Preferential Labilization and Stereochemical Change in the Photolysis of *trans*-Diacidotetraamminechromium(III) Ions[1]

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Abstract: Ligand-field band irradiation of five *trans*-$Cr(NH_3)_4XY^{n+}$ complex ions (where X and Y indicate various combinations of Cl^-, NCS^-, and H_2O) causes preferential (>90%) photoaquation of the acido groups, i.e., of the ligands on the weak average-field axis. The total quantum yields are in the 0.35–0.45 range and, for a given complex, are fairly constant throughout the visible region. Release of the axial ligands is always accompanied by trans → cis isomerization. Labilization of X and Y is concluded to occur in the lowest quartet, ^4E, excited state, in agreement with the predictions of Adamson's rules and of recent theoretical models. Also the relative efficiencies for aquation of different X and Y ligands conform to the photolysis rules and models. Stereochemical change appears to be a general characteristic of chromium(III) photosubstitutions. Ammonia aquation is a minor photoreaction mode, the study of which is complicated by secondary photolysis. The wavelength dependence of the quantum yields indicates that $^4B_2$ is the excited state mainly responsible for this process. Upon charge-transfer band irradiation, photorelease of Cl^-, but not of NCS^-, is considerably enhanced. In addition, labilization of equatorial NH_3 becomes highly efficient in the three species without thiocyanate, the quantum yields rising to 0.30–0.40. The differences from ligand-field photolysis are discussed.

Ligand-field band excitation of chromium(III) acidoamine complexes generally leads to replacement of more than one type of coordinated group by solvent.[2,3] That excited states are involved is shown by the fact that often the prevailing photoreaction path is absent thermally. Studies on sensitization[4-6] and quenching[7-9] of chromium(III) photoaquations have definitely indicated the lowest quartet excited state ($^4T_{2g}$ for O_h and ^4E for tetragonal symmetries, respectively) as the principal precursor to photosubstitution. The ligand labilization pattern can be accounted for by accumulation of electron density on the lower σ-antibonding orbital in such an excited state.[10,11] While some early semiempirical rules proved useful to systematize and predict the photochemical behavior (i.e., release of the strong-field ligand on the weak-field axis),[10] theoretical models have been recently developed which explain the photoreactivity in terms of both σ and π bonding changes in the various excited states.[12,13]

A point which is drawing increasing attention is the mechanism of chromium(III) photoreactions and its possible relations with the geometry of the thermally equilibrated quartet excited state.[14] An approach is represented by the investigation of the stereochemistry of photosubstitutions. Studies with the *trans*-$Cr(en)_2Cl_2^+$ [15] and $Cr(NH_3)_4(^{15}NH_3)Cl^{2+}$ [16] ions have shown that, while the predictions of the photolysis rules as to the ligands labilized are obeyed, the photoaquation reactions occur with trans → cis isomerization. Stereochemical change was suggested to be a general characteristic of chromium(III) photolysis,[17,18] as opposed to stereoretention, generally associated with thermal substitutions.[19] Moreover photoaquation appears to be efficient only if mobility of the octahedral framework is possible. In the *trans*-$CrN_4Cl_2^+$ series (where N_4 = $(en)_2$, tet, cyclam) an increasing degree of constriction imposed by the polyamine chains is accompanied by a progressive reduction of the quantum yield for Cl^- release.[14]

In order to obtain further information on the stereochemical aspects, we have investigated the ligand-field (LF) photolysis of five *trans*-$Cr(NH_3)_4XY^{n+}$-type complex ions, where X and Y denote various combinations of the Cl^-, NCS^-, and H_2O ligands. These systems offer several advantages. (i) The X and Y groups define the weakest field axis (i.e., that predicted to be photoactivated)[10] and, unlike in $Cr(NH_3)_5X^{2+}$ species, the original position (axial or equatorial) of all labilized ligands is unambiguously identified. (ii) The presence of only monodentate ligands rules out either limitations to stereomobility or potential mechanistic complications. (iii) The isomeric nature of the photoproducts can be characterized through their spectra, since the absorption features are now well known for all of the *cis*- and *trans*-diacidotetraammine ions possibly involved.

In addition, determination of the quantum yields for the various photoreaction modes provides a test for the abovementioned rules[10] and models;[12,13] particularly for those predictions regarding the relative extent of labilization of two different ligands on the same axis.

Also the photoreactions taking place upon charge-transfer (CT) band excitation have been investigated in some detail and have shown remarkable differences from LF photolyses.

Some preliminary results have already been reported[20] and used for discussion.[14,18] While this work was in progress, studies have appeared on analogous *trans*-$Cr(en)_2(NCS)Cl^+$,[21] *trans*-$Cr(en)_2ClF^+$,[22a] and *trans*-$Cr(en)_2(NCS)_2^+$ [22b] ions, providing valuable complementary knowledge.

Experimental Section

Preparation of Complexes. *trans*-Aquochlorotetraamminechromium(III) Perchlorate was obtained by cleavage of *trans*-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$ with concentrated $HClO_4$ and recrystallized, as reported elsewhere.[23] The solution absorption spectrum shows maxima at 555 (ϵ 20), 468 (ϵ 18), and 384 nm (ϵ 42) in accordance with the literature.[24]

***trans*-Dichlorotetraamminechromium(III) Perchlorate** was prepared by cleavage of the above binuclear species with concentrated HCl, according to a literature method.[23] The maxima of the absorption spectrum are at 590 (ϵ 25), 470 (ϵ 15), and 397 nm (ϵ 29) and agree with previous data.[24]

***trans*-Diaquotetraamminechromium(III) Perchlorate.** The preparation followed a described procedure consisting of controlled hydrolysis of the trans aquochloro complex.[23] The absorption spectrum exhibits one shoulder at 520 nm (ϵ 17) and two band maxima at 475 (ϵ 20) and 368 nm (ϵ 29) in agreement with literature values.[24]

***trans*-Chlorothiocyanatotetraamminechromium(III) Perchlorate.** A 5-g portion of *trans*-$[Cr(NH_3)_4(H_2O)Cl](ClO_4)_2$ was dissolved in 30 ml of 0.2 *M* $HClO_4$. Ten grams of sodium thiocyanate were added, and the mixture was heated at 70° for 5 min. *trans*-$[Cr(NH_3)_4(NCS)Cl]NCS$ precipitated on cooling and was filtered off. The thiocyanate salt was converted into the perchlorate by dissolving it in 25 ml of water and dropwise adding an excess of concentrated $HClO_4$. The product was collected, washed with a small amount of ice-cold ethanol (in which it is fairly soluble) then with ether, and air-dried. Recrystallization was accomplished by dissolving 2 g in 20 ml of water and dropwise adding concentrated $HClO_4$. The purple-red crystals were separated, washed, and dried as above. Anal. Calcd for $[Cr(NH_3)_4(NCS)Cl]ClO_4$: Cr, 16.60; NCS, 18.55; Cl^-, 11.30. Found: Cr, 16.4; NCS, 18.5; Cl^-, 11.0. The maxima of the ligand-field absorption bands occur at 537 (ϵ 51.2), 485 (shoulder, ϵ 29.0), and 383 nm (ϵ 53.5). In addition, the following high-intensity features are observed: 290 (ϵ 3350), 266 (ϵ 3600), 224 nm (ϵ 10,000).

***trans*-Aquothiocyanatotetraamminechromium(III) Perchlorate** was obtained by controlled acid hydrolysis of the *trans*-chlorothiocyanato complex. A 2-g portion of the perchlorate salt of the latter was dissolved in 120 ml of 0.2 *M* $HClO_4$ and the solution was heated at 80°C, in dim red light, for 15 min. Sixty milliliters of concentrated $HClO_4$ was then added dropwise and the mixture was kept overnight in a refrigerator. The pink-red solid was filtered off, washed with a small amount of ice-cold ethanol then with ether, and air-dried. The crude product was recrystallized as described above. Anal. Calcd for $[Cr(NH_3)_4(H_2O)(NCS)](ClO_4)_2$: Cr, 13.16; NCS, 14.70; N 17.72; H, 3.57. Found: Cr, 12.9; NCS, 14.4; N, 17.4; H, 3.4. The spectral absorption maxima are at 510 (ϵ 50), 371 (ϵ 46), 295 (ϵ 3120), 258 (ϵ 2350), 222 nm (ϵ 8750).

