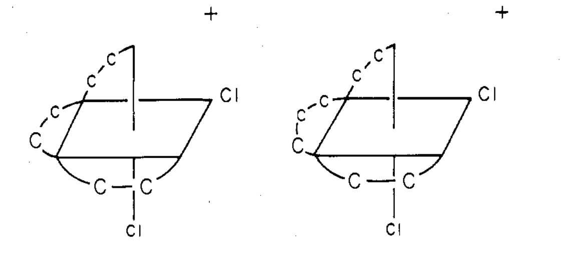
In an effort to probe the importance of coordinatively unsaturated species in the photochemistry of d^6 haloamine complexes, we have studied the ligand field photochemistry of *cis*-β-$[M(2,3,2\text{-tet})ClX]^{n+}$ (M = Co, Rh; X = Cl, H_2O).[8]

As shown in Figure 1, the 2,3,2-tet complexes differ only marginally from the previously studied[3,5] *cis*-β-$[M(trien)ClX]^{n+}$ ions, where photolysis leads to mixtures of *cis*-β- and *trans*-$[M(trien)Cl(H_2O)]^{2+}$. By use of the edge-displacement model, the formation of these two photoproducts results from the photoinduced labilization of the ligands at either end of the axis defined by a primary amine and a coordinated chloride. The isomeric composition of the photoproduct then reflects the discrimination between amine and chloride loss along the photoreactive axis, as chloride loss would lead directly to *cis*-β-$[M(trien)Cl(H_2O)]^{2+}$ and amine labilization would lead to edge-displacement and formation of *trans*-$[M(trien)Cl(H_2O)]^{2+}$.

The factors which affect the degree of discrimination between chloride and amine labilization are unknown, but the addition of a methylene group in the central chelate ring would not affect the reactivity pattern of an excited state formed upon the population of metal-centered orbitals. Thus, if the edge-displacement model is valid, photolysis of *cis*-β-$[M(2,3,2\text{-tet})ClX]^{n+}$ ions should closely mimic that of the corresponding *cis*-β-$[M(trien)ClX]^{n+}$ ions.

In contrast, if the photochemical reaction proceeds via a species of reduced coordination number, addition of a methylene group into the chelated amine could have profound effects upon the stereochemistry of the photoproducts. The trien ligand forms transition-metal complexes almost exclu-

0020-1669/79/1318-2195$01.00/0



cis-β-[M(trien)Cl$_2$]$^+$ cis-β-[M(2,3,2-tet)Cl$_2$]$^+$

Figure 1. Structural skeletons of *cis*-β-[Co(trien)Cl$_2$]$^+$ and *cis*-β-[Co(2,3,2-tet)Cl$_2$]$^+$.

sively in the cis configuration[9] as extensive steric strain is induced when trien is forced into the trans configuration, while the 2,3,2-tet ligand forms a variety of trans complexes,[10] and work with molecular models confirms that the extra methylene group relieves the strain inherent in the trans trien structure. This difference in the stable geometries of the trien and 2,3,2-tet ligands could lead to differences in the geometries of the photoinduced five-coordinate excited states, which would then be reflected in the stereochemical composition of the photoproducts.

As a part of this study on the effects of ligand configuration on excited-state reactivity, it was necessary to determine the effects of ligand configuration on ground-state reactivity under the conditions used for photochemistry. As a result, kinetic studies were done on the thermal aquations of *cis*-α- and *cis*-β-[Rh(trien)Cl$_2$]$^+$ and *cis*-β-[M(2,3,2-tet)Cl$_2$]$^+$ (M = Co, Rh) in acidic aqueous solution.

Experimental Section

Preparation of Complexes. ***cis*-α-Dichloro(triethylenetetramine)rhodium(III) Chloride.** The method of Johnson and Basolo,[11] as amended by Gillard,[9b] was used to prepare *cis*-α-[Rh(trien)Cl$_2$]Cl. Each sample was recrystallized from HCl before photolysis. The electronic spectrum agreed with the previously reported spectrum:[9,11] given, λ_{max} 352 nm (ϵ 240), λ_{max} 292 (210); found, λ_{max} 352 (235), λ_{max} 292 (195). The infrared spectrum was virtually identical with that reported for the cis-α complex.[11]

***cis*-β-Dichloro(triethylenetetramine)rhodium(III) Chloride.** Repeated crystallization of the mother liquor separated from *cis*-α-[Rh(trien)Cl$_2$]Cl eventually led to the isolation of *cis*-β-[Rh(trien)Cl$_2$]Cl.[9b] The electronic spectrum is similar to that previously observed: given, λ_{max} 350 nm (ϵ 270), λ_{max} 300 (290); found, λ_{max} 350 (273), λ_{max} 300 (290). The infrared spectrum was virtually identical with that reported for the cis-β ion. On the basis of the infrared and electronic spectra, we estimate any contamination by the cis-α ion to less than 5%.

