Contribution from the Department of Chemistry,
Revelle College, University of California, San Diego, La Jolla, California 92037

Photolysis of 1,6-Dichlorodiaquoethylenediaminechromium(III)

R. TOM WALTERS and R. G. LINCK*

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The photolysis of 1,6-dichlorodiaquoethylenediaminechromium(III) ion has been carried out at several wavelengths at 3–5°. Photolysis leads to rupture of the chromium(III)–chloride bond both with and without net stereochemical change. The quantum yields for formation of the two isomers of $Cr(en)(H_2O)_3Cl^{2+}$ are 0.12 and 0.10. These product isomers have been studied by kinetic methods of analysis and are assigned structures on that basis. The nature of the photolysis is discussed in terms of the concepts of an axis of activation and models of the photolytic behavior of Cr(III) complexes.

Introduction

What effect does perturbation of the electronic energy levels of Cr(III) complexes have upon photochemical behavior of those complexes? This question continues to demand attention from experimentalists in order that various models of photochemical processes on Cr(III) centers can be tested. In order to attempt to gain some insight into this question, we report in this paper results on the photolysis of 1,6-dichlorodiaquoethylenediaminechromium(III), $Cr(en)(H_2O)_2Cl_2^+$, hereafter labeled $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$.

This complex was chosen for a photolysis study in order to establish several features accented in models of Cr(III) photochemistry. First, we wished to learn if the concept of an "axis of labilization", a concept first introduced by Adamson[1] and since used extensively by most other workers in the area, had validity in complexes of microsymmetry lower than C_{4v}. Second, the trans arrangement of the chlorides along axial positions in this molecule offers a means to compare an in-plane perturbation with several other *trans*-dichloro complexes whose photochemistry has been reported, *trans*-$CrL_4Cl_2^+$ where L_4 is 4 NH_3,[2] 2 en,[3] 2,3,2-tet,[4] and cyclam.[4] Third, because the spectral features of $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ show almost no splitting of the transitions arising from the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of the parent octahedral complex, certainly as little as is found in *trans*-$Cr(en)_2F_2^+$,[5,6] $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ should be classified as an "octahedral-like" complex in the nomenclature of Wrighton, Gray, and Hammond.[7] If this is so, the photochemistry predicted by their model will involve retention of Cr–Cl bonds because of the depopulation of π^* orbitals in the excited state. On the other hand, the model we advanced earlier[6,8,9] predicts that the weaker Cr–Cl bond will become weaker yet in the σ^* vibrationally relaxed excited state—an excited state stretched along the Cl–Cr–Cl axis will be formed—and reaction from this state will tend to lead to rupture of the Cr–Cl bond. Thus $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ allows another[9] test of the distinction between these models. Finally, knowledge of the quantum yield for photolysis of $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ offers an opportunity to assess whether the replacement of coordinated amines by coordinated water allows a more efficient means of nonradiative deactivation. These questions will be discussed below on the basis of the results of the photolysis of $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$.

Experimental Section

Materials. The 1,6-dichlorodiaquoethylenediaminechromium(III) chloride was prepared, according to the procedure of House and Garner,[10] by treating $Cr(en)(OH_2)(O_2)_2 \cdot H_2O$ with concentrated HCl. (*Caution*! $Cr(en)(OH_2)(O_2)_2 \cdot H_2O$ can easily be exploded by impact. Striking a small sample with a hammer causes a sharp report. Another sample dried by passing air through it on a glass-fritted filter burned without explosion upon contact with a Teflon spatula.) The crude material was washed with a 1:1 mixture of concentrated HCl and 2-propanol and then with 2-propanol and dried. Anal. Calcd for $Cr(en)(H_2O)_2Cl_3$: Cr, 20.41. Found: Cr, 20.50. In addition the spectroscopic parameters for this species agreed very well with those reported in the literature—see Table I—and the material showed by ion-exchange chromatography only slight levels of an impurity that agrees in spectral characteristics with the aquation product[11] of $1,6\text{-}Cr(en)(H_2O)Cl_2^+$.

