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

Substitution Reactions of Metallic Complexes of β,β′,β″-Triaminotriethylamine. 11. Kinetics of the Stepwise Hydrolysis and Ligand Field Photolysis of the Difluoro(β,β′,β″-triaminotriethylamine)chromium(III) Cation[1]

MICHAEL J. SALIBY, PETER S. SHERIDAN,* and STANLEY K. MADAN*

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The kinetics of the hydrolysis of $[Cr(tren)F_2]^+$ (tren = β,β′,β″-triaminotriethylamine) have been investigated in both acidic and basic solutions. The aquation proceeds in two steps, the first occurring via an acid-catalyzed pathway involving an equilibrium between the $[Cr(tren)F_2]^+$ and $[Cr(tren)FFH]^{2+}$ ions. The rate of the reaction is described by the rate law $-d[complex]/dt = k_H K_{EQ}[H^+][complex]$, where k_H is the first-order rate constant for the aquation of the protonated complex and K_{EQ} is the equilibrium constant for the protonation reaction. In the second step, a water ligand enters with concurrent Cr–N bond rupture. In basic solution, $[Cr(tren)F_2]^+$ undergoes base-catalyzed release of fluoride. Rate constants and activation parameters were evaluated for all three reactions at 25 °C: $k_H K_{EQ}$ at ionic strength 0.5 M is 2.40×10^{-2} M^{-1} s^{-1}, $\Delta H^* = 14.5 \pm 0.5$ kcal mol^{-1}, and $\Delta S^* = -15.2 \pm 1.4$ cal deg^{-1} mol^{-1} for the aquation of $[Cr(tren)F_2]^+$; k_2 in 0.114 M HClO$_4$ is $(6.79 \pm 0.30) \times 10^{-4}$ s^{-1}, $\Delta H^* = 18.90 \pm 0.50$ kcal mol^{-1}, and $\Delta S^* = -9.7 \pm 1.9$ cal deg^{-1} mol^{-1} for the aquation of $[Cr(tren)F(H_2O)]^{2+}$; k_{OH} is 158.4 M^{-1} s^{-1}, $\Delta H^* = 22.75 \pm 1.60$ kcal mol^{-1}, and $\Delta S^* = 27.8 ● 3.0$ cal deg^{-1} mol^{-1} for the base hydrolysis of $[Cr(tren)F_2]^+$. The ligand field photolysis of $[Cr(tren)F_2]^+$ has been studied in acidic solution. Fluoride release occurs with a quantum yield (ϕ) of 0.21. Comparisons are made with amine complexes of chromium(III), cobalt(III), and rhodium(III).

Introduction

Amine complexes of Cr(III) which contain acido ligands often undergo Cr–N bond ruptures which interfere with the aquation of the acido ligands. Most of these studies have been done with complexes of linear polyamines such as dien,[2] trenen,[3] and trien.[4] For some time now, the kinetics of complexes containing the tripodal amine β,β′,β″-triaminotriethylamine (tren) have been studied in this laboratory. Much of this work has been done on Co(III) complexes,[5-8] but, until very recently,[9] very little has been done with the analogous Cr(III) species. More specifically, the kinetics of complexes containing coordinated fluoride have been studied extensively. In most cases, acid-catalyzed aquation of fluoride is observed.[5,10,11] However, in at least one case,[12] the rate of release of fluoride is acid independent at low pH. Furthermore, in *trans*-[Cr(en)$_2$F$_2$]$^+$,[13] the primary aquation pathway involves the breaking of a Cr–N bond. Thus, it was thought that [Cr(tren)F$_2$]$^+$ with its strained configuration would be an ideal system in which to study the competition between Cr–F aquation and Cr–N aquation, as well as to add to the knowledge of the reactions of Cr(III)–tren systems.

In addition, in light of the recent controversy[14] concerning Cr(III)–amine complexes containing fluoride ligands and since very few photochemical studies of complexes of the type *cis*-[CrN$_4$X$_2$]$^+$ have been done, it was thought that the ligand

field photolysis of this complex would contribute to the general knowledge of the photochemistry of Cr(III) complexes.

Experimental Section

Preparation of Compounds. All inorganic salts, acids, etc. were reagent grade. The complex [Cr(tren)F$_2$]ClO$_4$ was prepared according to the literature method.[15] Anal. Calcd for [Cr(tren)F$_2$]ClO$_4$: Cr, 15.6; ClO$_4^-$, 29.7; C, 21.46; H, 5.37; N, 16.69. Found: Cr, 15.8; ClO$_4^-$, 29.7; C, 21.67; H, 5.44; N, 16.60. The aquo complex [Cr(tren)F(H$_2$O)](ClO$_4$)$_2$ was synthesized according to the method of Zipp and Madan.[9] Anal. Calcd for [Cr(tren)F(H$_2$O)](ClO$_4$)$_2$: Cr, 11.98; ClO$_4^-$, 45.85. Found: Cr, 11.89; ClO$_4^-$, 46.03. [Cr(trenH)F(H$_2$O)$_2$]$^{3+}$ was generated in solution by allowing [Cr(tren)F(H$_2$O)](ClO$_4$)$_2$ to aquate in 0.1 M HClO$_4$ until the visible spectra were constant (about 2 h at 25 °C). λ_{max} (ϵ, M^{-1} cm^{-1}): 538 (51.9), 397 nm (27.4).