1,4,8,11-Tetraazaundecane. The tetradentate ligand was either purchased (Eastman Kodak, Rochester, NY) or prepared by the method of Van Alphen[12] as modified by Alexander.[13] Infrared spectra of purchased and synthesized ligand were indistinguishable, as was their reactivity.

***trans*-Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Chloride.** The synthesis of *trans*-[Co(2,3,2-tet)Cl$_2$]Cl was adapted from Bosnich's[14] synthesis of *trans*-[Co(3,2,3-tet)Cl$_2$]Cl·CoCl$_2$·6H$_2$O (12 g) in CH$_3$OH (25 mL). The resultant brown-violet solution was oxidized by the vigorous passage of air for 3 h. Concentrated HCl (13 mL) was added, and the solution was heated for 10 min on the steam bath. On standing, at 0 °C for 1 h, the resultant solution precipitated feathery, pale green needles, which were collected and washed with ethanol and air-dried. The complex was recrystallized from a minimum volume of hot 4 M HCl by the addition of 10 volumes of MeOH.

***cis*-β-Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Chloride.** The synthesis of *cis*-β-[Co(2,3,2-tet)Cl$_2$]Cl is a modification of Bosnich's[15] synthesis of the analogous *cis*-[Co(3,2,3-tet)Cl$_2$]Cl. A mixture of *trans*-[Co(2,3,2-tet)Cl$_2$]Cl (4 g), LiCO$_3$ (1.5 g), and activated charcoal (6.2 g) in 30 mL of H$_2$O was heated on a steam bath for 1 h. The violet solution that formed was filtered, concentrated HCl (10 mL) was slowly added to the filtrate, and the resulting solution was heated on a steam bath for 5 min. The violet solution was taken close to dryness under vacuum. The violet crystals were collected by filtration and washed with methanol. The electronic spectrum of *cis*-[Co(2,3,2-tet)Cl$_2$]Cl is λ_{max} 532 nm (ϵ 86) and λ_{max} 386 (89), which is typical for a *cis*-[Co(N)$_4$Cl$_2$]$^+$ chromophore.

***cis*-Chloroaquo(1,4,8,11-tetraazaundecane)cobalt(III) Cation.** All attempts to isolate *cis*-[Co(2,3,2-tet)Cl(OH$_2$)](NO$_3$)$_2$ in the solid state met with failure. A reported synthesis[10b] of the aquochloro isomer could not be repeated. However, the aquochloro isomer was prepared by the silver-induced aquation of *cis*-[Co(2,3,2-tet)Cl$_2$]Cl in dilute (0.1 M) nitric acid. Two equivalents of AgNO$_3$ was added to a room-temperature solution of the dichloro ion, and precipitation of 2 equiv of AgCl occurred. The resultant AgCl was separated by filtration, and a solution of known concentration of aquochloro isomer was obtained.

***cis*-β-Dichloro(1,4,8,11-tetraazaundecane)rhodium(III) Chloride.** The method used for the preparation of *cis*-α-[Rh(trien)Cl$_2$]Cl[9b] was adapted for the 2,3,2-tet complex, as LiOH was carefully added to a refluxing solution of RhCl$_3$·3H$_2$O (1.0 g) and 2,3,2-tet·4HCl (1.2 g) until a neutral solution was obtained. The solution volume was reduced and the temperature held at 2 °C, and the chloride salt crystallized slowly (ca. 4 weeks). The yellow crystals were collected by filtration, washed extensively with ethanol, and air-dried. The electronic spectrum (λ_{max} 348 nm (ϵ 218), λ_{max} 295 (241)) is consistent with a *cis*-[Rh(N)$_4$Cl$_2$]$^+$ chromophore. Assignment of the β configuration is based upon a comparison of its infrared spectrum with that of *cis*-β-[Co(2,3,2-tet)Cl$_2$]Cl. In the diagnostic regions used to distinguish cis-β from cis-α trien complexes,[16] the two 2,3,2-tet complexes had virtually superimposable spectra. The presence of lattice water is indicated by sharp OH stretching bands at 3450 and 3350 cm^{-1}. Anal. Calcd for C$_7$H$_{22}$N$_4$Cl$_3$ORh, [Rh(2,3,2-tet)Cl$_2$]Cl·$^1/_2$H$_2$O: C, 22.2; H, 5.0; N, 14.8. Found: C, 22.7; H, 5.2; N, 14.7. Before kinetic or photochemical study, trans impurities were separated by ion-exchange chromatography (Sephadex SP C-25 resin with 0.2 N H$_2$SO$_4$ as eluent).