Table I. Spectral Characteristic of Complexes

Complex	λ_{max}, Å	ϵ, M^{-1} cm^{-1} Our value	ϵ, M^{-1} cm^{-1} Lit. value	Ref
$1,6\text{-}[Cr(en)(OH_2)_2(Cl)_2]^+$	4200	22.7	22.7	
	5500 sh	37.0	37.6	10
	5800	39.1	39.1	
Magenta $[Cr(en)(OH_2)_3Cl]^{2+}$	4020	30.3	30.5	
	5350	38.4	38.9	11
$[Cr(en)(OH_2)_4]^{3+}$	3850	24.4	24.3	
	5120	41.0	41.7	10

Mercuric perchlorate solutions were prepared from reagent grade mercuric nitrate by repeated recrystallizations of HgO as described previously.[12] The solutions were standardized by titration of excess EDTA with standard Mg^{2+} solution.[13] All other chemicals were of reagent grade quality.

Techniques. Photolyses were carried out using a 500-W xenon source with interference filters to select the wavelength of interest. Samples were irradiated in 10-cm spectrophotometer cells held at constant temperature in a water-filled block. Stirring was achieved by a small magnetic stirring bar in the bottom of the cell.

Product analysis was achieved by ion-exchange chromatography on Dowex 50W-X2 resin, 200–400 mesh, partially screened by flotation. This resin was cleaned by the basic peroxide method outlined previously.[8] The columns were of 9-mm inside diameter and 10–15 cm long. All separations were made at 0–10° in a refrigerator with applied pressures of about 3 atm to avoid undue thermal aquation during the separation. Blank experiments were run in parallel with photolyses to check thermal aquations. Actinometry was achieved with *trans*-$Cr(NH_3)_2(NCS)_4^-$ as outlined in the literature.[14]

Kinetic experiments were performed in a thermostated cell compartment of a Cary Model 14 recording spectrophotometer. pH measurements were made with a Radiometer Model 51 meter.

Analyses. Analysis for Cr content of solutions was achieved spectrophotometrically at 3730 Å[15] after basic oxidation by peroxide to CrO_4^{2-}. Chloride analyses were performed by the technique described by Vogel.[16]

Results

Photolysis Products. When $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ is subjected to irradiation with visible light and the resulting solution chromatographed on an ion-exchange column, three bands are observed. The first and third are easily identifiable. The first, eluted with 0.5 M $HClO_4$, has spectral and chromatographic characteristics of starting material and this structure is assigned to it. The third band elutes from the column with 2.0–4.0 M $HClO_4$ and has the same spectral characteristics[10] and ion-exchange behavior[10] as $Cr(en)(H_2O)_4^{3+}$: see Table I.

The second band in an ion-exchange separation of photolyzed $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ is the dominant product band. It is eluted easily with 0.75–1.0 M $HClO_4$ and has chromatographic characteristics[17] similar to those of the product of thermal aquation of $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$, the molecule named[17] "magenta $Cr(en)(H_2O)_3Cl^{2+}$". We have independently synthesized magenta $Cr(en)(H_2O)_3Cl^{2+}$ by thermal aquation of $1,6\text{-}Cr(en)(H_2O)_2Cl_2^+$ as well as by Hg^{2+}-induced aquation

Table II. Hg^{2+}-Induced Kinetic Experiments on Photolysis Product Band 2 (25°)

$10^2[Hg^{2+}]$, M	k_{rapid}, M^{-1} sec^{-1}	k_{slow}, M^{-1} sec^{-1}
4.32	1.10	0.96×10^{-2}
4.45	1.10	1.11×10^{-2}
2.53	1.13	
2.10	1.03	
2.20	1.14	
3.60	1.02	
	Av 1.08 ± 0.05	Av $(1.04 \pm 0.11) \times 10^{-2}$

and found spectral characteristics in good agreement with those of House, Hughes, and Garner.[11] Table I lists these values. However, although the second chromatographic band of a photolyzed solution of 1,6-$Cr(en)_2(H_2O)_2Cl_2^+$ behaves chromatographically properly for identification as magenta $Cr(en)(H_2O)_3Cl^{2+}$, the spectral characteristics of this band are slightly, but significantly and reproducibily, different from pure magenta $Cr(en)(H_2O)_3Cl^{2+}$. For instance, in a typical experiment, the apparent extinction coefficient at 5400 Å (λ_{max}) is 46.7 M^{-1} cm^{-1} and at 4050 Å (λ_{max}) is 32.2 M^{-1} cm^{-1}; these values are to be compared with those in Table I for magenta $Cr(en)(H_2O)_3Cl^{2+}$. Since magenta $Cr(en)(H_2O)_3Cl^{2+}$ is the thermal product of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ and the length of time necessary for us to carry out a photolysis and separation is such that some thermal product is produced, magenta $Cr(en)(H_2O)_3Cl^{2+}$ must be a partial component of this second ion-exchange band. However, attempts to resolve this product band into two components by use of longer columns failed; and various cuts of the band showed little change (but the apparent ϵ did increase as further cuts were taken) in spectral characteristics indicating that only a partial resolution is achieved on Dowex 50W-X2 columns of the length employed by us. Analyses of the band indicated a Cl:Cr ratio of 1.02 ± 0.07, and thermal aquation or Hg^{2+}-induced aquation of the material in this band yielded a solution whose spectral characteristics matched those of $Cr(en)(H_2O)_4^{3+}$.