Analytical Methods. Chromium was determined spectrophotometrically as chromate at 372 nm after oxidation of the Cr(III) with alkaline peroxide. C, H, and N analyses were performed by Strauss, Oxford, England.

Ion-exchange procedures were carried out with Bio-Rad AG-50-W-X-8 (100–200 mesh) (H$^+$ or Na$^+$ form) cation-exchange resin which had been purified by the method of Kemp and King.[16] Jacketed columns (10 cm × 2 cm) were used, and ice water was circulated through the jacket for procedures done at low temperatures.

Elution characteristics of aquation products were determined by charging the column with the appropriately aged solution in 0.1 M HClO$_4$ at 0 °C and eluting with increasing concentrations of HClO$_4$. Recovery of Cr-containing species was always complete within experimental error.

Determination of released fluoride was carried out at 0 °C by charging the appropriately aged solution onto the column (Na$^+$ form), washing the column with H$_2$O until the washings gave a negative test for H$^+$, and titrating the washings with Th(NO$_3$)$_4$·4H$_2$O with sodium alizarin as an indicator.

Charge determinations on aquation products were done by the method of Lin and Garner.[2]

Electronic Absorption Spectra. Visible spectra were obtained on a Beckman Acta MIV recording spectrophotometer.

Kinetic Measurements. (A) Spectrophotometric Method. The basic kinetic techniques have been described previously.[7] Infinite time absorbances were obtained experimentally.

(B) Fluoride Ion Electrode Method. The aquation reaction was monitored in pH 3.0–11.5 by following the released fluoride ion concentration with a fluoride ion activity electrode (Orion Research, Inc.) used with a standard calomel reference electrode and a Beckman

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(2) Lin, D. K.; Garner, C. S. *J. Am. Chem. Soc.* **1969**, *91*, 6639.
(3) Ranney, S. J.; Garner, C. S. *Inorg. Chem.* **1971**, *10*, 2437.
(4) Kamp, D. A.; Wilder, R. L.; Tang, S. C.; Garner, C. S. *Inorg. Chem.* **1971**, *10*, 1396.
(5) Kuo, K.-W.; Madan, S. K. *Inorg. Chem.* **1971**, *10*, 229.
(6) Yuan, S.-T.; Miller, W. V.; Madan, S. K. *Inorg. Chim. Acta* **1973**, *7*, 134.
(7) Madan, S. K.; Reiff, W. M.; Bailar, J. C., Jr. *Inorg. Chem.* **1965**, *4*, 1366.
(8) Madan, S. K.; Peone, J., Jr. *Inorg. Chem.* **1967**, *6*, 463.
(9) Zipp, S. G.; Madan, S. K. *Inorg. Chem.* **1976**, *15*, 587.
(10) Basolo, F.; Matoush, W. R.; Pearson, R. G. *J. Am. Chem. Soc.* **1956**, *78*, 4883.
(11) Fehrmann, K. R. A.; Garner, C. S. *J. Am. Chem. Soc.* **1961**, *83*, 1276.
(12) Jones, T. P.; Phillips, J. K. *J. Chem. Soc. A* **1968**, 674.
(13) Pyke, S. C.; Linck, R. G. *Inorg. Chem.* **1971**, *10*, 2445.
(14) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1979**, *18*, 897 and references within.

(15) Glerup, J.; Josephsen, J.; Michelsen, K.; Pedersen, E.; Schaeffer, C. E. *Acta Chem. Scand.* **1970**, *24*, 247.
(16) Kemp, D. W.; King, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3433.
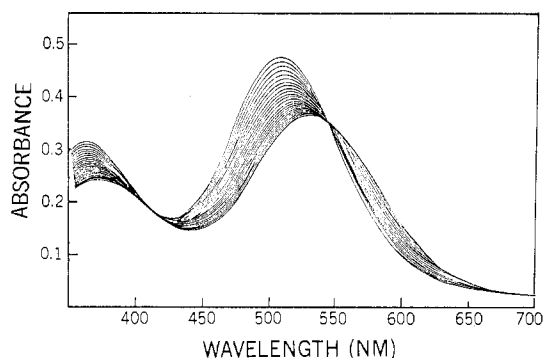
Figure 1. Spectral changes during the hydrolysis of [Cr(tren)F-$(H_2O)]^{2+}$ in 0.114 M $HClO_4$ at 25 °C.

Expandomatic SS-2 pH meter. Solutions of the appropriate buffer (pH 5–8) were allowed to come to the desired temperature, the complex was added and dissolved, and the released fluoride ion concentration was monitored with time. Alternatively, in solutions of acidic or basic pH, aliquots of the reaction solution were withdrawn at appropriate time intervals. These aliquots were quenched in ice, and ice-cold 0.1 M $HClO_4$ or 0.1 M NaOH was added until the pH of the resulting solution was 7.0. The fluoride ion concentration was then determined with the fluoride ion activity electrode.