Kinetic Studies. The rate of thermal aquation was monitored spectrophotometrically, and several wavelengths were monitored for each complex. Solid material was dissolved in thermally equilibrated solvent; the Co aquations were done in dilute perchloric acid, while sulfuric acid was used for the Rh(III) aquations. The ionic strength was adjusted with LiClO$_4$ and Li$_2$SO$_4$, respectively. Infinite time absorbances were experimentally determined and rate constants calculated from ln ($A - A_\infty$) vs. time graphs.

Photolyses. Irradiation was done with a 200-W Hg short-arc lamp (Illumination Industries Inc.). For the Rh complexes, wavelength selection was effected with an interference filter (Baird Atomic) with a transmittance maximum at 336 nm and fwhh of 20 nm; incident intensities were measured by ferrioxalate actinometry and averaged 3.0 × 10^{-9} einstein/s over a front window area of 2.9 cm^2. The photochemical efficiencies of the Co complexes were so low that even at 2 °C the thermal aquation swamped photochemical changes when an interference filter was used. Photon flux was increased by using a broad band-pass filter (Corning CS3-72) which transmitted light of wavelength greater than 450 nm. As with the Rh complexes, this corresponded to the lowest energy ligand field band. Reinekate$^-$ actinometry was used to estimate incident intensity, which averaged 9.0 × 10^{-7} einstein/s. To reduce interference from thermal reactions, a hot mirror (Baird Atomic) was placed in the optical path, and photolyses were run at 2 °C.

Product Analysis. The two previously described[3] graphical techniques were used to analyze solute composition: photoinduced spectral changes of the cis aquochloro ions were analyzed by a two-component scheme, while a three-component, triangular graph system was needed for the three species present upon photolysis of the dichloro ions.

Instrumentation. Electronic spectra were recorded on a Beckman Acta M IV spectrophotometer. A Radiometer PHM 64 pH meter with a GK2320C combined electrode (Radiometer) was used for pH measurements, and a F1012Cl Selectrode and a K701 calomel reference electrode were used for chloride determinations. Infrared spectra were recorded with a Beckman spectrometer on Nujol mull samples.

Results

Thermal Aquation. In acidic aqueous solution, *cis*-α- and *cis*-β-[Rh(trien)Cl$_2$]$^+$ and *cis*-β-[Rh(2,3,2-tet)Cl$_2$]$^+$ undergo chloride aquation with retention of cis configuration. The

Table I. Rates of Chloride Aquation of *cis*-α- and *cis*-β-[Rh(trien)Cl_2]$^+$ in Acidic Aqueous Solution

temp, °C	μ	pH	$10^4k_{\text{cis-}\alpha}$, s^{-1}	$10^4k_{\text{cis-}\beta}$, s^{-1}
90	0.15	1.3	9.7	
80	0.15	1.3	4.5	28.5
70	0.15	1.3	1.8	14.3
60	0.15	1.3	0.68	7.2
50	0.15	1.3		3.6
70	0.30	1.3	2.0	16.3
70	0.45	1.3	2.9	16.9
70	0.15	2.1	1.8	16.2
70	0.15	3.0	2.0	16.7
70	0.15	4.0	1.8	20.0
E_a, kcal/mol			21	16
$S^{\ddagger}$ (at 80 °C), eu			−17	−27

Table II. Rates of Chloride Aquation of *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$ in Acidic Aqueous Solution

temp, °C	μ	pH	10^4k, s^{-1}
58	0.30	1.0	0.99
63	0.30	1.0	1.6
70	0.30	1.0	3.3
76	0.30	1.0	4.7
70	0.30	2.0	3.7
70	0.30	3.0	3.7
70	0.15	2.0	3.7
70	0.03	2.0	3.1