***cis*-Aquochlorotetraamminechromium(III) Perchlorate** was prepared by treating oxalatotetraamminechromium(III) nitrate with concentrated HCl for 15 min at 50°.[25] The precipitated chloride salt was converted to the perchlorate with concentrated $HClO_4$, eliminating ionic chloride as HCl gas.[24] The absorption spectrum has maxima at 519 (ϵ 40) and 384 nm (ϵ 33) as reported in the literature.[24]

***cis*-Diaquotetraamminechromium(III) Perchlorate** was obtained by base hydrolysis of the cis aquochloro species, following a reported procedure.[24] The absorption maxima occur at 495 (ϵ 36) and 366 nm (ϵ 27) and agree with already reported values.[24]

***cis*-Aquothiocyanatotetraamminechromium(III) Ion.** This species, which could not be precipitated as a solid salt, was prepared by controlled aquation of the corresponding cis dithiocyanato complex, followed by isolation by means of cation-exchange chromatography, as described previously.[26] The spectral bands have maxima at 497 (ϵ 70 ± 2) and 372 nm (ϵ 47 ± 2).[27]

Analytical Procedures. The free chloride content of photolysis mixtures was measured by potentiometric titration with 2×10^{-3} *M* silver nitrate, using a silver electrode and a Radiometer TTT 1c automatic titrator. The aliquots, of 2 to 3 ml volume, were kept in an ice bath in order to minimize possible thermal reaction effects. Blank experiments showed that the results were not affected by the presence of complexes in solution.

Thiocyanate ion was determined spectrophotometrically at 450 nm (ϵ 4300) with iron(III) reagent.[28]

Simultaneous determination of free chloride and thiocyanate was accomplished by the above potentiometric procedure. In this case the complex ions were removed from the photolyzed samples by addition of a small amount (ca. 1 g) of a cation-exchange resin (Permutit Zeo-Karb 225 SRC 13) which was then filtered off. The titration curves yielded two sharp end points. In the range of concentrations dealt with (10^{-3} *M*), the average deviation was 3%. Independent spectrophotometric determinations of thiocyanate ion agreed within 5% error.

Photoreleased ammonia was measured as H^+ uptake, according to an earlier published method.[29] pH differences between dark and irradiated samples were monitored using a glass microelectrode (Schott U 9258/81) and an Orion Model 801 digital potentiometer. In all cases the ionic strength was kept constant at 0.2 by means of sodium perchlorate. Standardization plots of ΔpH vs. $[NH_3]$ were obtained by adding known amounts of ammonia to solutions of trans or cis complexes, having the same concentration and initial pH (~3) as in the actual photolysis runs. At these pH values NH_3 is completely protonated. If aquated chromium(III) ions (which are weak acids) are present, they exert a buffering action, so that the ΔpH's are smaller than expected, and found, in the absence of complexes. However, the fractions of deprotonated species are less than 1%. The pH changes are consistent with pK_a values of ca. 5 for all the $Cr(NH_3)_4(H_2O)X^{2+}$-type ions and of ca. 4 for the $Cr(NH_3)_4(H_2O)_2{}^{3+}$ ions.

Essentially identical procedures were employed for analyzing the Cl^- and NCS^- ligands of the complex salts, after alkaline decomposition.

Chromium was determined by titration with ferrous ion, following persulfate oxidation of the samples. Nitrogen was determined by standard organic microanalysis.

Apparatus. Either a 500-W high-pressure xenon lamp or an A-H6 high-pressure mercury arc was employed as light source in the visible or near-uv range, respectively. Wavelength selection was by means of Baird Atomic interference filters. The half-width of the irradiation bands was generally ca. 10 nm. The 254-nm radiation was obtained by filtering the emission of a Minerallight lamp through 2 cm of $CoSO_4$ and $NiSO_4$ saturated solution.

In most of the experiments light intensity was measured using an Eppley copper-constantan thermopile (1.5 × 2.0 cm surface) connected to a Keithley 150 B electrometer. The output of the latter was instrumentally integrated over a given period of time, yielding the incident light energy.

Optical densities of solutions were determined using a Beckman DU spectrophotometer. General absorption spectra were recorded by means of Beckman DB and Shimadzu MPS 50L instruments.

Photolysis Procedures. Three-milliliter samples ca. 10^{-2} *M* in complex, in 1×10^{-2} to 1×10^{-3} *M* $HClO_4$ were irradiated in 1-cm spectrophotometer cells, held in a thermostated brass compartment in which identical "dark" samples were simultaneously placed. The solutions were continuously stirred by means of a small magnet, and the temperature was kept constant within ±0.5°C. Photolyses were performed under conditions of incomplete light absorption, and the incident energy was determined as described elsewhere.[30] Light intensities were around 2×10^{-8} einstein sec^{-1}. The energy was measured either by the above-mentioned instrumental method or actinometrically, using the reineckate[28] and ferrioxalate[31] systems. After suitable periods of irradiation (usually 10-20 min) the samples were either brought to the spectrophotometer or chemically analyzed. While absorption spectra were recorded by a double beam instrument, actual concentration changes were usually followed at specific wavelengths.

The extent of conversion was usually less than 10% in order to minimize secondary photolysis (vide infra). The irradiated and the dark aliquots were simultaneously analyzed so as to allow for possible thermal reaction effects.

Results

The absorption spectra of the complexes studied, with the exception of *trans*-aquothiocyanatotetraamminechromium(III), exhibit three LF bands, assigned to the $^4B_1 \rightarrow {}^4E$, $^4B_1 \rightarrow {}^4B_2$, and $^4B_1 \rightarrow {}^4A_2, {}^4E$ transitions, in order of increasing energy, and designated as L_{c1}', L_1'', and L_2, respectively. The first two features arise from the splitting of the $^4T_{2g}$ state on descending from octahedral to tetragonal (D_{4h} or C_{4v}) symmetry.[32] The thiocyanate-containing species are characterized by a strong absorption around 290-295 nm, assigned to a ligand-to-metal, charge-transfer transition.[33] The photoreactivity was investigated using several irradiation wavelengths throughout the LF and the CT absorption regions.

An initial pH of 2-3 was chosen for the samples to be photolyzed, so as to neglect spectral changes due to deprotonation of complexes with H_2O ligands, whose pK_a's are in the 4-5 range. All photolyses were carried out at 20°, due to insufficient solubility at lower temperatures, specially for *trans*-$[Cr(NH_3)_4Cl_2]ClO_4$. Under the above pH and temperature conditions, the thermal aquation reactions,[23,34] all occurring with retention of configuration, are sufficiently slow to contribute to the overall products by no more than 2-5%.

As mentioned above, determination of NH_3 by the pH change method required a constant ionic strength of 0.2. A series of runs showed that, within the 0.01-0.5 range, there are no ionic strength effects on all photoprocesses.

Table I. Photolysis Quantum Yields[a] for *trans*-$Cr(NH_3)_4XY^{n+}$ Complex Ions, in Acid Aqueous Solution at 20°