Buffers were prepared by using mixtures of $HClO_4$, NaOH, various amines (pyridine, ammonia, 2-aminopyridine), and borax; solutions were adjusted to $\mu = 0.5$ with $NaClO_4$. Calculations of pseudo-first-order rate constants were performed as previously described.[5]

Photolysis. Irradiation at 520 nm was done with a 200-W Hg short-arc lamp (Illumination Industries, Inc.) with a hot mirror (Baird Atomic) to reflect infrared radiation and an interference filter (Baird Atomic) for wavelength selection. Solutions of approximately 7.0 × 10^{-3} M were photolyzed in 5- and 10-cm cells with continuous mixing by a magnetic stirrer. Aliquots of the photolyzed solutions were transferred to 1.0-cm cells for spectral analysis. Light intensities were measured with Reineckate actinometry and averaged about 2 × 10^{-8} einstein/s at 520 nm in a cell with a front window area of 2.9 cm^2.

Quantum Yields. Quantum yields for fluoride release were determined on the basis of spectral changes, as described elsewhere.[17] Released fluoride was determined by titration with $Th(NO_3)_4$·$4H_2O$.

Results

Aquation of Cr(tren)F_2^+ in Acidic Solution. When [Cr-(tren)F_2]ClO_4 is dissolved in 0.1 M $HClO_4$, the spectrum of the original red-violet solution gradually changes to that of [Cr(tren)F(H_2O)]$^{2+}$. Spectral scans of this reaction at 10 °C exhibited three isosbestic points, which held throughout the reaction and were in good agreement with those predicted from the spectra of the pure components: predicted, 493, 438, 364 nm; found, 491, 439, 365 nm.

When solutions of [Cr(tren)F_2]$^+$ in 0.1 M $HClO_4$ were allowed to aquate for 45 min (>10 half-lives at 25 °C) and charged onto a cation-exchange resin in the H^+ or Na^+ form, elution with increasing concentrations of $HClO_4$ showed that all Cr-containing species were present in a single pink band. This band could be eluted quantitatively with 2 M $HClO_4$ and was found to contain >97% of the Cr charged onto the column. No separation of this band was observed during the elution procedure. This behavior is similar to that exhibited by species of similar size and charge.[9,18]

When solutions of [Cr(tren)F_2]$^+$ underwent the first hydrolysis at 25 °C, charge per Cr atom determinations on this product gave values of 2.13 ± 0.08 (two determinations). Furthermore, titration of released fluoride ion with standardized $Th(NO_3)_4$·$4H_2O$ (see Experimental Section) gave an average of 1.01 ± 0.05 mol of F^- released/mol of complex. Runs done with NaF confirmed that F^- could be recovered

(17) Martins, E.; Sheridan, P. S. *Inorg. Chem.* **1978**, *17*, 2822.
(18) Esparza, M.; Garner, C. S. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2377.

Table I. Values of k_{obsd} for the First Aquation of [Cr(tren)F_2]$^+$ at Various Acid Concentrations and Ionic Strengths[a]

$\mu = 1.00$		$\mu = 3.00$	
[H^+], M	$10^3 k_{obsd}$, s^{-1}	[H^+], M	$10^3 k_{obsd}$, s^{-1}
0.103[b]	2.72 ± 0.07	0.114	3.31 ± 0.06
0.188	4.94 ± 0.06	0.245	7.05 ± 0.20
0.284	7.26 ± 0.09	0.400	11.6 ± 0.2
0.501	12.4 ± 0.7	0.501	14.3 ± 0.2
0.597	15.4 ± 0.4	0.746	21.3 ± 0.3
0.693	17.3 ± 0.6	0.978	28.9 ± 0.2
0.789	20.0 ± 0.3	1.55	45.5 ± 0.5
0.978	25.0 ± 0.4	2.07	60.0 ± 0.2
		2.61	76.5 ± 0.4

[a] Ionic strength adjusted with $NaClO_4$; $\lambda = 547$ nm; [complex] = 1.0 × 10^{-3} M. [b] [Complex] = 3.0 × 10^{-3} M; [H^+] = 0.103 M; $k_{obsd} = (2.68 ± 0.04) × 10^{-3} s^{-1}$.

Table II. Values of k_{obsd} for the First Aquation of [Cr(tren)F_2]$^+$ at Various Acid Concentrations and Temperatures[a]

[H^+], M	$10^3 k_{obsd}$, s^{-1}			
	20.0 °C	25.0 °C	30.0 °C	35.0 °C
0.125	2.00 ± 0.06	3.10 ± 0.03	4.84 ± 0.03	7.37 ± 0.16
0.198	3.13 ± 0.11	4.94 ± 0.10	7.61 ± 0.15	12.7 ± 0.3
0.299	4.87 ± 0.08	7.32 ± 0.05	10.8 ± 0.2	15.9 ± 0.4
0.395	6.44 ± 0.15	9.67 ± 0.25	14.2 ± 0.4	21.3 ± 0.6
0.500	8.27 ± 0.21	12.3 ± 0.5	18.2 ± 0.5	26.8 ± 0.8

[a] Ionic strength = 0.5 M (adjusted with $NaClO_4$); $\lambda = 547$ nm; [complex] = 1.0 × 10^{-3} M.

quantitatively from the ion-exchange column.

The rate of aquation of [Cr(tren)F_2]$^+$ was measured over a variety of complex concentrations, acid concentrations, ionic strengths, and temperatures. Pseudo-first-order rate constants were measured spectrophotometrically at 547 nm in order to avoid possible interference from the secondary aquation reaction, the scan of which has an isosbestic point at this wavelength (Figure 1). Rate plots were linear for more than 4 half-lives. The values of k_{obsd} over a range of acid concentrations and ionic strengths are presented in Table I. It can be seen that the reaction is acid catalyzed and that k_{obsd} increases with ionic strength. The reaction was monitored in 0.1 M p-toluenesulfonic acid in both H_2O and D_2O and was more rapid in D_2O ($k_{obsd} = 3.49$ (±0.07) × 10^{-3} s^{-1}) than in H_2O ($k_{obsd} = 2.59$ (±0.03) × 10^{-3} s^{-1}).