E_a = 19.5 kcal/mol (at 80 °C); $S = -20$ eu

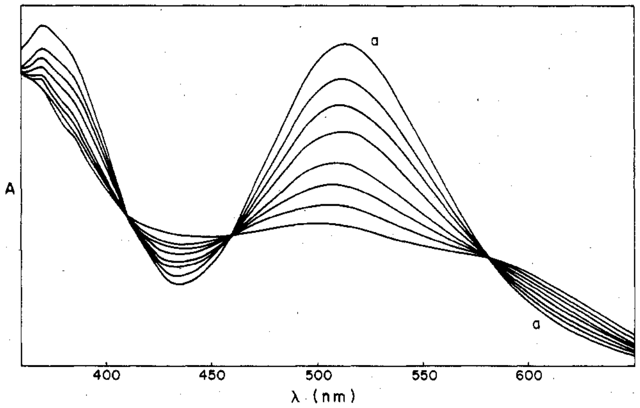


Figure 2. Spectral changes induced by ligand field photolysis of *cis*-β-[Co(2,3,2-tet)Cl(H_2O)]$^{2+}$ (a).

cis-α- and *cis*-β-[Rh(trien)Cl_2]$^+$ ions aquate to distinct cis products, implying retention of the α and β ligand configurations in the aquated products. All three ions give linear first-order plots for at least 4 half-lives, and representative rate constants and activation parameters are given in Tables I and II.

Photolyses. ***cis*-β-[M(2,3,2-tet)Cl(OH_2)]$^{2+}$.** Irradiation of the lowest energy ligand field bands of *cis*-β-[Co(2,3,2-tet)Cl(OH_2)]$^{2+}$ and *cis*-β-[Rh(2,3,2-tet)Cl(OH_2)]$^{2+}$ in acidic aqueous solution caused negligible pH or chloride concentration changes but caused the spectral changes shown in Figures 2 and 3. Isosbestics were maintained throughout the photolyses, and the intermediate spectra can be generated as linear combinations of the initial and final spectra. Comparison of the photoproduced spectra with previously reported Co(III) and Rh(III) systems allows unambiguous assignment of the photoproducts as *trans*-[M(2,3,2-tet)Cl(OH_2)]$^{2+}$ (eq 1).

$$\textit{cis-}\beta\text{-}[\mathrm{M(2,3,2\text{-}tet)Cl(OH_2)}]^{2+} \xrightarrow[\mathrm{H_3O^+}]{h\nu} \textit{trans-}[\mathrm{M(2,3,2\text{-}tet)Cl(OH_2)}]^{2+} \quad (1)$$

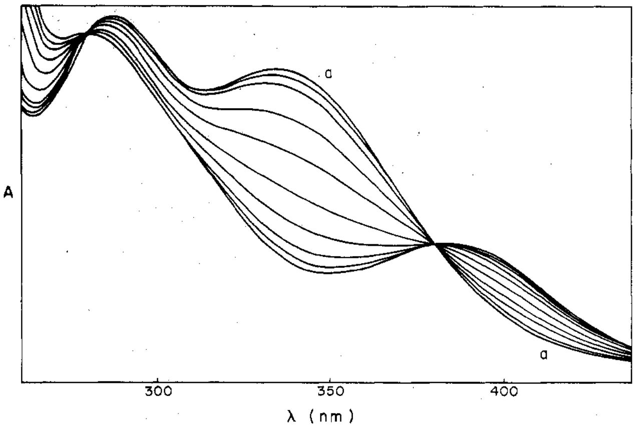


Figure 3. Spectral changes induced by the ligand field photolysis of *cis*-β-[Rh(2,3,2-tet)Cl(H_2O)]$^{2+}$ (a).

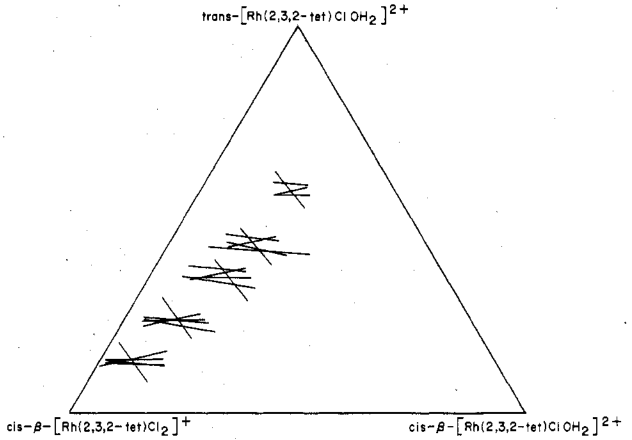


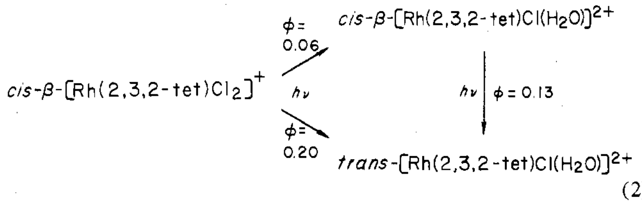
Figure 4. Three-component composition analysis for the solutions obtained upon photolysis of *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$. The region at the intersections of lines represents the fractional composition after a given photolysis period.

