state ($J = 4$) and, in $NpCp_3 \cdot 3THF$, was found to be weakly paramagnetic, like the isoelectronic Pu^{4+} ion.[17] For cubic symmetries, temperature-dependent paramagnetism is consistent only with the Np^{3+} in an O_h site and a field dominated by the fourth-order term for a Γ_5 ground level. T_d and O symmetries have the nonmagnetic singlet Γ_1 ground level, which can have TIP but not temperature-dependent paramagnetism in any symmetry. The experimental susceptibility for Np^{3+} in $NpCp_3 \cdot 3THF$ indicates two paramagnetic levels; descending in symmetry from O_h, the Γ_5 level is split into Γ_1 and Γ_3 (magnetic doublet) levels for hexagonal-class levels,[14] which, in this instance, implies a threefold axis. The symmetries D_{3v}, D_{3h}, C_{3v} and C_{3h} are all consistent with the magnetic susceptibility results for Np^{3+} in $NpCp_3 \cdot 3THF$. Lower symmetries split the Γ_5 level into nonmagnetic singlets and permit only TIP unless the splitting is so small as to allow temperature-dependent paramagnetism *via* "non-Kramers doublets."[18] An explanation of the magnetic properties of Np^{3+} in $NpCp_3 \cdot 3THF$ based upon a threefold axis (a D_{3v}, D_{3h}, etc., site) appears more probable.

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Thermal and Photochemical Aquation of Some Substituted Acetatopentaamminechromium(III) Ions

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The acid hydrolysis of four $Cr(NH_3)_5(OCOR)^{2+}$ complex ions, where R = CCl_3, $CHCl_2$, CH_2Cl, or CH_3, has been studied in 0.1–0.01 *M* $HClO_4$ at constant ionic strength, 0.13. For R = CCl_3, as usual, the reaction is one of aquation of the acido group and is acid catalyzed. Comparison with the R = CF_3 analog indicates that the rate varies inversely with the base strength of $RCOO^-$. NH_3 aquation is the primary step for the three other species with rates increasing with $RCOO^-$ basicity. The results are interpreted in terms of a progressive strengthening of the Cr–O bond and weakening of the Cr–N bond cis to the carboxylate, consistent with hydrogen bonding between the carbonyl oxygen and adjacent H of an ammonia ligand. Possible steric effects are discussed. Irradiation of the four complexes and of that with R = CF_3 in the long-wavelength ligand-field band leads mainly to ammonia aquation with quantum yields ranging between 0.25 and 0.45, unconnected with the elctron-withdrawing ability of R. The mode of photoreaction is that predicted by the chromium(III) photochemical rules. No conclusions can be drawn about stereospecific implications from the configuration of the photoproduct, *cis*-$Cr(NH_3)_4(H_2O)(OCOR)^{2+}$.

Introduction

All the known acidopentaammine complexes of chromium(III), like those of cobalt(III), rhodium(III), and iridium(III), are known to undergo the primary aquation of the acido group.[1,2] Among the $Cr(NH_3)_5X^{2+}$ systems, detailed acid hydrolysis studies have been reported for X = NCS,[3,4] F,[5] Cl, Br, I,[6,7] and ONO.[8]

Recently a series of variously substituted acetatopentaamminechromium(III) complexes of the general formula $Cr(NH_3)_5(OCOR)^{2+}$, where R = CH_3, $CHCl_2$, CCl_3, or CF_3, has been prepared[9] and it seemed proper to study the aquation reactions of such a homologous series of coordination compounds. The purpose of this research was (i) to study the effect of a virtually continuous variation of the basicity of the acetato ligand and (ii) to compare these reactions with the reported results for analogous $M(NH_3)_5(OCOR)^{2+}$ complexes, where either M = Co(III) and R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3[10] or M = Co(III), Rh(III), Ir(III) and R = CH_3, $C(CH_3)_3$, CF_3,[11] the aquation of which is subject to acid catalysis since the leaving acido group may be protonated.[11] Some of the reaction paths were reported to involve the cleavage of the oxygen to carbon (rather than metal to oxygen) bond.[11] Arguments have however been presented[12] that C–O bond breaking is much less common than previously assumed.[11]

The results reported here refer to the aquation reactions of (trichloroacetato)-, (dichloroacetato)-, (chloroacetato)-, and acetatopentaamminechromium(III) in acid solution. While this work was in progress, a note by other authors has appeared on the acid and alkaline hydrolysis of (trifluoroacetato)pentaamminechromium(III).[13] Also the photochemical behavior of the five new coordination compounds has been examined, on irradiation of their long-wavelength ligand-field band, indicated as L_1 and due to the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition in O_h symmetry. Chromium(III) photoreactions following light absorption in the

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d–d region are exclusively substitutional in type.[14] Of the $Cr(NH_3)_5X^{2+}$ complex ions, those with X = NCS,[15] Cl,[16,17] Br[18] have been photochemically studied in some detail, and in all cases the main reaction was found to be NH_3 release, whereas in the dark only X^- aquation is occurring.[3–7] The mode of photoaquation can be predicted by a set of semiempirical rules.[19] The study of five more complexes having X = OCOR can provide a further test for these predictions; in addition these compounds offer the possibility of checking whether or not the variation of the electron-withdrawing ability of the acido group has any effect on the photochemical behavior.

Experimental Section

Materials.—The general procedure followed for the preparation of the various carboxylatopentaamminechromium(III) salts was the anation of aquopentaamminechromium(III) which was obtained as the $[Cr(NH_3)_5(H_2O)](NO_3)_3 \cdot NH_4NO_3$ double salt by a literature method.[20]

The synthesis is successful only in the presence of a high concentration of the entering $RCOO^-$ ion, provided the complex is in the aquo and not in the hydroxo form.[9] During this work, the $Cr(NH_3)_5(OCOR)^{2+}$ series was completed with the preparation of the R = CH_2Cl term using ammonium monochloroacetate in aqueous medium; the use of the corresponding ammonium salt improved the synthesis of the complex with R = $CHCl_2$.