Table II gives values of k_{obsd} over a variety of temperatures and $HClO_4$ concentrations. Plots of k_{obsd} vs. [H^+] were linear. The slopes of these lines, corresponding to the second-order rate constants $k_H K_{EQ}$ (see below), were calculated at 20.0, 25.0, 30.0, and 35.0 °C and found to be 1.49 × 10^{-2}, 2.40 × 10^{-2}, 3.55 × 10^{-2}, and 5.33 × 10^{-2} M^{-1} s^{-1}, respectively. Excellent Arrhenius plots were obtained by using these values and yielded the following activation parameters: $\Delta H^* = 14.5 ± 0.5$ kcal mol^{-1}; $\Delta S^* = -15.2 ± 1.4$ cal mol^{-1} deg^{-1}.

Base Hydrolysis of [Cr(tren)F_2]$^+$. The rates of aquation of [Cr(tren)F_2]$^+$ in buffer solutions at various temperatures are listed in Table III. The kinetics in solutions of pH 4.0 and above were monitored by using a fluoride-sensitive electrode, since spectral changes in these solutions were small. In all cases, release of 1 mol of F^-/mol of complex was found to be complete (>98%). Furthermore, after these reactions were complete and the solutions acidified to pH 1 with $HClO_4$, the spectra were identical with that of [Cr(tren)F(H_2O)]$^{2+}$. In addition, ion-exchange experiments performed on these acidified solutions gave results consistent with the identification of the product as [Cr(tren)F(H_2O)]$^{2+}$. No separation of possible isomers was observed. These results are in agreement with the characterization of the product at higher pH's as [Cr(tren)F(OH)]$^+$.

Table III. Values of k_{obsd} for the Aquation of $[Cr(tren)F_2]^+$ in Buffers of Various pH at Various Temperatures[a]

pH	T, °C	$10^3 k_{obsd}$, s^{-1}
0.30	25.0	12.3 ± 0.5
0.40	25.0	9.67 ± 0.25
0.52	25.0	7.32 ± 0.05
0.70	25.0	4.94 ± 0.10
0.90	25.0	3.10 ± 0.03
2.0	25.0	1.93 ± 0.08
3.0	25.0	1.37 ± 0.05
4.0	25.0	1.10 ± 0.04
5.0	25.0	1.00 ± 0.05
6.0	25.0	1.08 ± 0.04
7.0	25.0	1.41 ± 0.06
8.0	25.0	2.07 ± 0.10
9.0	25.0	5.02 ± 0.13
9.84	25.0	11.2 ± 0.2
10.46	25.0	45.7 ± 0.5[b]
10.46	20.0	22.9 ± 0.6
10.46	15.0	11.6 ± 0.7
10.46	10.0	5.21 ± 0.07
10.46	5.0	2.52 ± 0.09[c]
11.00	5.0	8.65 ± 0.09[d]
11.50	5.0	26.9 ± 0.9[e]

[a] μ = 0.5 (adjusted with NaClO$_4$); [complex] = 1.0 × 10^{-3} M. [b] Second-order rate constant k_{OH} = 158.4 M^{-1} s^{-1}. [c] k_{OH} = 8.7 M^{-1} s^{-1}. [d] k_{OH} = 8.7 M^{-1} s^{-1}. [e] k_{OH} = 8.5 M^{-1} s^{-1}.
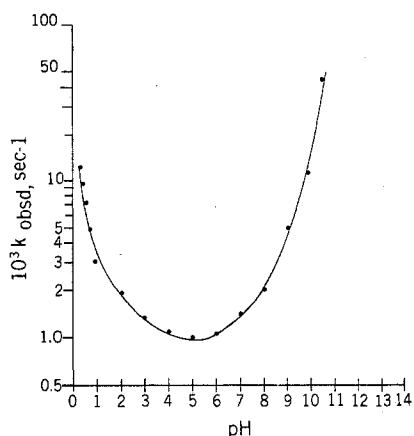
Figure 2. log k_{obsd} as a function of pH for the hydrolysis of $[Cr(tren)F_2]^+$.

Base hydrolysis data for $[Cr(tren)F_2]^+$ at 25 °C are plotted as log k_{obsd} vs. pH in Figure 2. The curve shown in Figure 2 is similar to those obtained by Basolo[10] and Garner[11] in the studies of *trans*-$[Co(en)_2F_2]^+$ and *cis*-$[Cr(en)_2F_2]^+$, respectively. First-order dependence of k_{obsd} on hydroxide ion concentration is observed at pH ≥9.84. In order to show this first-order dependence, second-order rate constants k_{OH} were determined at 5 °C at pH 10.46, 11.00, and 11.50. These constants were identical within experimental error. k_{OH} was determined over a range of temperatures at pH 10.46 and the activation parameters were calculated from the linear Arrhenius plots: ΔH^* = 22.76 ± 1.6 kcal mol^{-1}; ΔS^* = 27.8 ± 3.0 cal deg^{-1} mol^{-1}.