To gain further insight into the composition of band 2 of a chromatographically separated photolyzed solution of 1,6-$Cr(en)(H_2O)_2Cl_2^+$, we have performed several kinetic experiments. These experiments were designed to differentiate the two (or more) components of this band. Treatment of a sample of band 2 with Hg^{2+} showed a two-component kinetic curve of absorbance at 5700 Å vs. time. These kinetic experiments were run under pseudo-first-order conditions of excess Hg^{2+}. We extracted from plots of ln $(A_t - A_\infty)$ vs. t, where A_t and A_∞ are the absorbancies at time t and after completion of the reaction, respectively, two pseudo-first-order rate constants. One was obtained from the linear portion of the ln $(A_t - A_\infty)$ vs. time plot that results after the rapidly decaying component has died out; the second was obtained from plots of ln $(A_t - A_e)$ vs. time, where A_e is the absorbance at time t due to the slowly reacting component extrapolated from the long-time-linear portion of the ln $(A_t - A_\infty)$ vs. time plot. Both of these first-order rate constants were found to depend on $[Hg^{2+}]$ and each yielded second-order rate constants. Table II lists the values for several kinetic experiments; it should be noted that these experiments are under conditions of somewhat variable acidity and ionic strength (0.75–1.0 M) as dictated by the elution acidity. In separate experiments, authentic samples of magenta $Cr(en)(H_2O)_3Cl^{2+}$, prepared from thermal aquation of 1,6-$Cr(en)(H_2O)_2Cl_2^+$, were treated with Hg^{2+}. The curve resulting when ln $(A_t - A_\infty)$ was plotted vs. time was linear; no evidence was found for a rapidly reacting component. The second-order rate constant derived from these latter experiments was $(1.01 \pm 0.11) \times 10^{-2}$ M^{-1} sec^{-1}. This result allows us to identify the slowly reacting component as magenta $Cr(en)(H_2O)_3Cl^{2+}$.

Table III. Thermal Aquation of the Rapidly Reacting Component of Photolysis Product Band 2

Temp, °C	10^4k, sec^{-1}	Temp, °C	10^4k, sec^{-1}
25	1.19	25	1.16
25	1.15	25	1.16
25	1.18	35	2.93

Use of the kinetic plots mentioned above is also made to determine the fraction of chromium in each of the two components of the second band of the separation. Extrapolation of the value of $(A_t - A_\infty)$ from the linear (long-time portion) to zero time yields $(A_0' - A_\infty)$ where A_0' is the value of the absorbance if all the rapidly reacting component, R, has been converted to $Cr(en)(H_2O)_4^{3+}$ but none of the slowly reacting one, S, has been. A_0' is then given by

$$A_0' = \epsilon_S l[S]_0 + \epsilon_T l[R]_0$$

where ϵ_T is the extinction coefficient of $Cr(en)(H_2O)_4^{3+}$. Subtracting A_∞ from A_0' and rearranging yield

$$[S]_0 = (A_0' - A_\infty)/(\epsilon_S - \epsilon_T)l$$

Thereby, if ϵ_S is available, $[S]_0$ is available. The rapidly reacting concentration, $[R]_0$, is then determinable from $[S]_0$ and the total Cr in the band. Since we have identified the slowly reacting compound as magenta $Cr(en)(H_2O)_3Cl^{2+}$, ϵ_S at 5700 Å can be obtained from the product of thermal aquation; it has a value of 32.4 M^{-1} cm^{-1}.