Acetatopentaamminechromium(III) Perchlorate.—The corresponding nitrate salt was prepared in dimethylacetamide using anhydrous sodium acetate, by the described method, and then converted to the perchlorate by reprecipitation with $NaClO_4$. *Anal.* Calcd for $[Cr(NH_3)_5(C_2H_3O_2)](ClO_4)_2$: C, 6.06; H, 4.66; N, 17.65. Found: C, 5.9; H, 4.3; N, 17.7. The band maxima in the visible absorption spectrum occur at 494 nm (ϵ 56.6) and 364 nm (ϵ 41.9). The extinction coefficients are higher than previously reported.[9]

(Chloroacetato)pentaamminechromium(III) Perchlorate and (Dichloroacetato)pentaamminechromium(III) Perchlorate.—Five grams of the above double salt was dissolved in 20 ml of water at 50°. A 15-g portion (*ca.* tenfold molar excess) of the substituted ammonium acetate was then added and the mixture was kept at 60–70° for 5 min. After cooling in an ice bath, the deep red solution was treated with 20 ml of 8 *M* sodium perchlorate. The orange salt slowly precipitated and after 30 min it was filtered off, washed with a small portion of ice-cold 0.1 *M* $NaClO_4$, ethanol, and ether, and air-dried. The yield was 50–60%. Recrystallization of the crude product was necessary especially to remove possible amounts of ammonium perchlorate and was accomplished by dissolving 2.5 g in 15 ml of water at 40° containing 2 g of the corresponding acetic acid, filtering, cooling, and adding dropwise 15 ml of 8 *M* sodium perchlorate. The crystalline powder was collected, washed, and dried as above. *Anal.* Calcd for $[Cr(NH_3)_5(C_2H_2O_2Cl)](ClO_4)_2$: C, 5.59; H, 3.98; N, 16.30; Cr, 12.10. Found: C, 5.1; H, 3.0; N, 16.0; Cr, 12.1. Calcd for $[Cr(NH_3)_5(C_2HO_2Cl_2)](ClO_4)_2$: C, 5.18; H, 3.47; N, 15.0. Found: C, 5.3; H, 3.1; N, 14.5. The visible absorption spectra show maxima at 483 nm (ϵ 50.3), 360 nm (ϵ 32.7) and at 483 nm (ϵ 52.4), 361 nm (ϵ 35.7) for the monochloro- and the dichloroacetate complexes, respectively, the latter bands being more intense by *ca.* 15% than the early reported ones.[9]

(Trichloroacetato)pentaamminechromium(III) Perchlorate and (Trifluoroacetato)pentaamminechromium(III) Perchlorate.—The preparation and recrystallization of these salts followed the published procedure using the corresponding acids in aqueous medium. The spectral features of both complexes agree well with those previously described.[9]

All the other chemicals and solvents used were of reagent grade.

Analytical Procedures.—The free ammonia content of a solution was determined by a colorimetric method with sodium phenate–sodium hypochlorite reagent.[15] A separation procedure was necessary to prevent decomposition of any complex present by the alkaline reagent and was accomplished in dim red light by adsorbing 3- or 5-ml aliquots in a 1 cm × 4–5 cm column of Permutit Zeo-Karb 225 SRC 13 cation-exchange resin (14–52 mesh), previously washed with 0.7 *M* $HClO_4$, and eluting with 50–60 ml of the same solution. The reagent was added to the neutralized eluate and the analysis was performed in the described manner. Owing to the complexity of the method, the results were reproducible to 10%.

Any colorimetric procedure would have been suitable in aqueous solution for analyzing the released acetato ions, whose concentration was in the range 10^{-3}–10^{-4} *M*. However no procedure of this kind seems to have been described in the literature and a remaining possibility was the spectrophotometric determination in the uv region where the absorption onset of the free carboxylato species occurs at *ca.* 260 nm for R = CCl_3 and R = $CHCl_2$, at *ca.* 240 nm for R = CH_2Cl, and at *ca.* 230 nm for R = CH_3. The corresponding chromium(III) complexes have the same absorption with a bathochromic shift of 10–15 nm, and spectral variations in this wavelength range were somewhat imprecise due also to the steepness of the band tail.

Another procedure followed was to isolate the free ligand by eluting a reaction aliquot through a 1 cm × 3 cm column of the above-described cation exchanger, with 0.1 *M* perchloric acid. The resin was previously washed with 3 *M* $HClO_4$ until the effluent was spectrophotometrically pure in the 200–300-nm region. All the species, except free acetate (partly neutral and partly anionic), were retained in the column. The eluate was diluted to a known volume and its spectrum was measured between 200 and 260 nm. Both methods yielded at best semiquantitative results.

Chromium was determined spectrophotometrically using 1,5-diphenylcarbohydrazide as reagent, following persulfate oxidation of the sample.[21]

Apparatus.—The general photolysis equipment is described elsewhere.[22] Light selection in the L_1 absorption region was accomplished using the Corning filter combination CS-3-72 + CS-5-57 which gave a band centered at 460 nm (*T* = 50%; 55-nm half-width). The intensity was of the order of (3–5) × 10^{-8} einstein/sec and was determined by means of Reineckate actinometry.[21]

Optical densities of solutions were measured with a Beckman DU spectrophotometer. Visible and uv absorption spectra were obtained with either a Beckman DK 1A or DB recording instrument. Infrared spectra were recorded with a Beckman IR 10 apparatus and the details in the 1600–1800-cm^{-1} range were scanned using a Perkin-Elmer Model IR 521 spectrophotometer.

Kinetic Procedures.—Rate measurements were carried out as follows. Weighed amounts of complex, such as to give a concentration around 1 × 10^{-2} *M*, were placed in aluminum foil covered volumetric flasks which were immersed in a thermostated bath. Solutions were made up with 0.1–0.01 *M* perchloric acid previously brought to the desired temperature and containing sufficient sodium perchlorate to maintain the ionic strength at 0.13 (the total ClO_4^- concentration was 0.1 *M*). The temperature was constant to within 0.1°. Two procedures were employed to follow the decrease in optical density of the L_1 band whose maximum occurs in all cases at around 485 nm.

For the "slow" reactions, aliquots were periodically withdrawn and cooled to room temperature and their absorption spectra were recorded. In some experiments their absorbance was measured only at certain wavelengths. Some rate determinations for (trichloroacetato)pentaamminechromium(III) were done measuring, at given times and wavelengths, the optical density of a unique sample in a 1-cm spectrophotometer cell placed in a thermostated Beckman DU cell compartment and positioned in the light beam only during the actual measurement. The temperature precision was in this case ±0.2°. All these methods gave results in good agreement. For R = CCl_3 some rate determinations were done by measuring the optical density change below 250 nm. The scatter of the data was, in this case, higher than in the visible region, for the mentioned reason. In some instances rates for release of ammonia and/or carboxylate were measured removing 3- or 5-ml portions at various times, cooling, and analyzing them as described above.

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For the "fast" reactions, the absorbance at a fixed wavelength was recorded as a continuous function of time by placing the sample in a cell which was inserted in a holder of a double-beam spectrophotometer and maintained at a constant temperature.

When necessary, complex concentrations were corrected at zero time for the extent of reaction which occurred prior to measurement. Rate constants were obtained from plots of log $(A_t - A_\infty)$ *vs.* time. Activation enthalpies and entropies were derived from a least-squares analysis of log (k/T) *vs.* $1/T$.

Photolysis Procedures.—Irradiations were done either at room temperature using a 10-cm path length cylindrical spectrophotometer cell (27-ml volume) placed in a brass holder or in a cylindrical double-wall Pyrex cell (10-cm path length, 40-ml volume) kept at 18.0 ± 0.2°C by circulating thermostated water. The solutions were 0.1 M in perchloric acid and about 10^{-2} M in complex; thus, light absorption was greater than 99%. For (trifluoroacetato)pentaamminechromium(III) photolyses were carried out at the natural pH of the complex solutions because of solubility limitations. The solutions were stirred every 10 min and the photolysis time was usually 60 min. The total reaction was between 10 and 20% so that secondary photolysis and inner filter effects were minimal. In the case of acetatopentaamminechromium(III) the temperature was kept at 8 ± 1° and the irradiation time was limited to 15 min, to minimize the effect of the fast dark reaction. The simultaneous thermal reaction was taken into account in each case by analyzing the irradiated solutions in parallel with samples kept in the dark at the same temperature as during photolysis.