Aquation of $[Cr(tren)F(H_2O)]^{2+}$. Acidic solutions of $[Cr(tren)F(H_2O)](ClO_4)_2$ show spectral changes with a shift of the lowest energy d–d band to longer wavelengths. Spectrophotometric scans of the fluoro–aquo complex in 0.1 M HClO$_4$ at 25 °C demonstrate one isosbestic point (547 nm), which held throughout the reaction and agrees with that predicted from the spectra of pure $[Cr(tren)F(H_2O)]^{2+}$ and $[Cr(trenH)F(H_2O)_2]^{3+}$ (549 nm).

When aged (2 h), constant spectra solutions of $[Cr(trenH)F(H_2O)_2]^{3+}$ were charged onto an ion-exchange column in the H$^+$ form, one purple band was sorbed which was

Table IV. Values of k_2 for the Aquation of $[Cr(tren)F(H_2O)]^{2+}$ at Various Acid Concentrations, Ionic Strengths,[a] and and Temperatures

T, °C	[H$^+$], M	μ, M	$10^3 k_2$, s^{-1}
25.0	0.114	0.115	0.679 ± 0.030
25.0[b]	0.114	0.115	0.687 ± 0.027
30.0	0.114	0.115	1.10 ± 0.05
38.0	0.114	0.115	2.16 ± 0.02
38.0	0.114	1.00	1.53 ± 0.06
38.0	0.114	2.00	1.28 ± 0.02
38.0	0.973	2.00	1.27 ± 0.03
38.0	2.00	2.00	1.33 ± 0.04
38.0[c]	0.114	0.115	2.20 ± 0.06
38.0[d]	0.114	0.115	2.17 ± 0.04

[a] Adjusted with NaClO$_4$; λ = 500 nm; [complex] = 1.0 × 10^{-3} M. [b] $[Cr(tren)F(H_2O)]^{2+}$ prepared in situ from $[Cr(tren)F_2]^+$. [c] [Complex] = 3.0 × 10^{-3} M. [d] λ = 480 nm.

eluted with 3 M HClO$_4$. This band was found to contain >98% of the Cr that was charged onto the column. This behavior is consistent with that of other 3+ species of similar size.[9] Furthermore charge determinations on this product gave values of +3.08 ± 0.13 (two determinations).

When known amounts of aged $[Cr(trenH)F(H_2O)_2]^{3+}$ were charged onto an ion-exchange column and the washings analyzed for free fluoride, the results were the same, within experimental error, as those obtained with a blank.

Evidence for the presence of uncoordinated amine in this product comes from the fact that when solutions of $[Cr(trenH)F(H_2O)_2]^{3+}$ were adjusted to pH 7 with NaOH and then reacidified, the spectrum returned to that of $[Cr(tren)F(H_2O)]^{2+}$.

The kinetics of aquation of $[Cr(tren)F(H_2O)](ClO_4)_2$ were measured in HClO$_4$ under various conditions of complex concentration, acid concentration, ionic strength, and temperature. Measurements were made at 500 nm, where a large difference occurs between the absorbance of $[Cr(tren)F(H_2O)]^{2+}$ and $[Cr(trenH)F(H_2O)_2]^{3+}$. These data are compiled in Table IV. It is evident that there is no pH dependence over the region studied. This lack of acid dependence is expected for processes involving the breaking of a Cr–N bond.[19] It can also be seen that an increase in ionic strength from 0.1 to 2.0 M causes a 40% decrease in the value of k_2. This effect has been noticed in similar reactions.[9,19]

The following activation parameters were calculated from the linear Arrhenius plots: ΔH^* = 18.90 ± 0.50 kcal mol^{-1}, ΔS^* = -9.7 ± 1.9 cal mol^{-1} deg^{-1}.

Photolysis of $[Cr(tren)F_2]ClO_4$. Excitation of the lowest energy ligand field band ($^4B_{2g} \leftarrow {}^4B_{1g}$) of $[Cr(tren)F_2]^+$ in acidic aqueous solution leads to spectral changes reminiscent of the thermal aquation. Photolysis produces a blue shift in the d–d band maximum with isosbestic points at the same wavelengths (±3 nm) as observed during the thermal reaction. Prolonged photolysis leads to a spectrum indistinguishable from that of thermally produced $[Cr(tren)F(H_2O)]^{2+}$; additional photolysis causes no further spectral changes. Titration of the photoproduct solution with Th^{4+} shows that 1.0 mol (±0.10 mol) of fluoride is released per mole of complex initially present.

Photolyses were done at 2–5 °C in order to minimize thermal reactions, and identical solutions held in the dark underwent no detectable spectral change during the photolysis time. Quantum yields for this reaction are given in Table V.

To substantiate the supposition that the thermal and photochemical products were identical, we heated acidic solutions of photochemically produced $[Cr(tren)F(H_2O)]^{2+}$ to 35 °C. Spectral changes during the resulting reaction involved a red

(19) Garner, C. S.; House, D. S. *Transition Met. Chem.* **1970**, *6*, 221.