Another kinetic means of analysis of the products in the second band of an ion-exchanged solution of photolyzed 1,6-$Cr(en)_2(H_2O)_2Cl_2^+$ is by thermal aquation. It has already been established[17] that the aquation of magenta $Cr(en)(H_2O)_3Cl^{2+}$ is very slow at 25°: the extrapolated value is 3.4×10^{-7} sec^{-1}. If a solution of the second band is observed spectrophotometrically as a function of time, the spectrum changes too rapidly for significant aquation of magenta $Cr(en)(H_2O)_3Cl^{2+}$. A plot of ln $(A_t - A_\infty)$ vs. t for this more rapid process is linear; the data are presented in Table III. The average value of the slope corresponds to a rate constant of 1.17×10^{-4} sec^{-1} at 25°. [Thus during the time required to aquate the more rapidly reacting compound for 6 half-lives (about 10 hr), magenta $Cr(en)(H_2O)_3Cl^{2+}$ has aquated only 1.2%.] The solution resulting after the rapid aquation has taken place exhibits λ (ϵ) values of 3860 Å (24.9), 4520 Å (13.8), and 5260 Å (37.9). These values are to be compared with the recorded values for the isosbestic points of magenta $Cr(en)(H_2O)_3Cl^{2+}$ and $Cr(en)(H_2O)_4^{3+}$: at the same wavelengths, the ϵ values are,[17] respectively, 24.5, 14.3, and 38.8. These data, coupled with the fact that the ultimate spectrum after complete aquation agrees with that of $Cr(en)(H_2O)_4^{3+}$, allow us to conclude that the rapidly reacting component loses chloride to produce $Cr(en)(H_2O)_4^{3+}$. Since the solution aquated for 10 hr contains only $Cr(en)(H_2O)_4^{3+}$ and magenta $Cr(en)(H_2O)_3Cl^{2+}$ and $Cr(en)(H_2O)_4^{3+}$ arises primarily from the rapidly reacting component, analysis of the solution for $Cr(en)(H_2O)_4^{3+}$ gives a value for the initial amount of the rapidly reacting component.

Each of these two kinetic means of analysis of the second band have been utilized to obtain the amount of rapidly reacting material in various preparations. From this number the value of the extinction coefficient for the rapidly reacting component at 5700 Å was obtained. The values found from a number of experiments yield an average value of 46.5 ± 1.3 M^{-1} cm^{-1}. This value was then used with ϵ for magenta $Cr(en)(H_2O)_3Cl^{2+}$ to determine the fraction of rapidly reacting species in any mixture of this species with magenta $Cr(en)(H_2O)_3Cl^{2+}$.

The results of the above-mentioned analyses are rigorous if only two components are present within band 2 of a chromatographically separated photolyzed solution of 1,6-$Cr(en)_2(H_2O)_2Cl_2^+$. The kinetic means of analysis, the Cl^-:Cr ratio, the observation of $Cr(en)(H_2O)_4^{3+}$ as the sole product of both thermal and Hg^{2+}-assisted aquation, and the lack of any H^+ uptake during photolysis demand the result that the two isomers of stoichiometry $Cr(en)(H_2O)_3Cl^{2+}$ are the two, and only two, complexes contained within the second chromatographic band.

Photochemical Yields. Having established the nature of the materials found upon ion exchange of a photolyzed solution of 1,6-$Cr(en)(H_2O)_2Cl_2^+$, we need to establish the quantum yield for production of the various species. To do so, it is necessary to correct the observed products for any formed thermally during photolysis and separation. Since rate constants are available for the reactions[17]

$$\text{1,6-}Cr(en)(H_2O)_2Cl_2^+ \rightarrow \text{magenta } Cr(en)(H_2O)_3Cl^{2+} + Cl^-$$

$$\text{magenta } Cr(en)(H_2O)_3Cl^{2+} \rightarrow Cr(en)(H_2O)_4^{3+} + Cl^-$$

as a function of temperature and we have measured the rate of the reaction

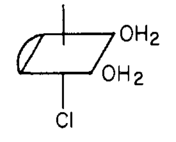
$$\text{rapid } Cr(en)(H_2O)_3Cl^{2+} \rightarrow Cr(en)(H_2O)_4^{3+} + Cl^-$$

as a function of temperature—see Table III—the data are available to determine the amount of aquation during photolysis and separation. The results of this analysis indicate that both the R isomer and the S isomer are photoproducts found in reasonable yield. In a typical experiment the total yield of material in the second ion-exchange band was 49 μmol. Of this amount, spectral analysis at 5700 Å, as described above, indicated that 18 μmol was the rapidly reacting isomer whereas the remaining yield of 31 μmol was the magenta (or slowly reacting) isomer. The time–temperature profile of the photolysis and separation was used as previously described[8] to determine that 4 μmol of the magenta isomer arose as a thermal product of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ (0.94% hydrolysis). Typically, as in this case, the thermal correction therefore is less than 20% of the observed yield of magenta $Cr(en)(H_2O)_3Cl^{2+}$. Thermal blanks agreed with these calculations.