Results

Thermal Reactions.—The aquation behavior is qualitatively different for (trichloroacetato)pentaamminechromium(III) and for the three complex ions with R = $CHCl_2$, CH_2Cl, CH_3. The results pertaining to $Cr(NH_3)_5(OCOCCl_3)^{2+}$ are presented first.

The spectral features of the R = CCl_3 complex are reported in Figure 1 along with those of trichloroacetic acid and aquopentaamminechromium(III). Its primary reaction consists exclusively of the aquation of the acido group, as indicated by the following facts. (1) As shown in Figure 2 the absorbance of solutions of (trichloroacetato)pentaamminechromium(III) in 0.1–0.01 M perchloric acid and at constant ionic strength of 0.13 progressively decreases with a slight blue shift. No crossing point is present, as would be expected for the substitution of the trichloroacetate ligand by water. (2) The optical density below 300 nm diminishes, in agreement with a lower extinction coefficient for both $Cr(NH_3)_5(H_2O)^{3+}$ and CCl_3COO^-. (3) Increasing amounts of free trichloroacetate ion were found in the solutions. (4) A tripositive ion, which may be aquopentaamminechromium(III), has been characterized in the mixture as follows. A solution aliquot containing approximately 30% of products was adsorbed in a 1 cm × 3 cm column of the above-described cation exchanger and eluted with 2 M perchloric acid. A parallel experiment indicated that 2 M $HClO_4$ did not elute $Cr(NH_3)_5(H_2O)^{3+}$ ion. The mixture was separated into two orange bands only one of which (corresponding to the dipositive starting complex) could be moved by elution. (5) The possibility of an appreciable occurrence of subsequent and/or simultaneous release of NH_3 from aquopentaamminechromium(III) could be excluded on the grounds that the spectrum of a solution containing only this complex remains unchanged for a period of time corresponding at least to 40–50% reaction of (trichloroacetato)pentaamminechromium(III). Also, not more than 1% of free NH_3 was present at 25% total reaction. (6) Any subsequent or simultaneous ammonia substitution should have produced a definite red shift of the absorption spectrum due to the lower position of water relative to NH_3 in the spectrochemical series.

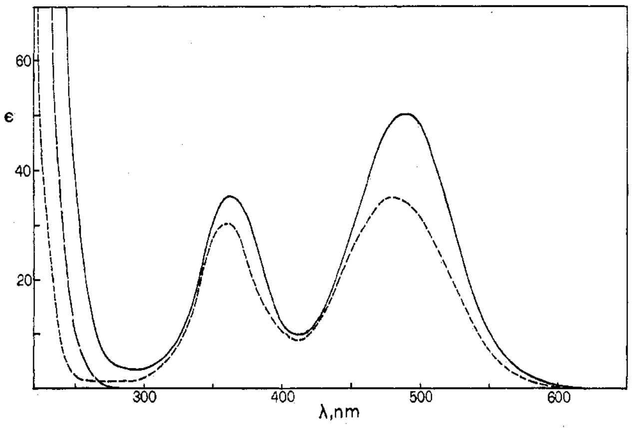

Figure 1.—Absorption spectra in 0.1 M $HClO_4$: ——, $Cr(NH_3)_5(OCOCCl_3)^{2+}$; - - - -, $Cr(NH_3)_5(H_2O)^{3+}$; — —, CCl_3COOH.

First-order rate plots based on spectral variations at 485 nm were linear up to at least 50% reaction. Determinations at 250 nm were less precise (see Experimental Section) but still in agreement within 15% error. Some measurements were done in duplicate and the average deviation was ±7%. The results for various acidities and temperatures are reported in Table I. In the range of acidity employed, the observed pseudo-first-order aquation rate constants increase with increasing H^+ concentration. A plot of k_{obsd} *vs.* $[H^+]$ is linear. Thus, k_{obsd} can be expressed as a sum of two terms

TABLE I

RATES FOR TRICHLOROACETATE AQUATION OF $Cr(NH_3)_5(OCOCCl_3)^{2+}$ [a]

Temp, °C	$[H^+]$, M	10^5k_{obsd}, sec^{-1}	Temp, °C	$[H^+]$, M	10^5k_{obsd}, sec^{-1}
25.0	0.10	0.415	55.0	0.10	15.5
40.0	0.10	2.90	55.0	0.08	14.3
40.0	0.08	2.76	55.0	0.06	13.8
40.0	0.06	2.55	55.0	0.04	13.5
40.0	0.04	2.48	55.0	0.02	12.9
40.0	0.02	2.26	69.0	0.10	51.0

[a] Constant ionic strength, 0.13, adjusted with $NaClO_4$.

$$k_{\text{obsd}} = k_{H_2O} + k_{H^+}[H^+] \qquad (1)$$

and a least-squares fit yields the values of $k_{H_2O} = (2.12 \pm 0.04) \times 10^{-5}$ sec^{-1} and $k_{H^+} = (7.8 \pm 0.6) \times 10^{-5}$ M^{-1} sec^{-1} at 40° for the uncatalyzed and acid-catalyzed rate constants, respectively.

For (dichloroacetato)-, (chloroacetato)-, and acetatopentaamminechromium(III) the primary reaction in aqueous solution and in the same conditions of acidity and ionic strength is one of aquation of the NH_3 ligand. The behavior for R = CH_3 could be only semiquantitatively studied because of the fairly high reactivity of this species, but it conforms to the same general pattern. The following observations are consistent with the above conclusion.

1. The visible absorption spectra shift to longer wavelengths during reaction as expected from a progressive replacement of coordinated ammonia with