Complex	X	Y	Irradiation wavelength (nm)	Band irradiated	ϕ_{Cl^-}	ϕ_{NCS^-}	$\phi_i{}^b$	ϕ_{NH_3}	Ratios
I	H_2O	Cl^-	578 ± 5	L_1'				0.012 ± 0.002	
			546 ± 5	L_1'	<0.004[c]		0.42 ± 0.02	0.023 ± 0.002	$\phi_i/\phi_{Cl^-} > 100$
			503 ± 5	L_1' L_1''			0.38 ± 0.01		
			480 ± 6	L_1''	<0.005[c]		0.40 ± 0.02	0.065 ± 0.003	>80
			380 ± 20	L_2	<0.005[c]		0.43 ± 0.01		>85
			366 ± 5	L_2			0.44 ± 0.02	0.045 ± 0.005	
			348 ± 11	L_2			0.46 ± 0.01		
			254	CT	0.21 ± 0.01			0.29 ± 0.02	
II	H_2O	NCS^-	546 ± 5	L_1		0.020 ± 0.001	0.42 ± 0.02	0.005 ± 0.002	$\phi_i/\phi_{NCS^-} = 21$
			480 ± 6	$L_1{}^d$		0.020 ± 0.001	0.41 ± 0.02	0.015 ± 0.005	= 21
			434 ± 5	$L_1{}^d$		0.020 ± 0.001	0.42 ± 0.02	0.040 ± 0.005	= 21
			390 ± 5	L_2		0.021 ± 0.001	0.44 ± 0.02	0.037 ± 0.006	= 21
			254	CT		0.056 ± 0.004	0.29 ± 0.03	0.045 ± 0.006	= 5
III	H_2O	H_2O	546 ± 5	L_1'			0.35 ± 0.02	<0.02	
			480 ± 6	L_1''			0.33 ± 0.02		
			366 ± 5	L_2			0.35 ± 0.02	0.1[e]	
			254	CT				0.3[e]	
IV	Cl^-	Cl^-	578 ± 5	L_1'	0.44 ± 0.02		0.44 ± 0.02	0.003 ± 0.002	
			480 ± 6	L_1''	0.44 ± 0.02		0.44 ± 0.02	0.067 ± 0.003	
			453 ± 5	L_1'' L_2	0.45 ± 0.02		0.45 ± 0.02		
			380 ± 20	L_2	0.40 ± 0.02		0.40 ± 0.02	0.065 ± 0.005	
			254	CT	0.95 ± 0.05			0.37 ± 0.02	
V	NCS^-	Cl^-	578 ± 5	L_1'	0.13 ± 0.01	0.230 ± 0.006	0.36 ± 0.02		$\phi_{NCS^-}/\phi_{Cl^-} = 1.8$
			546 ± 5	L_1'	0.15 ± 0.02	0.273 ± 0.016	0.42 ± 0.04	0.003 ± 0.002	= 1.8
			480 ± 6	$(L_1'')^f$	0.15 ± 0.02	0.280 ± 0.010	0.43 ± 0.03	0.046 ± 0.003	= 1.9
			434 ± 5	L_1'' L_2	0.14 ± 0.02	0.250 ± 0.010	0.39 ± 0.03	0.046 ± 0.002	= 1.8
			366 ± 5	L_2	0.14 ± 0.02	0.275 ± 0.012	0.41 ± 0.03	0.051 ± 0.003	= 1.9
			313 ± 7	CT	0.23 ± 0.02	0.210 ± 0.004			= 0.9
			254	CT	0.22 ± 0.02	0.223 ± 0.005		0.043 ± 0.005	= 1.0

[a] Average of at least four independent runs. [b] Quantum yield for formation of *cis*-aquoacidotetraammine ions. [c] Temperature 1°. [d] Short-wavelength side of the L_1 band, which is not split. [e] Extrapolated at zero photolysis time. [f] Absorption shoulder.

The quantum yields for the various photoreaction modes were corrected, according to an earlier published mathematical treatment, taking into account inner filter effects due to photochemical and thermal products.[30] The data are collected in Table I. Each entry represents the average of four or more independent experiments. The deviations were usually less than 10%.

For all the complexes the behavior is qualitatively different upon LF and CT excitation. The results are therefore presented separately.

LF Photolysis. For a given compound, essentially the same spectral variations occur upon irradiation with light of any wavelength between 550 and 350 nm. Figures 1-5 show the general evolution of the absorption spectra for the five *trans*-diacidotetraammine ions. Regardless of the energy of excitation the changes in optical density depend linearly on the absorbed quanta. The traces appearing in the figures are relative to L_1' band excitation, where the extent of NH_3 release is minimal (vide infra). The presence of two or three isosbestic points, up to 15% conversion, suggests that either single products or constant ratios of products are always involved. The well-defined crossing points and the stability of the spectra of photolyzed solutions may be taken to indicate that possible post-irradiation effects (and also any dark reactions) are slow compared to the time of analysis.

A general finding is that free ammonia is generated in small amounts and does not follow zero-order kinetics. From a detailed analysis (vide infra) most NH_3 results from secondary photolysis. The quantum yields for primary photorelease (see Table I) show that, in all cases, NH_3 photoaquation is a minor photoreaction mode, accounting for no more than 10% of the overall photoreactivity. The relative extent of primary, and especially that of secondary NH_3 photoaquation, is such that the absorption spectra, by which the main photoreaction (in particular isomerization) yields are evaluated, are affected only within experimental error. In fact, under our experimental conditions, secondary photoproducts never exceed 1-2% of all Cr(III) species present. The spectra remain virtually unaffected also by the small fractions (<1%) of aquo complexes deprotonated by NH_3 (see Experimental Section).

I. *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. The most significant spectral change is the disappearance of the splitting of the low-energy absorption band and the rise in optical density in the same wavelength region. The sharp isosbestic points at 578 (ϵ 17) and 470 nm (ϵ 18) are those expected for conversion to *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, the spectrum of which is reported for comparison in Figure 1.

Very little, if any, chloride is photoaquated and only an upper limit could be established for ϕ_{Cl^-}. The reason is that, even at 1°, the thermal chloride aquation of the product is not negligible at this level of reactivity.

The absorption spectra of photolyzed solutions can be fitted by linear combinations of those of the trans and cis aquochloro isomers. The quantum yields for photoisomerization, ϕ_i, were evaluated using the differences in absorbance at several wavelengths and after various irradiation periods. The ϕ_i values, relative to a given excitation wavelength, are virtually identical. This result, plus the low extent of chloride and ammonia photoaquation indicate that the photoprocess taking place ca. 90% of the time is

$$\textit{trans}\text{-}Cr(NH_3)_4(H_2O)Cl^{2+} \xrightarrow{h\nu} \textit{cis}\text{-}Cr(NH_3)_4(H_2O)Cl^{2+} \quad (1)$$

II. *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$. The spectral evolution, presented in Figure 2, does not exhibit differences as marked as in the previous case. The general trend and the crossing points at 525 (ϵ 47) and 430 nm (ϵ 17) (which become more evident in expanded-scale difference spectra)

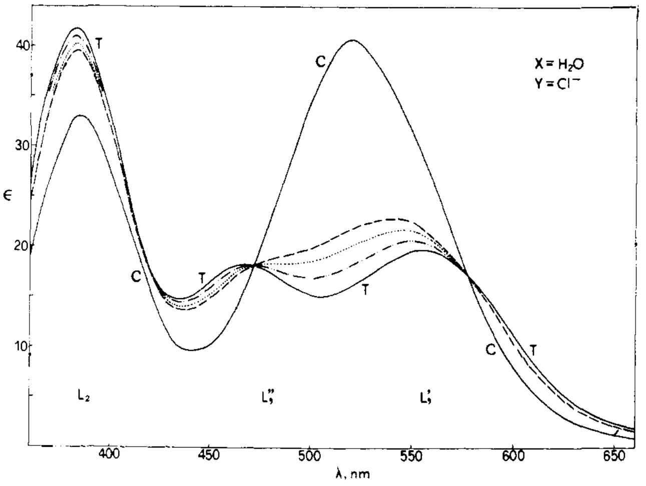

Figure 1. Absorption spectra in 10^{-2} *M* $HClO_4$: solid lines, T, *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$; C, *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$; broken lines correspond to 9.0, 17.1, and 24.1% conversion, on irradiation at 578 nm.

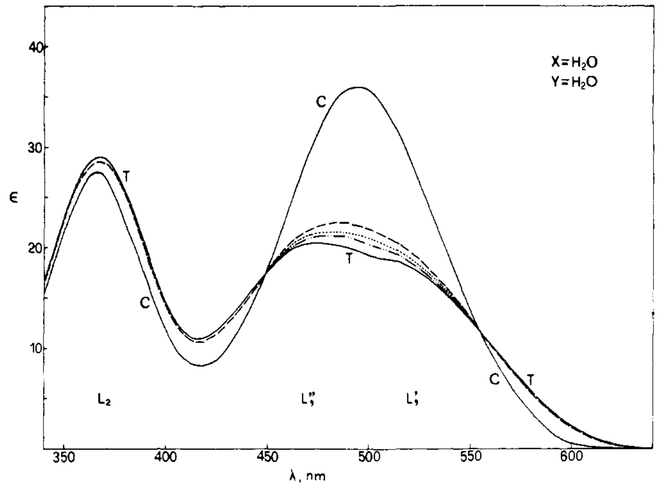

Figure 3. Absorption spectra in 10^{-2} *M* $HClO_4$: solid lines, T, *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$; C, *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$; broken lines correspond to 6.3, 9.8, and 15.2% conversion, on irradiation at 546 nm.