The other product of separation of the photolyzed solution is $Cr(en)(H_2O)_4^{3+}$. This material arises as the product of the labile R isomer during separation. Experiments in which a solution of the two monochloro isomers, freshly ion exchanged, are reexchanged indicate that a combination of column-induced and normal aquations of the R isomer accounts for the $Cr(en)(H_2O)_4^{3+}$ found. Thus the yield of the R isomer is obtained as the sum of the R isomer found in the dipositive-ion band of the ion-exchanged photolyzed solution and the $Cr(en)(H_2O)_4^{3+}$ obtained. The values found at several wavelengths are indicated in Table IV. As can be seen there is no observable dependence upon the fraction of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ photolyzed when the wavelength of irradiation is 5890 Å. This result follows from two considerations: (1) The value of ε for photoproducts is small compared to that of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ at this wavelength; (2) the concentrations under which photolysis took place were large enough so that greater than 99% of the light is absorbed even after destruction of 10–20% of starting material.

Discussion

Nature of the Activation and Identity of Products. 1,6-$Cr(en)(H_2O)_2Cl_2^+$ has a trans arrangement of chloride ligands as determined by an X-ray diffraction study.[18] This result suggests a treatment to achieve a consistent interpretation of the spectrum. The molecular structure

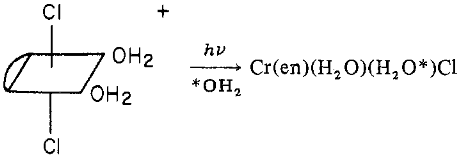


can be represented as a *trans*-$CrX_4Cl_2^+$ species where X is a ligand whose effective crystal field strength is the average of that of ethylenediamine and water.[19] This assumption would predict[20] spectral transitions in the visible region at 16,400, 19,880, 24,700, and 26,300 cm^{-1}. The observed spectrum has a broad peak, asymmetrical to the high-energy side, with a maximum at 17,200 cm^{-1} and a second peak at about 23,600 cm^{-1}. The low-energy peak is resolvable into components at about 16,800 and 19,000 cm^{-1}, in reasonable agreement with the predicted values. In addition, there are observed some low-intensity peaks at 14,500 and 14,700 cm^{-1} that are assigned to transitions to the doublet states (derivable from ^2E_g and $^2T_{1g}$ states of the octahedral parent species). The analysis of the spectrum presented above suggests that treatment of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ as a normal trans-disubstituted complex from the point of view of understanding the photochemistry is a reasonable *initial* approach. In this approach, we would expect the chloride–chloride axis to be labilized since these are the ligands which in the vibrationally relaxed excited state receive the greatest destabilization by population of their antibonding σ orbitals. Providing, then, that the axis of labilization concept is meaningful, a direct prediction of the photolysis pathway is available.

Table IV. Quantum Yield for Formation of the Isomers of $Cr(en)(H_2O)_3Cl^{2+}$ from Photolysis of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ (3–5°)

Wavelength, Å	ϕ_R	ϕ_S	Fraction unphotolyzed
5890	0.116	0.110	0.90
	0.081	0.095	0.89
	0.096	0.118	0.88
	0.115	0.135	0.88
	0.121	0.145	0.88
	0.100	0.120	0.86
	0.104	0.103	0.85
	0.108	0.128	0.95
	0.110	0.133	0.84
	0.079	0.108	0.82
	Av 0.103 ± 0.014	Av 0.120 ± 0.014	
5200	0.122	0.145	0.94
	0.117	0.143	0.97
	0.110	0.123	0.93
	Av 0.116 ± 0.006	Av 0.137 ± 0.012	
4000	0.158	0.217	0.97
	0.140	0.230	0.96
	0.159	0.206	0.95
	Av 0.152 ± 0.010	Av 0.218 ± 0.010	