***cis*-β-[M(2,3,2-tet)Cl_2]$^+$.** Ligand field irradiation of acidic aqueous solutions of *cis*-β-[M(2,3,2-tet)Cl_2]$^+$ eventually leads to the same photoproduct observed upon photolysis of the *cis*-β-aquochloro ions, *trans*-[M(2,3,2-tet)Cl(OH_2)]$^{2+}$. The photoinduced spectral changes are not clean, however, and isosbestic points are not observed during the photolyses of the dichloro ions.

The absorption spectra of *cis*-β-[M(2,3,2-tet)Cl_2]$^+$ could be obtained from the starting materials, and the spectra of the thermal aquation products, *cis*-β-[M(2,3,2-tet)Cl(OH_2)]$^{2+}$, and the final photoproducts, *trans*-[M(2,3,2-tet)Cl(OH)]$^{2+}$, could be reliably determined (±3%), so the triangular graph technique was used to analyze the composition of the photolyzed solutions. As shown in Figure 4, such an analysis confirms that both *cis*-β- and *trans*-aquochloro ions are generated in the photolysis solutions and that formation of *trans*-[M(2,3,2-tet)Cl(OH_2)]$^{2+}$ as the eventual photoproduct must result from secondary photolysis of the *cis*-β-aquochloro ion.

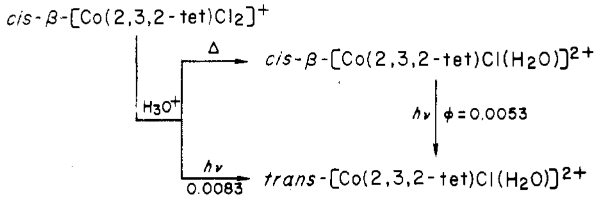
Generation of *cis*-β-[Rh(2,3,2-tet)Cl(OH_2)]$^{2+}$ via thermal aquation of the starting material was insignificant, so the photoproduct composition represented on the triangular graph is an accurate representation of the stereochemical consequences of ligand field irradiation. In the early stages of photolysis, a photoproduct ratio (trans/cis-β) of 3/1 was observed. This ratio was confirmed by quantum-yield determinations. Photoinduced isomerization of *cis*-β- to *trans*-aquochloro ion occurs with an isosbestic point at 380 nm, so analysis of the photoinduced spectral changes during the photolysis of *cis*-β-[Rh(2,3,2-tet)Cl_2]$^+$ at 380 nm gives a

ϕ_{total} which is independent of the isomeric composition of the aquochloro photoproducts (ϕ_{total} = 0.26). The thermal aquation of the *cis*-β-dichloro complex to the *cis*-β-aquochloro ion occurs with an isosbestic point at 366 nm, so determination of the quantum yield monitored at 366 nm gives the efficiency of photoinduced isomerization to *trans*-aquochloro ion (ϕ_{trans} = 0.20). This analysis gives a primary photoproduct composition of ((0.20/0.26) × 100=) 77% *trans*- and 23% *cis*-β-[Rh(2,3,2-tet)Cl(OH$_2$)]$^{2+}$, in excellent agreement with the 3/1 ratio determined from the triangular plot (eq 2).



(2)

The thermal aquation of *cis*-β-[Co(2,3,2-tet)Cl$_2$]$^+$ could not be ignored, however, for even at 2 °C, thermal formation of *cis*-β-[Co(2,3,2-tet)Cl(H$_2$O)]$^{2+}$ was not completely suppressed. Using information from a kinetic study of the thermal aquation of [Co(2,3,2-tet)Cl$_2$]$^+$ under photochemical conditions and confining the analysis to the early stages of the photolysis, we determined the extent of thermal formation of *cis*-β-[Co(2,3,2-tet)Cl(H$_2$O)]$^{2+}$ during the photolysis period; such calculations revealed that the concentrations of *cis*-β-aquochloro ion in the photolyzed solution were precisely (±2%) the concentrations generated upon thermal aquation. We therefore conclude that photolysis of *cis*-β-[Co(2,3,2-tet)Cl$_2$]$^+$ proceeds with virtually complete (at least 98%) isomerization to *trans*-[Co(2,3,2-tet)Cl(H$_2$O)]$^{2+}$ (eq 3).