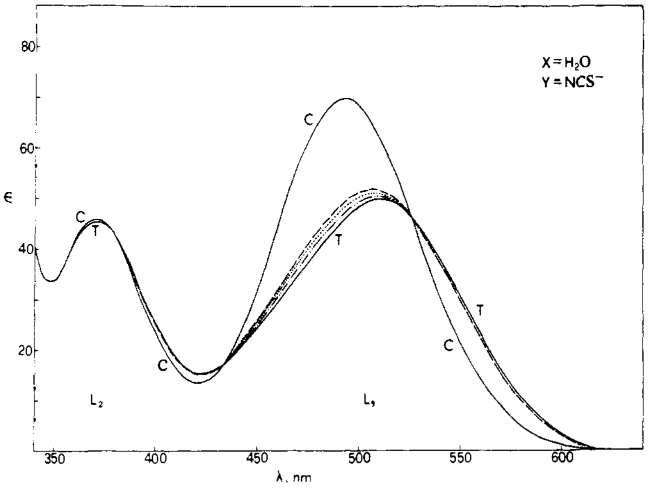

Figure 2. Absorption spectra in 10^{-2} *M* $HClO_4$: solid lines, T, *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$; C, *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$; broken lines correspond to 4.9, 9.7, and 14.2% conversion, on irradiation at 546 nm.

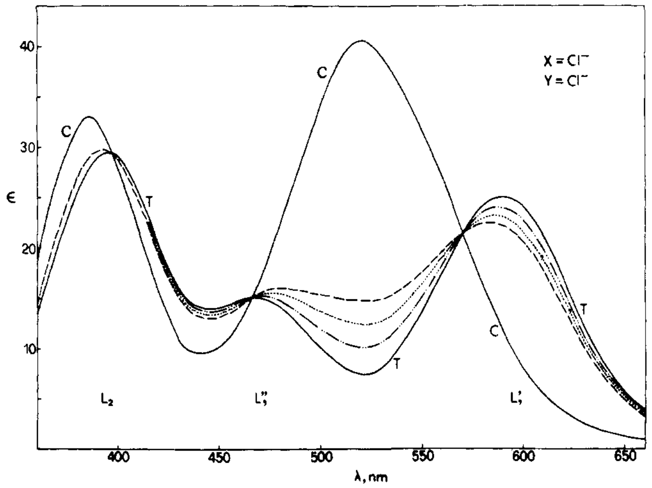

Figure 4. Absorption spectra in 10^{-2} *M* $HClO_4$: solid lines, T, *trans*-$Cr(NH_3)_4Cl_2{}^+$; C, *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$; broken lines correspond to 8.2, 15.1, and 22.1% conversion, on irradiation at 578 nm.

show that the main photoreaction is

$$trans\text{-}Cr(NH_3)_4(H_2O)(NCS)^{2+} \xrightarrow{h\nu} cis\text{-}Cr(NH_3)_4(H_2O)(NCS)^{2+} \quad (2)$$

Thiocyanate photoaquation accounts for ca. 5% of the photoreactivity and its dependence on the absorbed energy is linear.

Due to the relatively small amount of diaquotetraammine ion (produced by NCS^- aquation) it was practically impossible to establish its geometry. However, the reasonable assumption was made that *cis*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$ was the species involved, by analogy with the cis configuration of all the photoproducts encountered in the present study. With this assumption the photoisomerization quantum yields were determined from optical density data, taking into account the presence of the diaquo complex in the photolysis mixtures.

III. *trans*-$Cr(NH_3)_4(H_2O)_2{}^{3+}$. The general spectral behavior, shown in Figure 3, is consistent with the process

$$trans\text{-}Cr(NH_3)_4(H_2O)_2{}^{3+} \xrightarrow{h\nu} cis\text{-}Cr(NH_3)_4(H_2O)_2{}^{3+} \quad (3)$$

The isosbestic points at 555 (ε 12) and 448 nm (ε 17) are located precisely where the spectra of the trans and cis species cross. In this case either an upper limit or only one figure is given for the yield of NH_3 photoaquation, due to the considerable acid strength of the diaquo complexes. Photoisomerization is the largely predominant reaction. The spectra of irradiated samples can be well reproduced by linear combinations of those of the two diaquo isomers and allow the calculation of the quantum yields collected in Table I.

IV. *trans*-$Cr(NH_3)_4Cl_2{}^+$. Figure 4 shows that irradiation in the visible modifies the spectrum remarkably as in case I. Very clean isosbestic points are present at 570 (ε 21), 466 (ε 15), and 397 nm (ε 29). Chloride photoaquation is very efficient and obeys zero-order kinetics.

Although the spectral changes in general, and the crossing points in particular, agree with a cis configuration for the principal photoaquation product, in order to establish whether or not this is completely true, a more accurate analysis of the spectrophotometric data was carried out as follows. Assuming a product consisting of a mixture of trans and cis aquochlorotetraammine isomers (which have very different spectra; see Figure 1) at a given wavelength, the experimental difference in optical density, ΔA_i between a photolyzed and a dark sample is

$$\Delta A_i = [\mathrm{T}](\epsilon_\mathrm{T} - \epsilon_0)_i + [\mathrm{C}](\epsilon_\mathrm{C} - \epsilon_0)_i \qquad (4)$$

where [T] and [C] are the unknown concentrations of the trans and cis products, ϵ_T and ϵ_C the respective extinction coefficients, and ϵ_0 the absorbancy of the starting dichlorotetraammine ion. A least-squares fit, extended to several (30) wavelengths, yields the relations

$$\sum_i \{[\mathrm{T}](\epsilon_\mathrm{T} - \epsilon_0)_i{}^2 + [\mathrm{C}](\epsilon_\mathrm{T} - \epsilon_0)_i(\epsilon_\mathrm{C} - \epsilon_0)_i - \Delta A_i(\epsilon_\mathrm{T} - \epsilon_0)_i\} = 0 \qquad (5)$$

$$\sum_i \{[\mathrm{C}](\epsilon_\mathrm{C} - \epsilon_0)_i{}^2 + [\mathrm{T}](\epsilon_\mathrm{T} - \epsilon_0)_i(\epsilon_\mathrm{C} - \epsilon_0)_i - \Delta A_i(\epsilon_\mathrm{C} - \epsilon_0)_i\} = 0 \qquad (6)$$

whose solution gives [T] = 0 within 5% uncertainty, upon photolysis at 578 nm, in which either primary or secondary NH_3 photoaquations are minimal (vide infra). Values of [C] coincide, within experimental error, with the values found for photoreleased chloride (see Table I). The major photoreaction is thus

$$\textit{trans}\text{-}\mathrm{Cr(NH_3)_4Cl_2{}^+} + \mathrm{H_2O} \xrightarrow{h\nu} \textit{cis}\text{-}\mathrm{Cr(NH_3)_4(H_2O)Cl^{2+}} + \mathrm{Cl^-} \qquad (7)$$

V. *trans*-$Cr(NH_3)_4(NCS)Cl^+$. The process occurring thermally is one of slow chloride aquation, leading to *trans*-$Cr(NH_3)_4(NCS)(H_2O)^{2+}$.[34] Light excitation instead produces simultaneous release of Cl^- and NCS^- with zero order behavior for both ligands. Table I shows that the quantum yields for the two modes of photoaquation are of the same order of magnitude.

The evolution of the absorption spectrum is presented in Figure 5. Even though two well-defined crossing points at 522 (ϵ 48) and at 430 nm (ϵ 15) indicate that the complex products are formed in constant ratios, any spectral information about their nature is not as immediate as in the previously described systems where one of the reaction modes dominates.

That the two main photoreaction paths are parallel (i.e., do not simultaneously take place in the same molecule) was demonstrated by the following experiments. Photolysis mixtures were adsorbed on a column of a weak-acid, cation-exchange resin (Bio-Rex 70) in the hydrogen form. The 1+ charged, unreacted starting material was eluted by means of 5×10^{-3} *M* $HClO_4$. The purple band remaining at the top of the column was completely displaced by 0.1 *M* $HClO_4$. In parallel experiments such a concentration was found to move the dipositive aquochlorotetraammine and thiocyanatoaquotetraammine complexes, but not the tripositive $Cr(NH_3)_4(H_2O)_2{}^{3+}$ ions. The spectrum of the second fraction shows a strong absorption at 295 nm, which is associated to coordinated thiocyanate.[33] However, the extinction coefficient of this band (determined through the chromium content of the fraction) is about one-third of that (~3 × 10^3) generally found in complexes having one NCS^- ligand and suggests that at least another species is present. Thus, all photolysis products are 2+ ions; i.e., they must contain one anionic ligand; furthermore one of them must have the composition $Cr(NH_3)_4(H_2O)(NCS)^{2+}$. Definite support for the occurrence of parallel processes is found in the coincidence between ϕ_{NCS^-}/ϕ_{Cl^-} and the $[Cl^-]/[NCS^-]$ ratio, determined in the above eluate after decomposing the complexes.