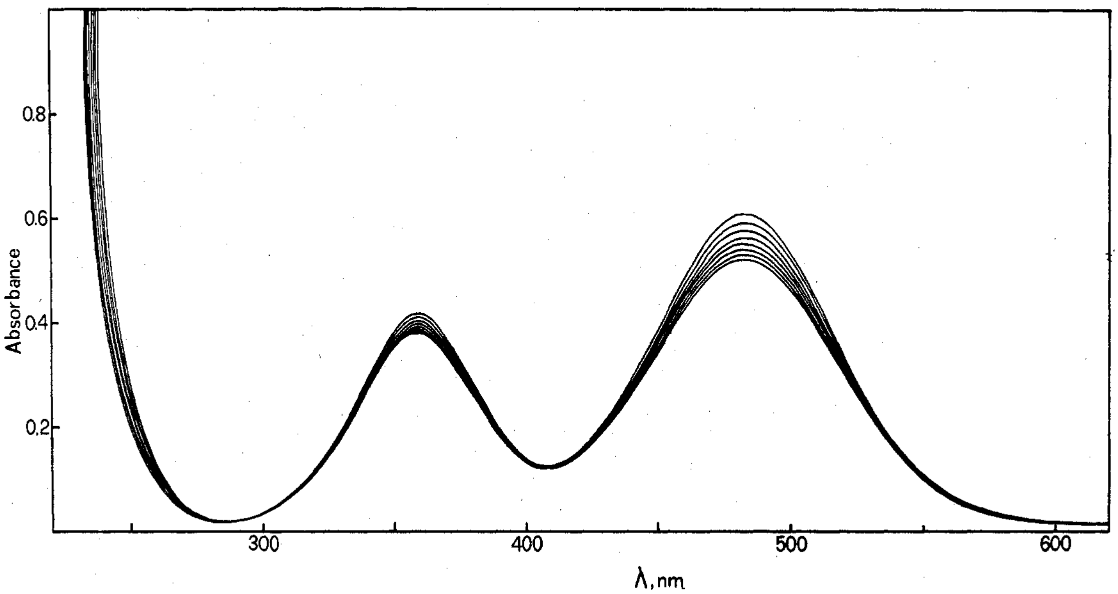

Figure 2.—Spectral changes during the aquation of $Cr(NH_3)_5(OCOCCl_3)^{2+}$ in 0.1 *M* $HClO_4$ at 55°. Reading downward reaction time is 0, 10, 20, 30, 40, 50, 60, and 70 min.

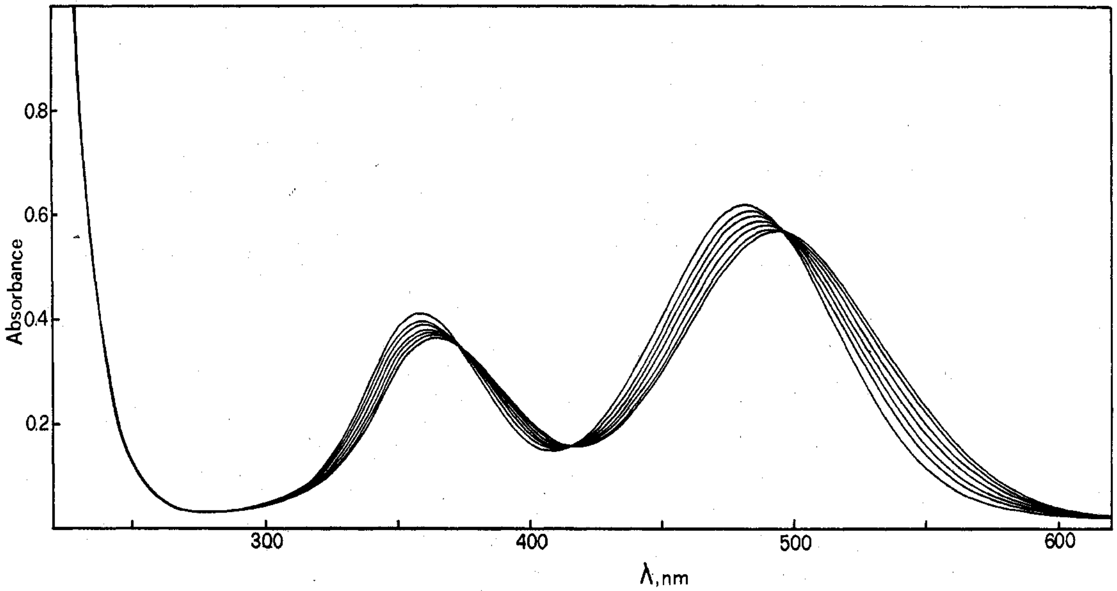

Figure 3—Spectral changes during the aquation of $Cr(NH_3)_5(OCOCH_2Cl)^{2+}$ in 0.1 *M* $HClO_4$ at 40°. Reading downward at 480 mn, reaction time is 0, 15, 30, 45, 60, 75, and 90 min.

water molecules. Figure 3 exemplifies the spectral evolution of the (chloroacetato)pentaammine species and shows three isosbestic points at 495 nm (ϵ 47.2), 415 nm (ϵ 11.6), and 375 nm (ϵ 26.4). For the R = $CHCl_2$ analog the spectra cross at 500 nm (ϵ 45.6), 412 nm (ϵ 11.8), and 375 nm (ϵ 27.9). Had the primary aquation product been aquopentaamminechromium(III), no crossing points and only a general decrease in optical density would have been recorded, as for R = CCl_3. That the red shift is the consequence of a subsequent ammonia release from a possible aquopentaammine product can be ruled out on the grounds that the observed reaction is faster approximately by a factor of 2 for R = $CHCl_2$ and by a factor of 6 for R = CH_2Cl than for R = CCl_3, whose aquation involves no spectral shift up to at least 50% reaction.

2. No appreciable change in optical density is occurring below 300 nm indicating that the acido group remains coordinated.

3. The concentration of free carboxylate was found to be negligible up to at least 30% reaction, whereas increasing amounts of free ammonia were present in the solutions.

4. By the same ion-exchange experiments used for the trichloroacetato complex, no tripositive ion was detectable among the reaction products.

5. The isosbestic points are still present at 40% reaction; thus, only one species or a constant ratio of products is formed. A simultaneous NH_3 and $RCOO^-$ substitution is highly improbable since the crossing points either with *cis*- or with *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$ (which are tripositive ions) are expected at longer wavelengths, especially in the L_1 region as shown in Figure 4.

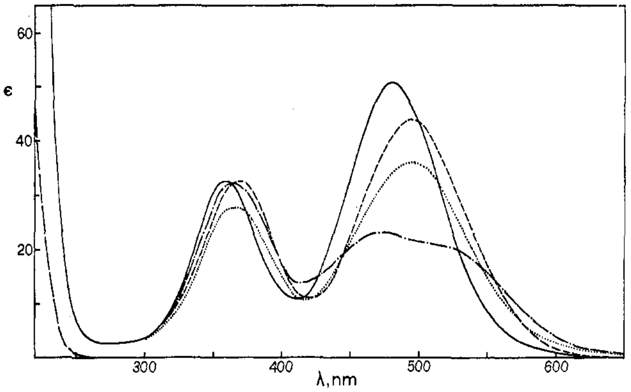

Figure 4.—Absorption spectra in 0.1 *M* $HClO_4$: ——, $Cr(NH_3)_5(OCOCH_2Cl)^{2+}$; ----, $Cr(NH_3)_4(H_2O)(OCOCH_2Cl)^{2+}$; ....., *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$; -·-·-, *trans*-$Cr(NH_3)_4(H_2O)_2^{3+}$; — —, $CH_2ClCOOH$.

For the same reason a fast subsequent $RCOO^-$ aquation can be excluded. Also two successive steps, the first one involving the replacement of the carboxylato group, can be ruled out as stated in point 1.