Table V. Absolute Quantum Yields upon Ligand Field
Photolysis of $[Cr(tren)F_2]^+$

pH	T, °C	ϕ_{F^-}
1.0	2.0	0.19
1.0	5.0	0.21
2.0	2.0	0.23
	av	0.21

shift of the d–d band maxima with an isosbestic point at 549 nm; identical spectral changes were observed upon the aquation of thermally prepared $[Cr(tren)F(H_2O)]^{2+}$. No fluoride ion was released during this reaction, and ion-exchange studies showed the final product has a 3+ charge, clearly implying that the final product is $[Cr(trenH)F(H_2O)_2]^{3+}$. As described earlier, these results mimic data from thermally prepared $[Cr(tren)F(H_2O)]^{2+}$ and support the supposition that the initial thermal and photochemical reactions of $[Cr(tren)F_2]^+$ are identical.

Discussion

Aquation of $Cr(tren)F_2^+$ in Acidic Solution. In acidic aqueous solution, $[Cr(tren)F_2]^+$ aquates (eq 1). Evidence for

$$[Cr(tren)F_2]^+ + H_3O^+ \rightarrow [Cr(tren)F(H_2O)]^{2+} + HF \quad (1)$$

this reaction includes the following: (1) three isosbestic points hold throughout the reaction and agree with the predicted values; (2) the movement of the d–d bands to higher energies, consistent with the replacement of fluoride by water; (3) the isolation of only one product by ion-exchange chromatography; (4) the occurrence of pseudo-first-order kinetics for at least 4 half-lives. These data suggest a mechanism involving an acid–base preequilibrium step (eq 2) followed by the rate-determining aquation of the HF ligand (eq 3), where K_{EQ} is

$$Cr(tren)F_2^+ + H^+ \underset{}{\overset{K_{EQ}, \text{ fast}}{\rightleftharpoons}} Cr(tren)FFH^{2+} \quad (2)$$

$$Cr(tren)FFH^{2+} + H_2O \xrightarrow[\text{slow}]{k_H} Cr(tren)F(H_2O)^{2+} + HF \quad (3)$$
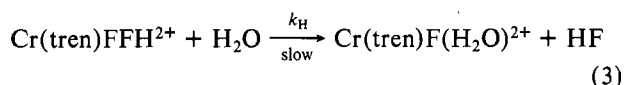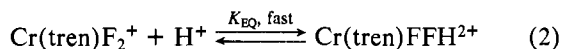
the equilibrium constant for the protonation reaction (2) and k_H is the first-order rate constant for reaction 3. Combination of (2) and (3) yields the rate law

$$-d[\text{complex}]/dt = k_{obsd}[\text{complex}] = k_H K_{EQ}[H^+][\text{complex}]$$

Thus, $k_{obsd} = k_H K_{EQ}[H^+]$, and a plot of k_{obsd} vs. $[H^+]$ will yield a straight line of slope $k_H K_{EQ}$ (see Results). The increased rate in D_2O is due to a larger concentration of the intermediate in this solvent,[20] as compared to water.

Unlike the analogous $[Co(tren)F_2]^+$,[5] the rate of the acid-independent aquation of $[Cr(tren)F_2]^+$ cannot be experimentally determined, as the base catalyzed hydrolysis becomes increasingly important above pH 5. Extrapolations of the linear portions of Figure 2 at low and high pH values intersect at a value in the neighborhood of 1.5×10^{-5} s^{-1} ($\pm 0.5 \times 10^{-5}$ s^{-1}). This hypothetical rate constant for the nonacid (and nonbase) catalyzed aquation of $[Cr(tren)F_2]^+$ is admittedly an approximation, but it does yield a ratio of aquation rates of about 10^3 for the dichloro to difluoro complexes. A similar value for the dichloro/difluoro aquation rate constant was also observed for the analogous $[Co(tren)X_2]^+$ ions (X = Cl$^-$, F$^-$).

Absolute isomeric assignment of $[Cr(tren)F(H_2O)]^{2+}$ is not possible without a single-crystal X-ray study, but a tentative assignment of the α isomer is possible on the basis of the electronic spectrum and considerations of the mechanism of the aquation of Cr(III) complexes. It was noted in the as-
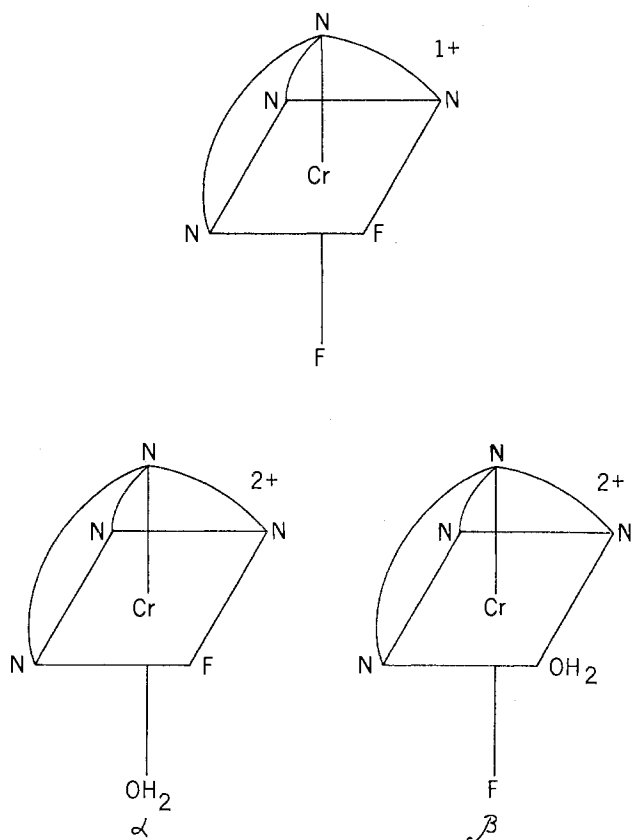
Figure 3. Geometrical isomers possible for $[Cr(tren)F(H_2O)]^{2+}$.