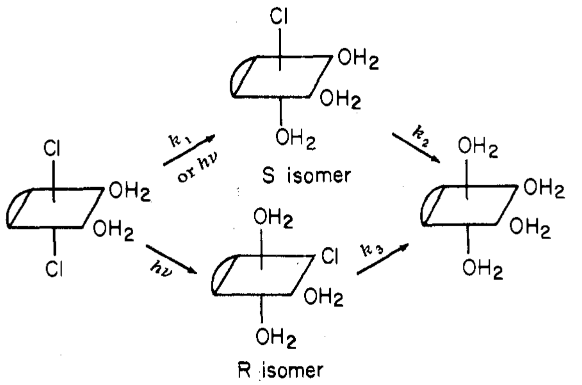
The results of photolysis of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ clearly establish that the products result from cleavage of the chromium–chloride bond. There is no evidence of any dichloro species except 1,6-$Cr(en)(H_2O)_2Cl_2^+$ [22] and there is no evidence for any species containing unidentate ethylenediamine as determined by lack of H^+ uptake and by failure to observe any band on the ion-exchange column characteristic of a one-ended species. These results support the concept of an axis of activation in low-symmetry complexes if we exclude the nondetectable (under our conditions) photoexchange of water, eq 1. This photoaquation could be occurring, and two



$$\xrightarrow[*OH_2]{h\nu} Cr(en)(H_2O)(H_2O^*)Cl_2^+ \quad (1)$$

lines of argument can be made that illuminate aspects of the importance of eq 1. First, the activation of a complex containing an amine–water axis is known to occur with chromium–nitrogen bond rupture; Edelson and Plane[23] have reported that photolysis of $Cr(NH_3)_5OH_2^{3+}$, in which the NH_3–H_2O axis is presumably activated, gives a quantum yield

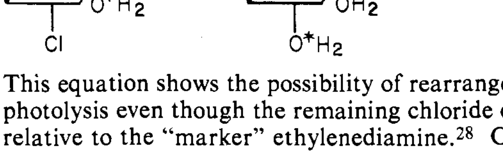
Scheme I



for NH_3 loss of 0.20. If "in-plane" activation were occurring in 1,6-$Cr(en)(H_2O)_2Cl_2^+$ as indicated in eq 1, some unidentate ethylenediamine would be expected to be produced. We found none. Second, if eq 1 were to take place, we would anticipate the possibility that some rearrangement would take place to produce one of the other isomers of $Cr(en)(H_2O)_2Cl_2^+$. Although such rearrangements are common in photolysis of Cr(III) complexes,[24,25] it has been established[6,8,9] that there are cases in which attendant rearrangement is not detectable. These cases are those which seem most applicable here: photoaquation of an "in-plane" ligand when the axial ligands have the capability to π donate. Therefore, it seems possible for eq 1 to take place without rearrangement but doubtful that "in-plane" activation of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ would lead exclusively to photoexchange of water rather than photoaquation of ethylenediamine.

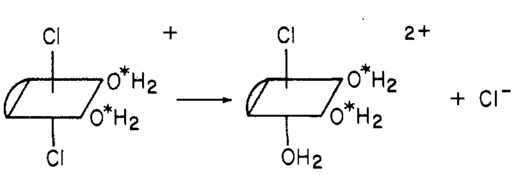
The dominant products of the photoaquation of chloride from 1,6-$Cr(en)(H_2O)_2Cl_2^+$ are the two isomers of $Cr(en)(H_2O)_2Cl^{2+}$. Therefore, we propose that the substitution chemistry, both thermal and photochemical, can be summarized as shown in Scheme I. That is, the S isomer, magenta[17] $Cr(en)(H_2O)_3Cl^{2+}$, is both a thermal product and photochemical product whereas the R isomer, a complex that has suffered rearrangement relative to 1,6-$Cr(en)(H_2O)_2Cl_2^+$, is only formed photochemically. This assignment of geometry is consistent with (1) the usual stereoretentive nature of thermal aquations of Cr(III) complexes,[26,27] (2) the usual rearrangement found when axial ligands are photoaquated from Cr(III) species,[24] and (3) the relative labilities of the R and S isomers, k_3/k_2.

These last two arguments require some amplification. In the photolysis of 1,6-$Cr(en)(H_2O)_2Cl_2^+$, to produce what is labeled in Scheme I as the R isomer, there is no question about rearrangement: chloride has shifted positions relative to the "marker", ethylenediamine. However, it is not as clear that the S isomer *can* also arise through a photochemical pathway involving rearrangement. This is easily shown, however, by labeling the water molecules in 1,6-$Cr(en)(H_2O)_2Cl_2^+$, eq 2.