The primary thermal aquation product could not be isolated and, therefore, its visible spectrum was unknown. However, photochemical experiments allowed us to deduce the spectrum of the main photoproduct, identified as $Cr(NH_3)_4(H_2O)(OCOR)^{2+}$ (see the following section). The fact that the evolution of the spectra is the same in the dark and under irradiation, plus the coincidence of the isosbestic points in the two cases, led to the reasonable assumption that aquocarboxylatopentaamminechromium(III) was the common product. With this assumption, first-order plots were derived from spectral variations at 485 nm and were linear up to *ca.* 40% conversion for R = $CHCl_2$ and R = CH_2Cl. Beyond this value, the isosbestic behavior is lost especially by the latter complex, because of a red shift of the L_1 band presumably in connection with the loss of further NH_3 molecules. The difference in optical density between reagents and products is rather small. As a consequence, the reproducibility of the rate data could be estimated as ±15%. Some first-order rate constants were also evaluated from the amounts of free ammonia. While for R = $CHCl_2$ the results agreed within experimental error, the apparent rate of ammonia release for R = CH_2Cl was somewhat larger than that measured spectrophotometrically. The results for three temperatures and for various acid concentrations are presented in Table II. Within our precision limits the rates seem not to be affected by the pH, at least in the interval of $[H^+]$ studied.

As already mentioned, the visible spectrum of acetatopentaamminechromium(III) evolves with the same general trend, but very rapidly even at room temperature. The crossing point around 500 nm becomes nonisosbestic earlier than for the previous complexes and shifts further. Evidently, a reaction sequence is taking place, more effectively than in the other two cases, involving the successive aquation of more than one NH_3 ligand. In fact the apparent rate for ammonia release was found to be higher by almost an order of magnitude than spectrophotometrically estimated. Pseudo-first-order constants could be computed from spectral changes occurring during the initial 10–15% reaction and only at two temperatures. Allowing an imprecision factor for the spectrum of the corresponding photoproduct (which was assumed to be also in this case identical with the thermal reaction product) the rate values could be off even by 50% although their ratio, and hence the activation energy, should not bear such an uncertainty. Thus, for R = CH_3, the results which appear in Table II, should be taken as semiquantitative. Also no acid effect seems to be present for this species between 10^{-2} and 10^{-1} *M* $HClO_4$. It was qualitatively observed that for a lower acid concentration the spectral changes are qualitatively different and occur much faster. Four isosbestic points were maintained at 542, 442, 395, and 330 nm almost to complete reaction and the product showed maxima at 570 and 413 nm. Possibly a very fast reaction cascade takes place at the high pH values induced by both free NH_3 and CH_3COO^- and leads either to $Cr(H_2O)_6^{3+}$ or to $Cr(H_2O)_5(OH)^{2+}$.

TABLE II

RATES FOR AMMONIA AQUATION OF $Cr(NH_3)_5(OCOR)^{2+}$ IONS[a]

Temp, °C	$[H^+]$, *M*	10^4k_{obsd}, sec^{-1}	Temp, °C	$[H^+]$, *M*	10^4k_{obsd}, sec^{-1}
		R = $CHCl_2$			
25.0	0.10	0.075	40.0	0.01	0.48
25.0	0.01	0.073	55.0	0.10	3.7
40.0	0.10	0.50	55.0	0.08	3.7
40.0	0.08	0.49	55.0	0.04	4.3
40.0	0.04	0.57	55.0	0.01	3.3
		R = CH_2Cl			
25.0	0.10	0.23	40.0	0.01	1.6
25.0	0.01	0.24	55.0	0.10	11
40.0	0.10	1.5	55.0	0.08	14
40.0	0.08	1.5	55.0	0.06	13
40.0	0.04	1.4	55.0	0.01	12
		R = CH_3			
25.0	0.10	2.3	40.0	0.10	12
25.0	0.01	2.3	40.0	0.01	11

[a] Constant ionic strength, 0.13, adjusted with $NaClO_4$.

Photochemical Reactions.—The photolysis behavior upon irradiation of the L_1 band is qualitatively the same for R = CF_3, CCl_3, $CHCl_2$, CH_2Cl, and CH_3. This band shifts to the red in all cases during irradiation, as in Figure 3, which is consistent with the replacement of coordinated ammonia by water. If only the oxygen-bound carboxylate were released, only a general decrease in absorption without any crossing would have been recorded, as in the dark aquation of the trichloroacetato complex (Figure 2). Three isosbestic points were observed for each complex at least until *ca.* 30% reaction. Particularly evident is the long-wavelength one at 503 nm for R = CF_3, at 502 nm for R = CCl_3, at 500 nm for R = $CHCl_2$, and at 495 nm for R = CH_2Cl. Thus, either a single product or a constant ratio of products is involved and secondary processes are negligible. The absorption features of the dark solutions remain virtually unchanged during photolysis, except for R = CH_3, being the thermal reaction fairly rapid in this case as mentioned above. Ammonia photoaquation quantum yields were estimated from the amounts of free NH_3. Determinations were carried out at least in duplicate using solutions around 0.01 *M* in complex either at room temperature or at 18°. The results agreed for both conditions and are summarized in Table III; the analytical method

TABLE III

QUANTUM YIELDS FOR NH_3 PHOTOAQUATION OF SOME $Cr(NH_3)_5(OCOR)^{2+}$ IONS IN 0.1 *M* $HClO_4$ AT 440–510 NM

R	Temp,[a] °C	% NH_3		ϕ
CF_3[b]	18.0	16.9		0.36
	rt	20.0		0.36
			Av	0.36 ± 0%
CCl_3	rt	14.2		0.25
	18.0	17.8		0.29
			Av	0.27 ± 8%
$CHCl_2$	18.0	12.5		0.43
	rt	26.3		0.46
			Av	0.44 ± 4%
CH_2Cl	rt	6.8		0.26
	18.0	12.5		0.28
			Av	0.27 ± 4%
CH_3	8	2.8		0.3

[a] rt denotes room temperature of 20–23°. [b] In water at the natural pH of the complex.

allowed a precision such that the average deviation was less than about 10%. Although for acetatopentaamminechromium(III) photolysis was performed at a lower temperature and to a smaller percentage of reaction because of the fast dark process, only one figure can be considered significant for ammonia quantum yield.

As explained in the Experimental Section, analytical limitations did not afford an exact determination of free carboxylate and only a semiquantitative estimate could be done for the $RCOO^-$ quantum yields. A conservative upper limit of 0.1 was established for all five complex ions; however the actual value could be lower even by an order of magnitude.