signment of α- and β-$[Rh(tren)Cl(H_2O)]^{2+}$[17] that the lowest energy d–d absorption band of the α isomer is less intense than that of the dichloro ion, while the spectrum of the β isomer is more intense. This difference is readily rationalized in terms of the distortions of the β isomer induced by the presence of a water molecule in a hydrophobic region of the molecule, while the α isomer, with a water in a hydrophilic pocket, would be less distorted (Figure 3). Aquation of $[Cr(tren)F_2]^+$ causes a dramatic decrease in the intensity of the d–d band ($\epsilon_{[Cr(tren)F_2]^+} = 116$; $\epsilon_{[Cr(tren)F(H_2O)]^{2+}} = 63.9$), consistent with the formation of α-$[Cr(tren)F(H_2O)]^{2+}$.

The current model[21] for Cr(III) aquations involves an associative interchange (I_A), so the fluoride in the hydrophilic pocket would be more susceptible to solvent interaction and would thus be more prone toward aquation. By analogy with the thermal aquation of $[Rh(tren)Cl_2]^+$,[17,22] these considerations suggest aquation of the fluoride trans to the tertiary amine, with the subsequent formation of α-$[Cr(tren)F-(H_2O)]^{2+}$. The rate of fluoride release from cis-$[Cr(tren)F_2]^+$ ion 0.1 M HClO$_4$ is over 500 times that of fluoride aquation of cis-$[Cr(en)_2F_2]^+$. Such accelerated aquations have been observed in other tren complexes and are often attributed to the strain induced by the tripodal tren.[7-9] Perhaps as important, however, is that the fluoride trans to the tertiary amine in $[Cr(tren)F_2]^+$ rests in a hydrophilic region of the ion's surface, so that associative interchange of that fluoride should be unusually rapid. This hydrophilic pocket is unique to tren complexes, thus accounting for the uniquely rapid aquation of one fluoride from $[Cr(tren)F_2]^+$.

Base Hydrolysis of $[Cr(tren)F_2]^+$. In basic solution, $[Cr(tren)F_2]^+$ reacts as follows:

$$[Cr(tren)F_2]^+ + OH^- \rightarrow [Cr(tren)F(OH)]^+ + F^-$$
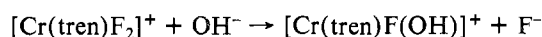
(20) (a) LaMer, V. K. *Chem. Rev.* **1936**, *19*, 363. (b) Wynne-Jones, W. F. K. *Chem. Rev.* **1935**, *17*, 115.

(21) Swaddle, T. *Coord. Chem. Rev.* **1974**, *14*, 273.
(22) Zipp, S. G.; Madan, S. K. *J. Inorg. Nucl. Chem.* **1975**, *37*, 181.

Evidence for this reaction comes from (1) release of 1 mol of fluoride/mol of complex, (2) ion-exchange behavior, and (3) linearity of pseudo-first-order rate plots.

At high pH's the release of fluoride from $[Cr(tren)F_2]^+$ is base catalyzed. The S_N1-cB mechanism is now generally accepted for the base hydrolysis reactions of Co(III)–amine complexes, but the base hydrolysis mechanism for Cr(III) complexes is not yet fully understood. Evidence has been cited for both dissociative[23,24] and associative[25] pathways. It has been postulated (vide infra) that the leaving group in the acid hydrolysis of $[Cr(tren)F_2]^+$ is the fluoride trans to the tertiary nitrogen. When solutions of thermally produced $[Cr(tren)F(H_2O)]^{2+}$ were adjusted to pH 13 with NaOH, the resulting spectra were identical with those obtained upon the base hydrolysis of $[Cr(tren)F_2]^+$. Furthermore, acidified solutions of $[Cr(tren)F(OH)]^+$, upon heating, show spectral changes indistinguishable from those observed during the aquation of $[Cr(tren)F(H_2O)].^{2+}$ These results imply either that the same fluoride is lost during the acid and base hydrolysis or that the α and β isomers of $[Cr(tren)F(H_2O)]^{2+}$ have identical spectra. While the two isomers of $[Cr(tren)F(H_2O)]^{2+}$ have not been characterized, they should have readily distinguishable spectra if analogy is drawn to the α and β isomers of $[Rh(tren)Cl(H_2O)]^{2+}.^{17}$ We conclude that the acid- and base-catalyzed hydrolyses both generate α-$[Cr(tren)F(H_2O)]^{2+}$. Our tentative assignment has the released fluoride coming from a hydrophilic region in a molecule, consistent with an associative interchange mechanism for the base-catalyzed reaction. Such a mechanism has been proposed for the base hydrolysis of other Cr(III) halo complexes.[25]

One interesting aspect of the application of an associative mechanism to the base hydrolysis of Cr(III)–tren complexes is that one would predict that release of the second halide would be very slow. It is located in a hydrophobic region, and interaction with solvent molecules would be inefficient. Although no attempts were made to study this reaction kinetically, qualitative experiments showed little further reaction over a period of 24 h at room temperature. Furthermore, preliminary studies of the base hydrolysis of $[Cr(tren)Cl_2]^+$ show that release of one Cl$^-$ at pH 11 and 25 °C is very fast (<1 min), while further reaction is much slower. These results are in agreement with an associative mechanism for the base hydrolysis reactions of Cr(III)–tren complexes.