(3)

Discussion

The thermal aquations of *cis*-α- and *cis*-β-[Rh(trien)Cl$_2$]$^+$ and *cis*-β-[Rh(2,3,2-tet)Cl$_2$]$^+$ occur with complete retention of the cis configuration at rates consistent with other *cis*-dichlorotetramine complexes of Rh(III). A previously reported[11] kinetic study of *cis*-[Rh(trien)Cl$_2$]$^+$ did not include an identification of ligand configuration, but comparison of kinetics data confirms that the earlier complex had the cis-α configuration. As observed with the analogous Co(III) complexes,[17] the rate of chloride loss from the cis-β ion is more rapid than from the cis-α ion, but the difference is less than an order of magnitude (Table I), in marked contrast to the differences observed for the analogous Cr(III) ions.[9c] Incorporation of an additional methylene group has little effect upon the thermal behavior, as *cis*-β-[Rh(2,3,2-tet)Cl$_2$]$^+$ aquates at a rate and with activation parameters between those of the cis-α and cis-β trien complexes.

Despite an earlier kinetic study,[18] the rate of chloride aquation of *cis*-β-[Co(2,3,2-tet)Cl$_2$]$^+$ was also studied, as first-hand information about this reaction was necessary to accurately subtract its contribution from the photoinduced spectral changes. Our study confirmed that the ion photolyzed was the same species as that observed by Tobe,[18] as the two kinetic studies were in excellent (±5%) agreement. The reaction rate is pH independent between pH 1 and 4, is relatively independent of ionic strength, and is not catalyzed by Co(II) at the pH values studied. The rates and activation parameters are also similar to those found for *cis*-β-[Co(trien)Cl$_2$]$^+$;[17] under identical conditions (pH 1, μ = 0.1, 25 °C) the rate of chloride aquation from *cis*-β-[Co(trien)Cl$_2$]$^+$ is 1.48×10^{-3} s^{-1}, compared to a value of 1.2×10^{-1} for the analogous 2,3,2-tet complex. We conclude that the configuration and detailed structure of the tetramine in the cis configuration has only minor effects on the thermal aquations of these *cis*-dichloro complexes of Co(III) and Rh(III).

Photolyses

The chemical reactions induced by ligand field photolysis of *cis*-β-[M(2,3,2-tet)ClX]$^{n+}$ (M = Co, Rh; X = Cl, H$_2$O) are nonthermal processes. In the absence of radiation, the dichloro ions aquate to *cis*-β-[M(2,3,2-tet)Cl(OH$_2$)]$^{2+}$, and photoinduced isomerization to *trans*-[M(2,3,2-tet)Cl(OH$_2$)]$^{2+}$ indicates excited-state aquations.

The identity of the photoreactive state is not known, even though irradiation was always into the lowest energy allowed ligand field transition ($^1T_1 \leftarrow {}^1A_1$). For ions of the series [Rh(NH$_3$)$_5$X]$^{2+}$, photoreaction has been proposed to occur from low-lying triplet states populated by rapid intersystem crossing.[19] In view of the similarities in the stereochemistry of the ligand field photolysis of these Co(III) and Rh(III) systems, it is reasonable that states of similar multiplicity are involved in both systems and that the higher efficiency of Rh(III) photolyses reflects the larger spin–orbit coupling and more efficient intersystem crossing of a second-row transition metal.

Despite the similarities in the thermal reactions of the 2,3,2-tet and trien complexes of Co(III) and Rh(III), the photochemical reactivities of the 2,3,2-tet ions differ from those of the trien systems. Ligand field photolysis of *cis*-[Co(en)$_2$Cl$_2$]$^+$ and *cis*-β-[Co(trien)Cl$_2$]$^+$ leads to both *cis*- and *trans*-aquochloro ions;[2d,3] photolysis of *cis*-β-[Co(2,3,2-tet)Cl$_2$]$^+$ occurs with efficiencies typical for a Co(III) amine complex, but there is no detectable photochemical production of *cis*-β-aquochloro ion. Photolysis proceeds with at least 98% isomerization to *trans*-[Co(2,3,2-tet)Cl(H$_2$O)]$^{2+}$. For the Rh(III) complexes, ligand field irradiation of *cis*-β-[Rh(trien)Cl$_2$]$^+$ leads to both *cis*-β and *trans*-aquochloro ions in a trans/cis ratio of 1/2,[5] while for the 2,3,2-tet ion the trans/cis photoproduct ratio is 3/1. That is, for both the cobalt and rhodium complexes, incorporation of a single methylene group in the central chelate chain causes a marked increase in the percentage of isomerized *trans*-aquochloro ion produced in the primary photolysis step.