Since the spectral variations are relatively small, only difference spectrophotometry proved sufficiently diagnostic for establishing the configuration of both photoproducts. In parallel to the absolute spectra, Figure 5 shows an expanded-scale curve, recorded by comparing a solution, photolyzed at 546 nm, with an identical dark sample. The curve can be fitted by the changes in absorbance expected assuming a product mixture of 63% *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ and 37% *cis*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$, the ratio being taken equal to the experimental ϕ_{NCS^-}/ϕ_{Cl^-}. Other mixtures of possible photoaquation products, consisting of 63-37% combinations of cis and trans, trans and cis, trans and trans aquochloro- and aquothiocyanato compounds, are associated to spectral patterns in disagreement with the experimental data.

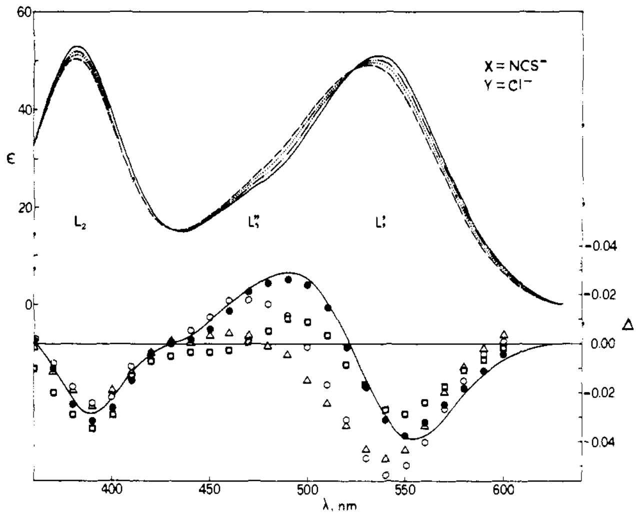

Figure 5. Absorption spectra in 10^{-2} *M* $HClO_4$: upper part, solid line. *trans*-$Cr(NH_3)_4(NCS)Cl^+$; broken lines correspond to 7.5, 13.2. and 19.5% of total photoreaction, upon 546-nm irradiation: lower part, experimental differential spectrum for 19.5% conversion; symbols represent spectral variations calculated for the same extent of conversion to 63–37% mixtures of $Cr(NH_3)_4(H_2O)Cl^{2+}$ and $Cr(NH_3)_4(H_2O)(NCS)^{2+}$ in the cis and cis (●), cis and trans (□), trans and cis (○), trans and trans (△) configurations.

Thus, the behavior of *trans*-chlorothiocyanatotetraamminechromium(III) can be summarized by eq 8–11.

$$\textit{trans}\text{-}\mathrm{Cr(NH_3)_4(NCS)Cl^+} + \mathrm{H_2O} \xrightarrow{kT} \textit{trans}\text{-}\mathrm{Cr(NH_3)_4(NCS)(H_2O)^{2+}} + \mathrm{Cl^-} \qquad (8)$$

$$\xrightarrow{h\nu} \begin{cases} \textit{cis}\text{-}\mathrm{Cr(NH_3)_4(NCS)(H_2O)^{2+}} + \mathrm{Cl^-} & (9) \\ \textit{cis}\text{-}\mathrm{Cr(NH_3)_4(H_2O)Cl^{2+}} + \mathrm{NCS^-} & (10) \\ \mathrm{Cr(NH_3)_3(H_2O)(NCS)Cl^+} + \mathrm{NH_3} & (11) \end{cases}$$

Secondary Photolysis and NH_3 Quantum Yields. Plots of NH_3 produced by LF irradiation vs. the absorbed light quanta are, in general, not linear, showing an upward curvature. The implication is that at least part of the ammonia photoaquation is due to secondary photolysis. Such a process is not negligible even in the very early reaction stages for the following reasons. First, the primary photolysis products are always in the cis configuration and the optical densities of *cis*-diacidotetraammine species are much higher than those of the trans compounds, especially in the L_1 absorption region (i.e., small percentages of products intercept considerable fractions of incident light; see specially Figures 1 and 4). Second, ϕ_{NH_3} is larger for the cis than for the trans complex ions, by at least one order of magnitude. While this behavior was already known for some ethylenediamine analogs,[15,21b,35] the photolysis of *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, carried out during the present study, gave a value of 0.30 ± 0.02 for ϕ_{NH_3} in the L_1 band region.

Since one of the main purposes was to establish whether or not photolabilization occurs at all on the plane perpendicular to the weak-field axis, NH_3 photoaquation was investigated in detail.

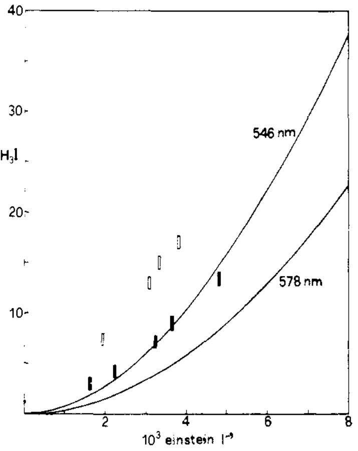

Figure 6. Ammonia photoaquation of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. Solid lines, contribution of secondary photolysis at different irradiation wavelengths, according to eq 16: □, experimental values at 546 nm; ■, experimental values at 578 nm.

In a given photolysis, NH_3 is produced according to eq 12, where T and C indicate the starting (trans) complex and

$$T \begin{array}{l} \xrightarrow{\phi_{NH_3}} (NH_3)_I \\ \xrightarrow{\phi_i} C \xrightarrow{\phi_{II}} (NH_3)_{II} \end{array} \qquad (12)$$

the main primary (cis) photoproduct(s), ϕ_{NH_3} is the quantum yield for primary NH_3 photoaquation, ϕ_i that for appearance of cis compounds, and ϕ_{II} the yield for secondary NH_3 release. Assuming that the incident radiation is absorbed only by T and C (which in the actual experiments constitute more than 98% of all complexes present), the fractions of light, I_T and I_C, instantaneously absorbed by the two species are defined by

$$I_T = \frac{\epsilon_T([T]_0 - [C])}{\epsilon_T[T]_0 + (\epsilon_C - \epsilon_T)[C]} I$$
$$I_T + I_C = I \qquad (13)$$

where ϵ denotes the molar extinction coefficients at the irradiating wavelength, I is the light intensity absorbed per unit volume (einstein sec^{-1} $l.^{-1}$), and $[T]_0$ is the initial concentration of the trans complex. If nonstrictly monochromatic light is employed, average ϵ values can be deduced from either bolometric or actinometric measurements of the transmittance. The time concentrations of the products are given by

$$d[C]/dt = \phi_i I_T \qquad (14)$$

and

$$d[NH_3]_{II}/dt = \phi_{II} I_C \qquad (15)$$

The concentration of ammonia due to secondary photolysis, after a period, t, of irradiation, is obtained combining eq 13 and 15.

$$[NH_3]_{II} = \phi_{II} \int_0^t \frac{\epsilon_C[C]}{\epsilon_T[T]_0 + (\epsilon_C - \epsilon_T)[C]} I\, dt \qquad (16)$$

[C] can be expressed as a function of t by means of the relation

$$\frac{\epsilon_T - \epsilon_C}{\epsilon_T}[C] - \frac{\epsilon_C[T]_0}{\epsilon_T} \ln\left(1 - \frac{[C]}{[T]_0}\right) = \phi_i It \qquad (17)$$

which is derived from eq 13 and 14. Equation 16 can be conveniently solved by numerical integration.

As an example, in Figure 6 are reported the plots of $[NH_3]_{II}$ vs. the absorbed energy, calculated by means of eq 16 and relative to *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, at two excitation wavelengths in the L_1 region. It should be noticed that at 546 nm, where $\epsilon_C > \epsilon_T$ (see Figure 1), secondary photolysis takes place to a larger degree than at 578 nm where $\epsilon_C < \epsilon_T$. Comparison with the experimentally measured total ammonia concentrations indicates that $[NH_3]_{II}$ predominates in all cases and that the importance of the subsequent photoprocess becomes larger and larger as photolysis proceeds. A very high ϕ_i/ϕ_{NH_3} ratio makes this effect not negligible even when irradiation is limited to the minimum extent necessary to generate measurable amounts of NH_3.