(2)

This equation shows the possibility of rearrangement during photolysis even though the remaining chloride does not shift relative to the "marker" ethylenediamine.[28] Of course it is also possible that the S isomer arises from a photolytic act in which rearrangement does not occur; in terms of labeled water molecules, the equation is shown by (3). Thus the occurrence of stereochemical change is consistent with both isomers being formed, but that one (the R isomer) which is formed only by the photochemical act argues in favor of the geometrical assignment given in Scheme I. The relative rates of aquation of the R and S isomers also are used to support the geometrical assignments. The difference in rates is suggestive of the well-known greater lability of *cis*-$Cr(en)_2X_2^+$ isomers compared to *trans*-$Cr(en)_2X_2^+$ isomers.[26] In the R isomer, the chloride is in a spatial position equivalent to a chloride in *cis*-$Cr(en)_2Cl_2^+$, that is, trans to one amine N, whereas in the S isomer, the spatial position is equivalent to the corresponding trans complex.[29] The greater lability of the R isomer is consistent with the assignment made on the basis of stereoretention in thermal aquations of Cr(III) complexes and the rearrangement that accompanies photoaquation of Cl^- from other Cr(III) complexes. Taken together, these lines of evidence strongly support the concept that Scheme I accurately reflects the dominant thermal and photochemical processes occurring during photolysis of 1,6-$Cr(en)(H_2O)_2Cl_2^+$.



(3)

Modeling the Axis of Activation. Since the dominant photochemical process occurring upon irradiation of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ is loss of Cl^-, this molecule provides a second,[9] and in some ways more conclusive, example of a violation of the rationalization of Wrighton, Gray, and Hammond[7] concerning the nature of the activation process in d^3 systems. Their argument to explain the difference in photolytic stoichiometry in complexes of the type *trans*-$CrL_4X_2^+$ where 2L = en and $X^- = Cl^-$ or F^- is as follows. When the ligand field properties of L and X^- are similar and when the ^4E_g and $^4B_{2g}$ states are approximately degenerate, then there is nonselective axial and in-plane bond weakening in a σ sense. However, since X^- species are π donors and their bonding is strengthened in the excited quartet state by removal of electron density from π^* orbitals, not the nonselective σ-bond weakening but rather axial π-bond strengthening leads to preferential loss of L. This is the $X^- = F^-$ case in which the ^4E_g and $^4B_{2g}$ states differ by only 2.9 kK at ground-state geometries.[5] In the case of $X^- = Cl^-$, the energy gap between the ^4E_g and $^4B_{2g}$ states is large (4.8 kK at ground-state geometries[30]), the lowest lying excited quartet state gives selective weakening in a σ sense of the Cr–Cl bond, and this breaks because it is not sufficiently compensated by π stabilization.

If one starts with *trans*-$Cr(en)_2Cl_2^+$, there are two ways to design new complexes in which the ^4E_g and $^4B_{2g}$ states (in D_{4h} symmetry) are made nearly degenerate: increase the ligand field strength of the axial ligands or decrease that of the in-plane ligands. Changing the complex to *trans*-$Cr(en)_2F_2^+$, we[6] have done the former; replacing an ethylenediamine by two water molecules, we have accomplished the latter. According to the model of Wrighton, Gray, and Hammond, either of these two "new" complexes should lead to Cr–N bond rupture. Actually, only *trans*-$Cr(en)_2F_2^+$ does: the photolysis of 1,6-$Cr(en)(H_2O)_2Cl_2^+$ does not obey the nonselective σ-bond weakening, π-stabilization arguments of these authors.

We would predict the axis of labilization and the stoichiometry of the photochemical process by reaching a decision about the nuclear configuration of the lowest lying vibrationally relaxed excited quartet state in the multidimensional space defined by those nuclear coordinates. The simplifications we adopt are that the dominant nuclear motions which will occur after excitation with stretch either axial ligands or in-plane ligands and that a decision about which motion generates the lowest energy minimum can be made by considering the dominant bonding interaction, the σ interaction. Since chloride is a considerably weaker σ-bonding ligand than is the average of ethylenediamine and water, it is the axial stretched minimum that is lower in energy in both 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$ and *trans*-$\mathrm{Cr(en)_2Cl_2^+}$. Reaction occurs from this configuration to lead to further stretching and ultimate rupture of the Cr–Cl bond.