Interpretation of the stereochemical rearrangements of d^6 complexes cannot be based upon the ligand field and σ/π bonding schemes developed by Zink.[20] These models attempt to identify the photolabilized ligand in octahedral complexes but do not deal with stereochemical rearrangement and, in fact, make the tacit assumption that stereoretentive aquation occurs as soon as the labilized ligand vacates the primary coordination sphere.

The edge-displacement model[2d,3] was developed in an attempt to reconcile the apparent requirement of (at least) six-coordination, with the stereochemical rearrangements common to d^6 photochemistry. This model, involving a quasi-seven-coordinate species does account for the formation of *trans*-[M(2,3,2-tet)Cl(OH$_2$)]$^{2+}$ upon photolysis of the cis-β ions, but it does not easily account for the differences between the cis-β trien and 2,3,2-tet complexes. It is not apparent why such a minor structural difference should increase the degree of discrimination of amine over chloride labilization along the photoreactive axis, yet such increased discrimination would be required to account for the increased trans/cis photoproduct ratio observed for both *cis*-β-[M(2,3,2-tet)Cl$_2$]$^+$ ions.

If the requirement of a coordinatively saturated metal center is loosened, photoinduced isomerizations are less difficult to rationalize. An empirical model, involving concerted ligand

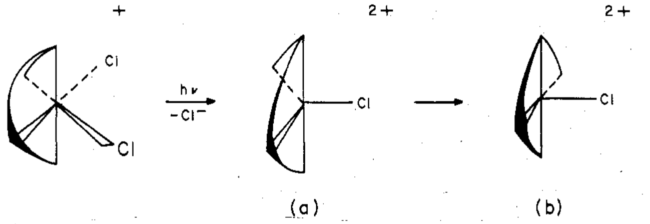


Figure 5. Representation of the photoinduced distortions of *cis*-β-$[M(2,3,2\text{-tet})ClX]^{n+}$ (M = Co, Rh; X = Cl, H_2O) which accounts for the high percentage of *trans*-$[M(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ photoproduct. Water attack at (a) would lead to a mixture of cis and trans photoproducts, while attack at (b) would lead to pure *trans*-$[M(2,3,2\text{-tet})Cl(H_2O)]^{2+}$.

loss and distortion of the remaining five-coordinate excited state, was proposed for some cis trien and tren complexes of Rh(III).[5] In addition, a theoretical analysis of Vanquickenborne and Ceulemans[6,7] implies a dissociative mechanism, with the distortion of the excited state treated as a separate process after loss of the photolabilized ligand. Within these dissociative models, the differences between the trien and 2,3,2-tet complexes would result from the different geometric preferences of the quadridentates, which, in turn, would effect the structure of the five-coordinate excited states.

Thermodynamic data is not available concerning the lowest energy configuration of trien and 2,3,2-tet, but preparation of trans trien complexes is difficult, and when formed, trans trien complexes are generally unstable toward isomerization to the cis-β geometry[17]. In contrast, the 2,3,2-tet ligand seems to prefer the trans geometry, and the synthesis of cis complexes is plagued by the readily formed trans species. The preference of 2,3,2-tet for the trans configuration (and of trien for cis) should then be reflected in the geometry of the photoproduced five-coordinate excited state. As represented in Figure 5, a trans geometry for the 2,3,2-tet ligand is readily attained through distortion toward a SP, with the chloride in the unique axial site and the 2,3,2-tet occupying the four equatorial sites. Just such a SP structure is calculated[6] to be the lowest energy configuration for the sterically unconstrained $[Rh(NH_3)_4Cl]^{2+}$ species, so the high percentage of *trans*-aquochloro photoproduct resulting from the ligand field photolysis of *cis*-β-$[M(2,3,2\text{-tet})Cl_2]^+$ (M = Co, Rh) is consistent with the calculations of Vanquickenborne.[6] The formation of 23% *cis*-β-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$ upon photolysis of *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]^+$ is then attributed to the existence of a second SP species (with the chloride in one of the equatorial coordination sites) which is in equilibrium with the more prevalent SP species with the axial chloride. The lower percentage of trans photoproduct observed for the trien complexes[5] must then be attributed to the ligand-imposed steric constraints which hinder formation of the normally low-energy SP species.