The quantum yields for primary aquation, ϕ_{NH_3}, were determined using the differences between the experimental $[NH_3]$ and the calculated $[NH_3]_{II}$ values. The results, presented in Table II, show that, while the apparent photoaquation quantum yields depend on the percentages of conversion (i.e., on the extent of inner filter effect), the corrected ϕ_{NH_3} are fairly constant, although $[NH_3]_I$ represents small differences between relatively large numbers.

The same treatment was applied to all the systems investigated. The corrected quantum yields are reported in Table I. In all cases secondary photolysis was primarily responsible for NH_3 photoaquation.

CT Photolysis. On irradiation with 313 and 254 nm light, photoaquation of axial ligands, such as NCS^- and Cl^-, is still taking place, and generally with higher efficiencies than upon LF excitation. Particularly relevant is the increase from less than 0.004 to 0.2 of the quantum yield for chloride release of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$. In addition, relatively large amounts of free ammonia are generated in I, III, and IV, with virtually identical quantum yields, and now according to zero-order kinetics, i.e., in primary processes.

For I, III, and IV, the spectral changes are definitely different from those observed during LF photolysis. Specifically, in the aquochlorotetraammine system the L_2 band undergoes a blue shift, accompanied by a decrease in intensity, whereas upon visible excitation no shift and a slight drop in optical density are observed. Another difference is that now the crossing points occur at 548 and at 405 nm. The disappearance of the splitting in the L_1 region suggests that the initial trans configuration is not maintained.

In the case of *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$ it was possible to estimate the quantum yield for photoisomerization on 254 nm irradiation. This is, in fact, the only system in which the quantum yields for aquation of both ammonia and the acido group are still as small as in the visible region and are such that the spectral changes essentially reflect the stereochemical change.

The experimental quantum yield for chloride release of *trans*-$Cr(NH_3)_4Cl_2^+$, reported in Table I, is close to unity. The possible reasons for this unusually large value are discussed below.

The quantum yield for NH_3 aquation of *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ was extrapolated to zero irradiation time (only one figure is given), since the large buffering effect of the highly acidic $Cr(NH_3)_3(H_2O)_3^{3+}$ photoproduct introduces a considerable uncertainty in the measurements of the pH changes.

Discussion

Ligand Labilization. A first important remark is that LF irradiation causes a highly specific labilization, localized on the X-Y axis. Photoaquation of equatorial NH_3 always corresponds to less than 10% of the overall photoreactivity. In the dichloro (IV) and chlorothiocyanato (V) systems the sum of the quantum yields for photoaquation of the X and

Y ligands coincides with that for production of cis aquoacido species, independently determined (see Table I). It seems then reasonable to infer that, for the other three complexes, isomerization (which is the predominant, observable reaction mode) is accompanied by exchange of axial H_2O with solvent.

The *trans*-$Cr(NH_3)_4(NCS)Cl^+$ ion shows typical "antithermal" behavior. While the dark reaction is one of Cl^- release, the favored photochemical path is one of NCS^- replacement.

The results conform to the general predictions of Adamson's rules[10] and of the photolysis models.[12,13] The ligands preferentially labilized are those on the weakest average-field axis,[10] along which the d_{z^2} (a_{1g}*) orbital is directed. For all five complexes the energy ordering of the d orbitals[36] is such that precisely the above σ-antibonding orbital is selectively populated in the lowest quartet (^4E) excited state,[12,13] which is well recognized to be the principally photoactive one.[4-9]

A second point concerns the simultaneous photoaquation of two (or more) ligands. The behavior of the dichloro (IV) and specially that of the chlorothiocyanato (V) ions indicate that the photoreactions are parallel, i.e., that the two axial ligands are not released from the same molecule. While this may be difficult to establish with systems such as $Cr(NH_3)_5X^{2+}$ (because of the very low quantum yields for X^- aquation, compared with that for NH_3 replacement),[26,29,37] it is unambiguously proven by the absence of $Cr(NH_3)_4(H_2O)_2{}^{3+}$ ions among the photolysis products of the above compounds.

Stereochemistry. The key observation is that stereochemical change is largely dominant in the LF photolysis of all the complexes investigated. For I, II, and III, trans → cis isomerization takes place at least 90% of the time. For IV, and V, each complex molecule undergoing aquation of the axial X or Y ligands results to undergo stereorearrangement within 5% experimental uncertainty. The stereochemistry of the main photoreactions is in sharp contrast with that of thermal aquation, which is essentially configuration retentive, leading to more than 90% trans products.[23,24] Also, predominantly *cis*-diacidotetraammine isomers are formed in the photolysis of *trans*-$Cr(en)_2(H_2O)(OH)^{2+}$ [38] and are the products of *z*-axis labilization of *trans*-$Cr(en)_2Cl_2{}^+$ (>70%),[15] *trans*-$Cr(en)_2(NCS)Cl^+$,[21] *trans*-$Cr(en)_2FCl^+$ (~90%),[22a] *trans*-$Cr(en)_2(NCS)_2{}^+$,[22b] and *trans*-$Cr(tet)Cl_2{}^+$ (≥80%).[14] Additionally, the *cis*-$Cr(NH_3)_4(H_2O)X^{2+}$ ions are the major photoaquation products of $Cr(NH_3)_5X^{2+}$-type complexes,[27,29,37,39] where NH_3 has been found to be preferentially released from the position trans to X^-, at least in the X = Cl case.[16] Even chromium(III) binuclear species undergo trans → cis photoisomerization.[40] Only *trans*-$Cr(cyclam)Cl_2{}^+$ photoaquates Cl^- with retention of configuration, however, with an exceptionally low efficiency.[14]

As has been pointed out elsewhere,[22b] even an experimental uncertainty of 5-10% in establishing the stereospecificity of chromium(III) photolyses may, in principle, preclude univocal mechanistic interpretations. However, at least within the above, hardly surmountable error limits, our data provide further support to the conclusion that a general and uniform photoaquation mechanism, requiring stereomobility, applies to all chromium(III) acidoamines when labilization along the *z* axis is involved. Stereochemical change accompanying release of axial ligands may be indeed regarded as an additional rule for chromium(III) photolysis.

As far as the products of equatorial photolysis are concerned, the relatively small fraction (<10%) of photoreleased NH_3 makes it impossible to conclude about their stereochemistries. Similarly, the configuration of the ethylenediamine photoaquation product could not be established for *trans*-$Cr(en)_2(NCS)Cl^+$.[21] Only in the cases of *trans*-$Cr(en)_2FCl^+$ [22a] and *trans*-$Cr(en)_2(NCS)_2{}^+$ [22b] were such products inferred to have the X and Y groups trans to each other.

Table II. Ammonia Photoaquation of *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ on L_1 Band Irradiation

578 ± 5 nm (ϵ_T = 17.7; ϵ_C = 14.5)[a]			546 ± 5 nm (ϵ_T = 19.8; ϵ_C = 31.1)[a]		
$[C]/[T]_0 \times 10^2$	$10^2\phi_{app}{}^b$	$10^2\phi_{NH_3}{}^c$	$[C]/[T]_0 \times 10^2$	$10^2\phi_{app}{}^b$	$10^2\phi_{NH_3}{}^c$
4.8	1.8 ± 0.3	1.2 ± 0.3	5.7	3.8 ± 0.3	2.5 ± 0.3
9.3	2.3 ± 0.2	1.2 ± 0.2	8.8	4.2 ± 0.2	2.3 ± 0.2
10.5	2.4 ± 0.2	1.1 ± 0.2	10.6	4.6 ± 0.1	2.4 ± 0.1
13.5	3.1 ± 0.1	1.4 ± 0.1	15.6	5.4 ± 0.1	2.2 ± 0.1
17.4	3.2 ± 0.1	1.1 ± 0.1			

[a] Measured under photolysis conditions. [b] Overall quantum yield. [c] Primary photoaquation quantum yield.

While the possible mechanisms have been discussed elsewhere,[14] the present results indicate that either associative or concerted reaction pathways (involving expansion of the coordination sphere) are more compatible with the stereochemical uniformity of products of axial labilization, than the merely dissociative processes implicitly assumed by the models.[12,13] Rearrangement through a pentacoordinated intermediate is more likely to yield a mixture of isomers, rather than a unique species of specific (cis) configuration.