TABLE IV

SPECTRAL FEATURES OF PHOTOPRODUCED $Cr(NH_3)_4(H_2O)(OCOR)^{2+}$ IONS IN 0.1 *M* $HClO_4$

	$^4A_{2g} \rightarrow {}^4T_{2g}$ band		$^4A_{2g} \rightarrow {}^4T_{1g}$ band	
R	λ, nm	ε	λ, nm	ε
CCl_3	500	43	370	29
$CHCl_2$	495	47	370	31
CH_2Cl	500	43	370	31

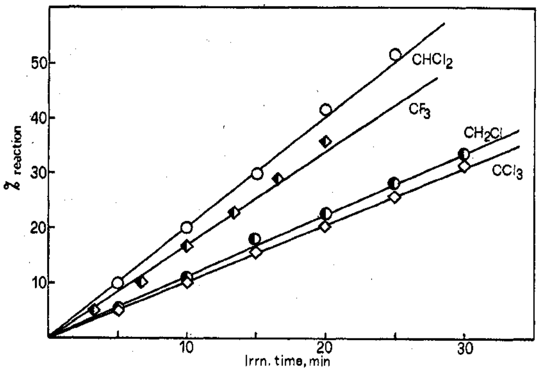

Figure 5.—Photoaquation of $Cr(NH_3)_5(OCOR)^{2+}$ ions in 0.1 *M* $HClO_4$ (except for R = CF_3) at 440–510 nm. Per cent of reaction is deduced from spectral changes at 485 nm. Light intensity is slightly different in each run.

The visible absorption spectrum of the photoproducts was deduced, within 10% approximation, by relating the spectral differences occurring during irradiation to the corresponding amounts of free ammonia. The assumption was made that the product, in all cases, consists principally of $Cr(NH_3)_4(H_2O)(OCOR)^{2+}$. This assumption is supported by the coincidence of the isosbestic points (for R = $CHCl_2$ and CH_2Cl) during the photoreaction and the thermal reaction, which is not likely simultaneously to produce two species in a constant ratio. The spectral data of the photoproducts are reported in Table IV, except those for R = CF_3 and CH_3, which may be in error by much more than 10%. In the former case fairly rapid secondary reactions take place in the absence of $HClO_4$, whereas in the latter, the simultaneous dark processes are important. These data were employed in the calculation of the rates of thermal ammonia aquation for R = $CHCl_2$, for R = CH_2Cl, and, with a larger approximation, for R = CH_3 as described in the previous section. By the use of the same data, the photoreactions, except for R = CH_3, appeared to be of zero order up to 30–40% completion. Figure 5 shows that the amounts of photoaquation *vs.* time are linear, although the inner filter effect is expected steadily to diminish the primary photolysis rate earlier than observed. Thus the products should themselves be photosensitive, probably undergoing further ammonia aquation, and the linearity could well be coincidental within error limits.

Discussion

The principal finding relative to the aqueous thermal chemistry of the four chromium(III) ions studied is a striking qualitative difference between the trichloroacetato complex and the three other homologs. While the former undergoes the acid hydrolysis

$$Cr(NH_3)_5(OCOCCl_3)^{2+} + H_2O \longrightarrow Cr(NH_3)_5(H_2O)^{3+} + CCl_3COO^- \quad (2)$$

in the case of R = $CHCl_2$, CH_2Cl, and CH_3 the results seem clearly to indicate that the aquation reaction is

$$Cr(NH_3)_5(OCOR)^{2+} + H_2O \longrightarrow Cr(NH_3)_4(H_2O)(OCOR)^{2+} + NH_3 \quad (3)$$

Thus (trichloroacetato)pentaamminechromium(III) conforms to the general behavior of the other acidopentaamminechromium(III) ions, whose preferred aquation mode is the replacement of the acido group. In Table V the rate constants for its uncatalyzed (k_{H_2O}) and acid-catalyzed (k_{H^+}) aquation and the activation parameters are compared with the corresponding data for other substituted acetatopentaammine complex ions. Extrapolation to 70° was necessary because of the unavailability of activation energies in ref 10; also, the rate constants of this reference are those for $[H^+]$ = 0.004–0.008 *M* where no acid catalysis was observed. Therefore they are assumed to be sufficiently close to k_{H_2O}. The rates for the chromium(III) complexes are higher by an order of magnitude than for the corresponding cobalt(III) ions and the activation enthalpies are smaller, as usually found in the comparison of d^3 with d^6 systems. The reaction for R = CCl_3 is slightly slower than for R = CF_3; *i.e.*, the rate decreases with increasing base strength of the leaving ligand anion as in the cobalt(III) series. Both this trend and the negative entropy of activation are consistent with reaction 2. In the range of H^+ concentration examined, an acid catalysis effect is present. For example, at 40° the acid-dependent term contributes by *ca.* 30% to the observed first-order rate at $[H^+]$ = 0.1 *M*. For R = CF_3 no such effect

TABLE V

RATE CONSTANTS AT 70°[a] AND ACTIVATION PARAMETERS FOR AQUATION OF SOME $M(NH_3)_5(OCOR)^{2+}$ COMPLEXES

R	Ligand aquated	k_{H_2O}, sec^{-1}	$\Delta H^{\ddagger}_{H_2O}$, kcal/mol	$\Delta S^{\ddagger}_{H_2O}$, eu	k_{H^+}, $M^{-1}\ sec^{-1}$	$\Delta H^{\ddagger}_{H^+}$, kcal/mol	Ref
				M = Cr			
CF_3	$RCOO^-$	8.4×10^{-4}	20.2	−25			13
CCl_3	$RCOO^-$	4.9×10^{-4}	21.5 ± 0.9	−11.3 ± 2.8	2×10^{-3}	21.6 ± 4.1	This work
$CHCl_2$	NH_3	1.7×10^{-3}	24.7 ± 0.6	0.9 ± 2.0			This work
CH_2Cl	NH_3	5.9×10^{-3}	25.3 ± 0.5	4.8 ± 1.7			This work
CH_3	NH_3	2×10^{-2}	19 ± 1				This work
				M = Co			
CF_3	$RCOO^-$	5.7×10^{-5}	26	−2	3×10^{-5}		11
CCl_3	$RCOO^-$	$5.3 \times 10^{-5\,b}$					10
$CHCl_2$	$RCOO^-$	$1.6 \times 10^{-5\,b}$					10
CH_2Cl	$RCOO^-$	$5.8 \times 10^{-6\,b}$					10
CH_3	$RCOO^-$	8.0×10^{-6}	25	−8	9.3×10^{-4}	25	11

[a] Calculated using the average values of activation parameters. [b] In 0.004–0.008 M $HClO_4$.

was noticed over the same interval of acidity[13] and it was barely detectable in the corresponding cobalt(III), rhodium(III), and iridium(III) complexes.[11] These results are in agreement with the higher basicity of CCl_3COO^- with respect to CF_3COO^- and with the occurrence of acid-catalyzed aquation pathways when the departing ligand either hydrogen bonds or is strongly basic. Thus, among the other $Cr(NH_3)_5X^{2+}$ ions this effect was observed for X = F[5] and was found to predominate completely over the uncatalyzed aquation for X = ONO.[8] Also $Cr(H_2O)_5X^{2+}$ systems undergo this kind of catalysis when X = F,[23] CN,[24] N_3,[25] SO_4,[26] H_2PO_4,[27] CH_3COO.[28]