In terms of the empirical model[5] involving concerted ligand loss and rearrangement, the distortions necessary to form the low-energy SP structure are logical continuations of the distortions proposed for the $[Rh(tren)ClX]^{n+}$ and *cis*$[Rh(trien)ClX]^{n+}$ systems. That the distortion should continue past the TBP to the SP geometry is again attributed to the preference of the 2,3,2-tet ligand for the trans configurations. In contrast to the theoretical model, the empirical model does not involve the existence of thermally equilibrated SP intermediates but calls for water attack at some coordinately unsaturated species which need not exist long enough to attain thermal equilibration. The formation of isomeric mixtures is attributed to water attack from different directions at species near a TBP geometry, while isomerically pure photoproducts (as upon photolysis of *cis*-β-$[Co(2,3,2\text{-tet})Cl_2]^+$) result from water attack near the vacant site of excited states near a SP geometry. The concerted labilization/distortion model avoids the problems inherent in postulating the thermal equilibration of two coordinatively unsaturated divalent cations in aqueous solution. It also accounts for the relative photoinertness of both *cis*-α-$[M(trien)Cl_2]^+$ ions,[5] which is not readily explained with the theoretical model.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Additional support from the Cottrell Grants Program of the Research Corp. and an institutional Biomedical Research Support Grant provided by the National Institutes of Health is gratefully acknowledged. We also thank Mr. Mark Rerek for assistance and the Department of Biological Sciences (SUNY—Binghamton) for the use of their infrared spectrophotometer.

Registry No. *cis*-β-$[Co(2,3,2\text{-tet})Cl_2]Cl$, 60409-16-7; *cis*-β-$[Rh(2,3,2\text{-tet})Cl_2]Cl$, 70613-66-0; *cis*-β-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, 70561-53-4; *cis*-β-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, 70528-07-3; *cis*-α-$[Rh(trien)Cl_2]^+$, 67951-70-6; *cis*-β-$[Rh(trien)Cl_2]^+$, 56026-84-7; *trans*-$[Co(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, 70614-59-4; *trans*-$[Rh(2,3,2\text{-tet})Cl(H_2O)]^{2+}$, 70614-58-3; *trans*-$[Co(2,3,2\text{-tet})Cl_2]Cl$, 15041-27-7.

References and Notes

(1) (a) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1454 (1973); (b) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1979 (1972); (c) J. Sellan and R. Rumfeldt, *Can. J. Chem.*, **54**, 519, 1061 (1976); (d) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 3027 (1974); (e) R. A. Pribush, R. E. Wright, and A. W. Adamson, *ibid.*, **99**, 2495 (1977); (f) J. D. Petersen and F. P. Jakse, *Inorg. Chem.*, **16**, 2845 (1977).
(2) (a) M. M. Muir and H. L. Huang, *Inorg. Chem.*, **12**, 1831 (1973); (b) John Petersen, private communication; (c) D. Strauss and Peter C. Ford, *J. Chem. Soc., Chem. Commun.*, **194** (1977); (d) P. S. Sheridan and A. W. Adamson, *J. Am. Chem. Soc.*, **99**, 2495 (1977).
(3) P. S. Sheridan and A. W. Adamson, *Inorg. Chem.*, **13**, 2482 (1974).
(4) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(5) E. Martins and P. Sheridan, *Inorg. Chem.*, **17**, 2822, 3631 (1978).
(6) L. G. Vanquickenborne and A. Ceulemans, *Inorg. Chem.*, **17**, 2730 (1978).
(7) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **100**, 475 (1978).
(8) Abbreviations used throughout: 2,3,2-tet = 1,4,8,11-tetraazaundecane, trien = 1,4,7,10-tetraazadecane.
(9) (a) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965); **6**, 787 (1967); (b) P. M. Gidney, R. D. Gillard, B. T. Heaton, P. S. Sheridan, and D. H. Vaughn, *J. Chem. Soc., Dalton Trans.*, 1462 (1973); (c) W. Fordyce, P. S. Sheridan, E. Zinato, P. Riccieri, and A. W. Adamson, *Inorg. Chem.*, **16**, 1154 (1977).
(10) (a) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965); (b) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966); (c) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).
(11) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).
(12) J. Van Alphen, *Recl. Trav. Chim. Pays-Bas*, **55**, 835 (1936).
(13) H. G. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, 5, 2060 (1966).
(14) B. Bosnich, J. MacB. Harrowfield, and H. Boucher, *Inorg. Chem.*, **14**, 815 (1975).
(15) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 836 (1975).
(16) D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, **88**, 2156 (1966).
(17) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).
(18) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).
(19) T. L. Kelly and J. F. Endicott, *J. Phys. Chem.*, **76**, 1937 (1972).
(20) M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, **13**, 2489 (1974); J. I. Zink, *ibid.*, **12**, 1018 (1973).