Isomerization is very probably related to the distortion of the thermally equilibrated excited state. A naive explanation for the ease of change in geometry may be based on simple LF considerations. In O_h approximation, the loss of ligand-field stabilization energy (LFSE) in the lowest quartet excited state ($^4T_{2g}$) with respect to the ground state, leaves only $^2/_{12}$ (or ca. 17%) of the initial stabilization. During relaxation, the octahedron would be allowed to switch to a more stable (possibly pentagonal bipyramidal)[41] geometry, leading to the cis aquoproduct. The same arguments are consistent with the fair degree of stereoretention observed in Co(III) photosubstitutions.[42] In octahedral d^6 species the lowest excited states (singlet and triplet) still possess $^{14}/_{24}$ (or ca. 58%) of the ground state LFSE and possible geometry changes during thermalization should be less favored.

Another explanation, based on a molecular orbital approach, has been recently put forward.[43] It accounts for photoisomerization specially when ligand release occurs along the *z* axis, in the ^4E state of D_{4h} or C_{4v} complexes. The $d_{xz} \rightarrow d_{z^2}$ electronic transition would cause stereochemical change by combining repulsion of the equatorial ligands from the axial belt of the d_{z^2} orbital, with attraction toward the lobes of the emptied d_{xz} orbital. (Again, in cobalt(III) such a rearrangement would be unfavored, since in the lowest excited state the d_{xz} orbital is still populated by one electron.)

An alternative possibility, which should be further tested, is that the product configuration depends simply on a larger thermodynamic stability of the cis vs. the trans isomers rather than on the stereospecificity of the photoreaction (and the excited state distortion).

Quantum Yields. All complexes are quite photosensitive, the total reaction yields being in the 0.35-0.45 range. The efficiencies for aquation of the axial ligands and/or isomerization appear to be fairly constant over the whole LF wavelength range. The implication is that the observed photoprocesses arise mostly, if not exclusively, from the lowest excited state within a spin manifold. There seems to be little question that the state involved is a quartet.[4-9] In view of the many variables involved, a simple interpretation of the minor variations in quantum yields would be doubtful.

More specifically, the virtual constancy of the ϕ_{NCS^-}/ϕ_{Cl^-} *ratio* (1.8-1.9) for the *trans*-$Cr(NH_3)_4(NCS)Cl^+$ ion indicates that release of both ligands proceeds from the same excited state. This is not the case with the two reaction modes observed in $Cr(NH_3)_5X^{2+}$ complexes.[4,26,29,37]

Systems I, II, and V provide support for the predictions concerning the relative efficiencies of labilization of the axial ligands within a given complex. While for the chlorothiocyanato (V) complex the results are unequivocally interpretable, the discussion includes compounds I and II to the extent that the quantum yields for isomerization are taken as a measure of the efficiencies of water exchange (ϕ_{H_2O}). As stated above, such an assumption is not unreasonable, considering that in IV and V the experimentally accessible quantum yields for replacement of the axial groups are identical with those for generation of cis aquoacido products.

Adamson's second rule,[10] based upon the relative position of the ligands in the spectrochemical series ($H_2O > NCS^- > Cl^-$) correctly predicts that ϕ_{H_2O}/ϕ_{Cl^-} in I is larger than ϕ_{H_2O}/ϕ_{NCS^-} in II, and that in V ϕ_{NCS^-}/ϕ_{Cl^-} is greater than unity.[44]

The basic consideration of the photolysis models[12,13] is that the $^4B_1 \rightarrow {}^4E$ transition, promoting an electron from the d_{xz} or d_{yz}, π-antibonding, orbital to the d_{z^2}, σ-antibonding one, has a double effect. While the σ bonds in the z direction are weakened, the loss of electron density in the d_{xz} and d_{yz} orbitals strengthens the π-bonding along the same axis. Preferential labilization would be determined by the relative degree of π bonding of the two axial ligands. The present data conform to such expectations, because the H_2O ligand is recognized as a σ-donor only, and the NCS^- ion has a lower π-donor ability than Cl^-.[45] Preferential labilization of NCS^- over Cl^- has been observed also with *trans*-$Cr(en)_2(NCS)Cl^+$.[21]

It may be noticed that using trans diacidotetraammine species, the effects determining competition in the labilization of the acido groups can be tested for two different types of ligands at a time, within the same complex (and relative to the same excited state). The test is more severe than comparison between the quantum yields for X^- photoaquation in different compounds, as in the $Cr(NH_3)_5X^{2+}$ series.[12] Since the experimentally accessible quantum yields are ratios of rate constants of competing processes, the latter comparison must rest on the arbitrary assumption that each nonreactive process, relative to the excited state involved, occurs with the same rate in all the terms of the series.

Comparison with the quantum yields for photoaquation of the axial ligands of *trans*-$Cr(en)_2Cl_2^+$ ($\phi_{Cl^-} = 0.31$-0.35)[15] and of *trans*-$Cr(en)_2(NCS)Cl^+$ ($\phi_{NCS^-} = 0.17$-0.19; $\phi_{Cl^-} = 0.04$-0.05)[21] shows that the absence of aliphatic links between the coordinated nitrogen atoms is associated to relatively large photoaquation efficiencies, in conformity to a well-characterized pattern of reactivity.[14]

A point of interest is that *cis*-$Cr(NH_3)_4(H_2O)Cl^{2+}$ is the common product of the LF photolysis of $Cr(NH_3)_5Cl^{2+}$,[37,39] *trans*-$Cr(NH_3)_4Cl_2^+$, and *trans*-$Cr(NH_3)_4(H_2O)Cl^{2+}$, with essentially the same quantum yield of 0.4. A possible interpretation of this constancy, in spite of the considerable differences between the labilized ligands (NH_3, Cl, and, supposedly, H_2O), is that the quantum yield may be determined by a photophysical process, i.e., by a virtually identical competition between vibrational equilibration (and distortion) of the ^4E state and radiationless deactivation to the ground state. The equilibrated excited state would then be reactively deactivated, with an efficiency approaching unity, through a common intermediate, whose collapse would yield the cis aquochloro complex in all cases.

As far as NH_3 photoaquation is concerned, the considerable wavelength dependence observed in general over the LF range, implies that such a reaction mode is, at least in part, unconnected to the labilization of X^- and Y^-. The efficiencies increase steadily for all complexes on passing from the long-wavelength side of the L_1' ($^4B_1 \rightarrow {}^4E$) absorption to the L_1'' ($^4B_1 \rightarrow {}^4B_2$) band; then, in the L_2 ($^4B_1 \rightarrow {}^4A_2$, ^4E) region, the quantum yields either remain virtually constant (as in II, IV, and V) or drop slightly (as in I).

The general trend indicates the $^4B_2$ excited state as the major precursor to NH_3 photoaquation and is in agreement with theoretical expectations.[12,13] In such a state the electron density is enhanced in the $d_{x^2-y^2}$ (b_{1g}*), σ-antibonding orbital, localized on the equatorial, xy plane. The Cr-N bonds are thus expected to be weakened. Depopulation of the in-plane d_{xy} orbital, with respect to the ground state, would produce no effect since the NH_3 ligands do not possess π electrons. The same explanation has been proposed for ethylenediamine photoaquation of *trans*-$Cr(en)_2(NCS)Cl^+$.[21]

Following the above interpretation, the results show that, while the upper $^4A_2$ and ^4E ($^4T_{1g}$) states are converted to lower LF levels with very high efficiency, the lowest, "spin allowed", vibrationally equilibrated, $^4B_2$ and ^4E excited states are probably close enough in energy to allow simultaneous population and establishment of thermal equilibrium between them. The latter occurrence is suggested by the small but finite ϕ_{NH_3} value obtained even upon irradiation of the low-energy side of the L_1' absorption band. The lack of decrease of ϕ_{NH_3} in the L_2 region for compounds III and IV may reflect a small amount of incursion of CT character into the high energy LF region. In fact, uv excitation of the above species leads to highly efficient NH_3 photoaquation, presumably through a different mechanism (vide infra).

As a last comment, the quantum yield for NH_3 release of *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ in the L_1 region is smaller by one order of magnitude than the value of 0.15 reported in the literature for $Cr(NH_3)_4(H_2O)_2^{3+}$, the configuration of which was not specified.[46] The latter complex was thus the cis isomer, whose relatively high NH_3 photoaquation efficiency is also congruent with the empirical [10] and theoretical[12,13] predictions.