It might be interesting to know whether in the case of chromium(III) systems the acetate aquation paths involve metal-to-oxygen or carbon-to-oxygen bond fissions. The conclusions drawn for the cobalt(III) analogs[11,12,29] do not necessarily apply to Cr(III). On the other hand, oxygen-18 experiments are likely to be inconclusive in this respect, in view of the relatively rapid exchange of ^{18}O with the aquation products under the same experimental conditions. Oxygen-18 has in fact been reported to exchange with both $Cr(NH_3)_5(H_2O)^{3+}$ (with $k = 6.3 \times 10^{-5}$ sec^{-1} at 25° and $\mu = 0.1$, comparable with the rate constants for carboxylate aquation)[30] and free CF_3COOH and CCl_3COOH.[29]

The three acetato complexes with R = $CHCl_2$, CH_2Cl, and CH_3 behave in an apparently unusual manner: contrary to the predictions by analogy with the cobalt(III) series, a qualitative change in the reaction mode takes place on passing from R = CCl_3 to R = $CHCl_2$. The acido group is no longer replaced by water, but rather the predominant, if not the sole, primary step is one of ammonia aquation. The discontinuity is evident from an inspection of the apparent first-order rate constants which are reported in Table V, with the activation enthalpies and entropies. Had the acetato group been released first, the aquation rate would have decreased with increasing basic strength of the carboxylato ligand as is true for cobalt(III). This is just the *reverse* of what was actually observed. Also significant in this respect might be the absence of any acid catalysis in these chromium(III) systems. There is little doubt that for R = CCl_3 it occurs between 0.01 and 0.1 M H^+. Thus for a type (2) reaction path, catalysis should become more and more important as the number of chlorine atoms decreases. Furthermore the activation parameters are definitely different in this second group, at least for R = $CHCl_2$ and CH_2Cl. Although only semiquantitative results could be obtained for R = CH_3, the three compounds appear to establish a definite trend.

The reaction products could be characterized only on the basis of their absorption features. *cis-* or *trans*-diaquotetraammine species could be ruled out as already explained. A rough but pessimistic estimate, based on spectral evidence, suggests a cis configuration for at least two-thirds of $Cr(NH_3)_4(H_2O)(OCOR)^{2+}$. As an example the case of R = CH_2Cl, Figure 4, shows that the aquation product has a spectrum similar in shape to that of *cis*-$Cr(NH_3)_4(H_2O)_2^{3+}$. The wavelengths of the maxima almost coincide, there is no indication of splitting of the L_1 band as in the *trans*-diaquo isomer and the extinction coefficients are higher than those of *cis*-diaquotetraamminechromium(III) in agreement with a certainly lower symmetry for an aquoacetatotetraammine than for a diaquotetraammine ion.

A reasonable explanation for the unexpected behavior may be found in the following additional observations. (i) A linear free energy relationship exists between the rate constants for ammonia aquation and the basic strength of the coordinated carboxylate, as illustrated

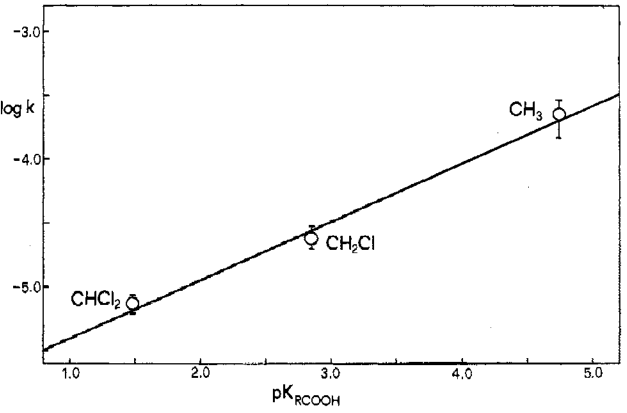

Figure 6.—Rates for ammonia aquation of $Cr(NH_3)_5(OCOR)^{2+}$ in 0.1 M $HClO_4$ at 25° *vs.* base strengths of $RCOO^-$.

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(26) J. E. Finholt and S. M. Deming, *ibid.*, **6**, 1533 (1967).
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in Figure 6. (ii) The carbonyl stretching frequency of the coordinated acetato group decreases as the basicity of the ligand increases, whereas in the corresponding methyl esters the same frequency is virtually unaffected when R changes (see Table VI).

TABLE VI

C–O STRETCHING FREQUENCIES (CM^{-1})

		ν	
R	RCOOH dissocn const	RCOOCH$_3$	Cr(NH$_3$)$_5$-(OCOR)$^{2+}$
CF$_3$	5×10^{-1}	1768	1715
CCl$_3$	2×10^{-1}	1768	1695
CHCl$_2$	3.3×10^{-2}	1768	1665
CH$_2$Cl	1.4×10^{-3}	1765	1665
CH$_3$	1.8×10^{-5}	1765[a]	1635

[a] Ethyl ester.

Although the ir measurements were carried out using solids, the variations of the C–O bond length should occur in solution, as well, since the differences appear to be greater than possible structural changes incurred on going from solution to the solid state. We conclude that the increase of the NH$_3$ aquation rate is directly related to a progressive lengthening of the C–O bond in the chromium(III) complex. Figure 7 shows the possibility of an intramolecular hydrogen-bond type interaction between the carbonyl oxygen and a H atom belonging to an ammonia cis to it. The extent to which this interaction is effective depends on the amount of negative charge localized on the oxygen atom; *i.e.*, it is inversely proportional to the electron-withdrawing ability of the R group. The implication is that the release of ammonia is "assisted" by hydrogen-bond formation with the acetate in cis position which in turn would weaken the chromium–nitrogen bond. The opening of the octahedral configuration in the transition state would be facilitated to make more room for an entering solvent molecule. This explanation is tentative but consistent with the trend of the apparent rate constants, with the cis configuration of the aquation product and with the lack of any acid effect, since the carbonyl oxygen is already "engaged" with another hydrogen atom. In addition, the absence of H$^+$ effects supports the conclusion that a primary step of RCOO$^-$ substitution is improbable. The acid hydrolysis of the corresponding Co(III) complexes is in fact very sensitive to protonation over the same pH range.[11] The successive aquation of further NH$_3$ molecules, observed especially for R = CH$_3$, might be accounted for by the establishment of other hydrogen bonds after the departure of the first ligand because of the high base strength of CH$_3$COO$^-$.

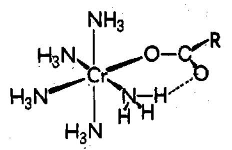

Figure 7.—Possibility of intramolecular hydrogen-bonding interaction in Cr(NH$_3$)$_5$(OCOR)$^{2+}$ ions.

In summary, the preferred reaction mode may be the result of two opposite trends: the labilization of the carboxylato group and that of an ammonia cis to it. The increasing basicity of the acetate progressively strengthens the Cr–O bond while it weakens the adjacent Cr–N one through the effect illustrated. It is possible that, especially for R = CHCl$_2$, both modes are simultaneously taking place, the first with a much slower rate, not detectable with the methods employed.