Quantum Yields. Table IV gives the quantum yields for production of each of the two isomers of $\mathrm{Cr(en)(H_2O)_3Cl^{2+}}$. The values for irradiation at 5890 Å, a wavelength in which population of the lowest lying quartet band is achieved, yield a ratio of 1-chloro-2,3,6-triaquoethylenediaminechromium(III), the S isomer, to 1-chloro-2,3,4-triaquoethylenediaminechromium(III), the R isomer, of 1.17. Although the quantum yield values increase slightly upon irradiation at 5200 Å, irradiation that presumably populates a higher lying quartet, the ratio remains fixed. Only upon irradiation at 4000 Å does this ratio change; at this wavelength of irradiation the quantum yield increase is greater for the S isomer than for the R isomer.

The constant ratio for the relative amounts of the S isomer and R isomer at two different wavelengths of irradiation suggests that reaction occurs from a common intermediate, independent of whether population takes place via $^4B_{1g} \rightarrow {}^4E_g$ (assuming the *trans*-$\mathrm{CrX_4Cl_2^+}$ approximation—see the first paragraph of Discussion) at 5890 Å or $^4B_{1g} \rightarrow {}^4B_{2g}$ at 5200 Å. Presumably this intermediate is the vibrationally relaxed molecule with rather extensive stretching of Cr–Cl bonds along the *z* axis, for these bonds are the easiest to weaken in the starting complex; this type of distorted molecule is in the most stable valley in the hypersurface of the lowest lying excited quartet state. Irradiation into the upper levels of the quartet states derived from the $^4T_2$ level of the parent octahedral molecule must therefore lead to rapid internal conversion to the lowest lying quartet surface and generation of this common intermediate.

On the other hand, irradiation initially to populate the levels derived from the lowest $^4T_1$ level of the octahedral parent molecule does not show a ratio common with the other two wavelengths. Rather the production of an increased amount of both isomers, with a more marked increase in the production of the S isomer, is observed: the ratio of S to R isomer increases to 1.45. These data are most easily accommodated by the suggestion that irradiation into the 4000-Å transition leads to photoreactivity from some higher excited state as well as from the lowest excited quartet state that is populated by internal conversion of the initially formed state. It is an open question as to which higher excited state is responsible for the reactivity at 4000 Å: either the higher d–d states or charge-transfer states or both are possibilities to consider. It has been suggested previously that charge-transfer states are efficient in causing photochemistry in competition with nonradiative deactivation into the d–d manifold: the aquations of $\mathrm{Br^-}$ from $\mathrm{Cr(NH_3)_5Br^{2+}}$[31] and of both $\mathrm{NCS^-}$ and $\mathrm{Cl^-}$ from *cis*-$\mathrm{Cr(en)_2(NCS)Cl^+}$[32] are two examples.

A second feature of the observed quantum yield that needs consideration is the overall value for loss of $\mathrm{Cl^-}$ from 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$ compared with values for other Cr(III) complexes containing a *trans*-dichloro grouping. This comparison can be made with the data summarized by Kutal and Adamson,[4] who pointed out that there was a relationship between the logarithms of the aquation rate constant and the logarithms of the quantum yield upon lower energy quartet irradiation for several *trans*-dichloro isomers. This correlation holds, at best, marginally for 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$. The rate of thermal aquation of this complex is somewhat greater than that of *trans*-$\mathrm{Cr(en)_2Cl_2^+}$, but the quantum yield is somewhat lower. However the deviation observed is relatively small and suggests that no special effects of large magnitude occur in 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$ to lead to rapid nonradiative deactivation of the lowest lying quartet excited state. Although it has been suggested that replacement of an ammonia by a water leads to an increase in nonradiative decay in Rh(III) complexes,[33] our results on 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$ suggest that replacement of an ethylenediamine by two waters in these Cr(III) complexes has no such effect on the nonradiative rate constant (or, improbably, an equal effect on both the nonradiative and photochemical rate constants).

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Registry No. 1,6-$\mathrm{Cr(en)(H_2O)_2Cl_2^+}$, 55401-10-0; $\mathrm{Cr(en)(H_2O)_3Cl^{2+}}$ (R isomer), 55449-63-3; $\mathrm{Cr(en)(H_2O)_3Cl^{2+}}$ (S isomer), 55449-64-4.

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