CT Excitation. Uv irradiation produces, in general, less selective bond breakage than does LF photolysis. In I, III, and IV both the z axis and the equatorial plane are affected to comparable extents. The nature of the electronic transition and the qualitatively different reactivity suggest that labilization may occur, at least partially, through a different mechanism, involving primary homolytic bond fission. The cleavage would be a consequence of the promotion of an electron from the π orbitals of the Cl^- or NCS^- ligands to the σ antibonding orbitals of chromium(III). Due to the high reducing power of Cr(II) the electron would have virtually unit probability of being recaptured by the labilized ligand before this leaves the solvent cage and a water molecule enters the coordination sphere. According to this picture our results would indicate that either the d_{z^2}, or the $d_{x^2-y^2}$ orbitals of chromium are populated with almost equal probability, leading to bond rupture both along the z axis and the xy plane. An interesting comparison may be made with $Cr(NH_3)_5Cl^{2+}$, which undergoes loss of comparable amounts of axial ($\phi = 0.15$-0.18) and equatorial ($\phi = 0.19$-0.22) NH_3 ligands at 254 nm, whereas the principal photoreaction, on L_1 band excitation, is aquation of axial NH_3.[16]

The anomalous ϕ_{Cl^-} value of IV may be accounted for by assuming that homolytic bond fission affects both chloride ligands simultaneously. Another explanation, that we prefer, is that CT photolysis produces a chromium(III) species which undergoes very fast thermal release of chloride. This species is likely to consist of a complex originated by NH_3 photoaquation. In view of the ease of stereochemical change such dichloroaquotriammine species may well have the chloride ligands cis to each other. A qualitative indication of the occurrence of rearrangement is given by the disappearance of the splitting of the L_1 band, even upon uv excitation. *cis*-Dichloroaminechromium(III) ions are known to be very reactive.[19b] Also, *cis*-$Cr(NH_3)_4Cl_2^+$ undergoes thermal aquation of the first chloride ligand with a half-life of a few minutes at 0°.[47] The presence of a fast thermal reaction prevents a reliable extrapolation of ϕ_{Cl^-} at zero irradiation time, even at 1°. The efficiency for primary Cl^- photoaquation can be thus evaluated only by subtracting ϕ_{NH_3} from the apparent ϕ_{Cl^-}. The figure, of about 0.5, is consistently larger than that found upon LF photolysis.

The question as to whether or not CT states convert to LF ones can be adequately answered only in the case of the NCS^- containing complexes (II and V). In fact, in these systems the absence of drastic variations in quantum yields for all the reaction modes on changing type of excitation indicates the occurrence of an efficient CT → LF conversion. As far as the other three species are concerned, even if such a conversion is likely to take place as well, the high quantum yields for photoreactions, which are certainly peculiar of the CT states, preclude any definite conclusion.

A survey of the quantum yields for release of the acido groups in I, II, V (and possibly in IV) indicates that, on passing from LF to CT excitation, ϕ_{Cl^-} is enhanced much more than ϕ_{NCS^-}. It is somehow surprising that, specially in II, irradiation of an absorption band assigned to a $NCS^- \rightarrow Cr$ transition[33] produces so little effect on ϕ_{NCS^-}. A possible explanation arises from the fact that for the two thiocyanate complexes the increase of ϕ_{NH_3} at 254 nm is much smaller than for the other systems. The CT excited state produced by the ligand-to-metal (or rather intraligand?) transition may rapidly deactivate, in part to LF states as already discussed, and in part even to the ground state, by dissipating the excitation energy through NCS-localized vibrations, before chemical change takes place.

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References and Notes

(1) Presented in part at the XIV International Conference on Coordination Chemistry, Toronto, Canada, June 1972 (see ref 20).
(2) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).
(3) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
(4) J. E. Martin and A. W. Adamson, *Theor. Chim. Acta*, **20**, 119 (1971).
(5) V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *J. Am. Chem. Soc.*, **93**, 339 (1971).
(6) N. Sabbatini, M. A. Scandola, and V Carassiti, *J. Phys. Chem.*, 77, 1307 (1973).
(7) S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).
(8) H. F. Wasgestian, *J. Phys. Chem.*, **76**, 1947 (1972).
(9) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, 77, 2947 (1973).
(10) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).
(11) S. C. Pyke and R. G. Linck, *J. Am. Chem. Soc.*, **93**, 5281 (1971).
(12) (a) J. I. Zink, *J. Am. Chem. Soc.*, **94**, 8039 (1972); (b) *Mol. Photochem.*, **5**, 151 (1973).
(13) M. Wrighton, H. B. Gray, and G. S. Hammond, *Mol. Photochem.*, **5**, 165 (1973).
(14) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).
(15) A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, **48**, 1524 (1971).
(16) E. Zinato, P. Riccieri, and A. W. Adamson, *J. Am. Chem. Soc.*, **96**, 375 (1974).
(17) A. D. Kirk, *J. Am. Chem. Soc.*, **93**, 283 (1971).
(18) A. D. Kirk, *Mol. Photochem.*, **5**, 127 (1973).
(19) (a) R. D. Archer, *Coord. Chem. Rev.*, **4**, 243 (1969); (b) C. S. Garner and D. A. House, *Transition Met. Chem.*, **6**, 59 (1970).
(20) P. Riccieri and E. Zinato, Proceedings of the XIV International Conference on Coordination Chemistry, Toronto, Canada, 1972, p 252.
(21) (a) M. T. Gandolfi, M. F. Manfrin, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **94**, 7152 (1972); (b) M. T. Gandolfi, M. F. Manfrin, A. Juris, L. Moggi, and V. Balzani, *Inorg. Chem.*, **13**, 1342 (1974).
(22) (a) G. Wirth and R. G. Linck, *J. Am. Chem. Soc.*, **95**, 5913 (1973); (b) C. Bifano and R. G. Linck, *Inorg. Chem.*, **13**, 609 (1974).
(23) D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, 7, 2506 (1968).
(24) D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem.*, **8**, 505 (1969).
(25) A. Benrath and H. Steinrath, *Z. Anorg. Allg. Chem.*, **194**, 351 (1930).
(26) E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Am. Chem. Soc.*, **91**, 1076 (1969).
(27) E. Zinato and P. Riccieri, *Inorg. Chem.*, **12**, 1451 (1973).
(28) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(29) P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, **9**, 727 (1970).
(30) P. Riccieri and E. Zinato, *Z. Phys. Chem.* (*Frankfurt am Main*), **79**, 28 (1972).
(31) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser A*, **235**, 518 (1956).
(32) (a) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968); (b) R. Perumareddi, *ibid.*, **4**, 73 (1969).
(33) C. K. Jorgensen, *Prog. Inorg. Chem.*, **12**, 101 (1970).
(34) P. Riccieri and E. Zinato, to be submitted for publication.
(35) M. F. Manfrin, M. T. Gandolfi, L. Moggi, and V. Balzani, *Gazz. Chim. Ital.*, **103**, 1189 (1973).
(36) D. A. Rowley, *Inorg. Chem.*, **10**, 379 (1971).
(37) H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem.* (*Frankfurt am Main*), 57, 282 (1968); **62**, 127 (1968).
(38) A. W. Adamson, *Adv. Chem. Ser.*, **No. 49**, 237 (1965).
(39) M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).
(40) P. Riccieri and E. Zinato, *Inorg. Chim. Acta*, 7, 117 (1973).
(41) A. W. Adamson, *Pure Appl. Chem.*, **20**, 25 (1969).
(42) R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, *J. Am. Chem. Soc.*, **97**, 3027 (1974).
(43) J. I. Zink, *J. Am. Chem. Soc.*, **96**, **4464** (1974).
(44) It should be kept in mind that the rules are *empirical*, as is the spectrochemical series. Although the NCS^- ligand is generally reported to occupy a spectrochemical position either close or slightly higher relative to H_2O, in the present cases the merely *empirical* correlation holds. In the series of analogous $Cr(NH_3)_5X^{n+}$ ions the L_1 band maximum is, in fact, at 484 nm for $X = H_2O$,[46] at 487 nm for $X = NCS^-$,[26] and at 512 nm for $X = Cl^-$.[37]
(45) W. W. Fee and J. N. MacB. Harrowfield, *Aust. J. Chem.*, **23**, 1049 (1970).
(46) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).
(47) Unpublished results from this laboratory.