It may be noticed that the free energy plot, if extended to include a point for the (trichloroacetato)-pentaamminechromium(III) ion, predicts that ammonia aquation occur with $k \approx 0.3 \times 10^{-5}$ sec^{-1}, *i.e.*, at an experimentally observable rate (of the same order of magnitude as for the CCl$_3$COO$^-$ release). However spectral changes and direct ammonia determination show that this is not, in fact, the case; thus the R = CCl$_3$ complex does not fit the plot. The drastic change in reaction modes may be explained by invoking steric effects which prevent the necessary hydrogen-bond interaction. A framework molecular model indicates that there could be hindrance caused by the three relatively bulky Cl atoms which limit complete mobility of the carboxylato ligand. As more H atoms replace the halogens, the hydrogen-bonding interaction is facilitated. The same steric interference could favor the expulsion of the acido group.

It is significant that the "decomposition" of Cr(NH$_3$)$_5$X^{2+} ions, consisting of a stepwise loss of coordinated ammonia, has been observed with X = F[31] and ONO,[8] *i.e.*, with acidic ligands capable of hydrogen bonding.

The mechanism postulated might be very similar to the SN2 FS (front side displacement) mechanism proposed by Adamson[32] involving cooperative intermolecular hydroged-bonding interaction between the solvent and the departing ligand.

A survey of the photochemical behavior of the five carboxylatopentaamminechromium(III) ions provides a positive answer to the question whether or not they conform to the predictions of the chromium(III) photolysis rules.[19] In all cases, light excitation to a d–d state leads mainly to ammonia aquation; *i.e.*, the predominant photoreaction is of type (3). The ligands released are of the same kind as those lying on the axis having the weakest average crystal field, and preferential aquation occurs for the ligand of greater field strength. Although only an upper limit could be established for the quantum yield of RCOO$^-$ photoaquation, certainly the ratio $\phi_{\mathrm{NH_3}}/\phi_{\mathrm{RCOO^-}}$ is higher than 1 but could be higher even by an order of magnitude as was found for other Cr(NH$_3$)$_5$X^{2+} systems with X = NCS,[15] Cl,[17] and Br,[18] where $\phi_{\mathrm{NH_3}}/\phi_{\mathrm{X^-}}$ = 22, 70, and 35, respectively.

For R = CF$_3$ and CCl$_3$ as for the other acidopentaammines of chromium(III) studied thus far, the preferred thermal and photochemical reaction modes are qualitatively different, while in the case of the other three compounds they appear to be identical. However in this latter group the coincidence might be only formal, *i.e.*, limited to the overall stoichiometry. The results of Table III show that, at least for the release of ammonia, no relation seems to exist between the quantum yields and the electron-withdrawing ability of R. The thermal aquation rate constants follow instead a definite trend, indicating that the labilization of NH$_3$ proceeds through different paths in the two

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cases. These observations could be taken as additional evidence that the chemistry of excited states is definitely different from that of the ground state.[14]

Although cobalt(III) photochemistry is in general rather different from that of chromium(III),[14] in a recent paper ligand-field excitation of the analogous $Co(NH_3)_5(OCOCH_3)^{2+}$ ion is reported to cause mainly NH_3 aquation (with $\phi = 0.01$).[33] It is suggested that for d–d states of cobalt(III) acidoammines NH_3 release may be a much more common process than previously thought.[14]

The present results are pertinent to the dispute as to whether or not Adamson's rules imply stereochemical consequences in the configuration of photolysis products.[14,15,34–36] The main products of acidopentaammine photoaquation, *i.e.*, $Cr(NH_3)_4(H_2O)X^{2+}$, were reported to be the trans isomer when X = NCS[15,37] and the cis isomer when X = Cl[16,35] and Br.[18] Our results for X = RCOO suggest that *cis*-$Cr(NH_3)_4(H_2O)(OCOR)^{2+}$ is the species preferentially formed. It has been pointed out[36] that stereomobility in chromium(III) photolysis may be the rule, rather than the exception, in contrast to the retention of configuration observed for thermal aquation. The behavior of *trans*-$Cr(en)_2Cl_2^+$ provides the first clear-cut demonstration of such a stereochemical change: the photoreaction is one of chloride aquation (the weak-field axis is the one labilized), yet most of the photoproduct is the cis isomer.[38] A dramatic example that stereomobility may be necessary for photosubstitution to occur is offered by the photoinertness of *trans*-$Cr(cyclam)Cl_2^+$ in which stereorigidity of the octahedral framework is imposed by the cyclam ring.[39,40] In the present case, while the mode of photoreaction is correctly predicted by the rules, no information can be gained knowing only the isomer produced, the final configuration of which could depend on how collapse takes place in the structure of the thermally equilibrated (quartet) excited state produced after light absorption.[39] The stereospecificity or otherwise cannot be decided, unless the particular NH_3 ligand photoreleased can be determined. It follows that the acidopentaammine complexes are not adapted for testing any stereochemical aspects of photolysis.

Investigations in our laboratory on several more suitable systems, such as *trans*-$Cr(NH_3)_4XY$,[41] do confirm that stereomobility is always involved. The ligands preferentially aquated are, in all cases, again those predicted by the empirical rules, while the photoproducts are exclusively in the cis configuration.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
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Carboxamido Complexes of (Arene)tricarbonylmanganese(1+). A Correlation with Infrared Data[1]

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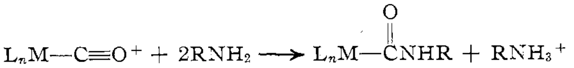
The (π-arene)$Mn(CO)_3^+$ complexes react with primary alkylamines, (arene)$Mn(CO)_3^+ + 2RNH_2 \rightleftarrows$ (arene)$Mn(CO)_2CONHR + RNH_3^+$, to give carboxamido complexes, where the arene is toluene, *p*-xylene, mesitylene, durene, or $C_6(CH_3)_6$. In a few cases, the carboxamido complex may be isolated, but generally the reversibility of the reaction allows the isolation of only starting (arene)$Mn(CO)_3^+$ when the solutions are evaporated to dryness. Qualitative equilibrium studies indicate the reaction proceeds further to the right when the electron density at the carbonyl carbon atom is reduced by decreasing the number of CH_3 groups in the arene. Since the electron density at a carbonyl carbon is reflected by its C–O stretching force constant, these constants have been correlated with the tendency of carbonyl groups to react with amines to form carboxamido complexes. This correlation extends to complexes of Fe, Ru, Mn, Re, Pd, Pt, Mo, and W. The (arene)$Mn(CO)_3^+$ complexes also react with hydrazine to yield (arene)$Mn(CO)_2(NCO)$ derivatives.

Introduction

Recently we have reported the reactions of a variety of cationic metal carbonyl complexes with primary and secondary alkylamines to form carboxamido complexes.



$$L_nM{-}C{\equiv}O^+ + 2RNH_2 \longrightarrow L_nM{-}\overset{O}{\overset{\|}{C}}NHR + RNH_3^+ \quad (1)$$

This route has been used to prepare carboxamido complexes of Fe,[3] Ru,[4] Mn,[5] Re,[6] Pd,[7] Pt,[7] Mo,[8] and W.[8]

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3187.

[2] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

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