Aquation of $[Cr(tren)F(H_2O)]^{2+}$ in Acidic Aqueous Solution. The aquofluoro ion, generated upon the acid-catalyzed aquation of $[Cr(tren)F_2]^+$, or the base hydrolysis followed by acidification, undergoes a slow second reaction (eq 4). The

$$[Cr(tren)F(H_2O)]^{2+} + H_3O^+ \xrightarrow{k_2} [Cr(trenH)F(H_2O)_2]^{3+}$$
(4)
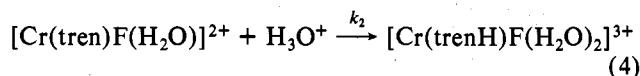
following results support the formation of $[Cr(trenH)F(H_2O)_2]^{3+}$: (1) shifting of the d–d bands to lower energies, consistent with the replacement of an amine group by water; (2) the presence of a single isosbestic point which holds throughout the reaction and agrees with the predicted value; (3) isolation of only one product during ion-exchange chromatography; (4) linearity of pseudo-first-order rate plots for over 4 half-lives; (5) detection of uncoordinated amine.

Comparison of the rate of Cr–N bond rupture observed in this system with that observed for $[Cr(tren)Cl(H_2O)]^{2+}$ shows that there is very little difference between the two systems. Although the data are limited, the results so far indicate that the rate of Cr–N bond rupture in these complexes is inde-

pendent of the nature of the remaining halide ion. Similar behavior has been observed in systems of the type trans-$[Cr(en)_2X_2]^+$ (X = F$^-$, Br$^-$, Cl$^-$, NCS$^-$).[13]

Rupture of the Cr–N bond in this system stops after production of $[Cr(trenH)F(H_2O)_2]^{3+}$. This is in contrast to Cr(III) complexes of linear polyamines, which undergo consecutive Cr–N bond ruptures until the amine is completely released,[2,3,26] but consistent with the analogous Cl$^-$ system. Thus, this is further evidence that consecutive Cr–N bond-breaking reactions may occur in a linear fashion, for in this case, the tertiary amine contains a coordinated primary amine on each side and would be less prone to aquation.

Four geometric isomers are possible for $[Cr(trenH)F(H_2O)_2]^{3+}$ as the tricoordinate tren could occupy a meridional edge (1,2,6 isomer), with the fluoride cis or trans to the tertiary amine or the tren could occupy three facial sites (1,2,3 isomer) with the fluoride cis or trans to the tertiary amine. Unequivocal isomer identification of the thermally produced $[Cr(trenH)F(H_2O)_2]^{3+}$ is not yet possible, but the relatively weak ligand field absorption bands of $[Cr(trenH)F(H_2O)_2]^{3+}$ suggest that the tren ligand is in the 1,2,3 configuration. Work with molecular models shows that the facial arrangement would be less sterically strained; comparison of the ϵ value of 52 cm M^{-1} for the d–d band in $[Cr(trenH)F(H_2O)_2]^{3+}$ is even lower than the 72 cm M^{-1} reported for the analogous $[Cr(trenH)Cl(H_2O)_2]^{3+}$, which was also identified as a facial (1,2,3) isomer.[9]

Under the conditions employed in this study, no separation of possible isomers was observed; this contrasts with the separations reported for some Co(III)–trenhaloaquo complexes. Furthermore, neither $[Cr(tren)F(H_2O)]^{2+}$ (prepared in situ from $[Cr(tren)F_2]^+$) nor $[Cr(tren)F(H_2O)](ClO_4)_2$ showed any deviation from first-order kinetics upon aquation. The existence of two isomers of $[Co(tren)Br(H_2O)]^{2+}$ [27] (and of $[Co(tren)Cl(H_2O)]^{2+}$ [28]) was indicated by the observation that the aquation of either ion occurred at a rate which was not pseudo first order but was the sum of two simultaneous first-order processes. No such deviation from first-order behavior is detectable upon aquation of $[Cr(tren)F(H_2O)]^{2+}$. In addition, aquation of $[Cr(tren)F(H_2O)]^{2+}$ causes a single sharp isosbestic point in the electronic spectrum, which would not be expected if more than one isomer of $[Cr(tren)F(H_2O)]^{2+}$ were aquating; such an isosbestic was not observed during the aquation of either of the Co(III)–tren complexes just discussed. We conclude, therefore, that the aquation of $[Cr(tren)F_2]^+$ is stereospecific, producing a $[Cr(tren)F(H_2O)]^{2+}$ ion of at least 98% isomeric purity.

Photolyses. Upon irradiation of the lowest energy ($^4B_{2g} \leftarrow {}^4B_{1g}$) d–d band, $[Cr(tren)F_2]^+$ undergoes fluoride aquation:

$$[Cr(tren)F_2]^+ + H_3O^+ \xrightarrow{h\nu} \alpha\text{-}[Cr(tren)F(H_2O)]^{2+} + HF$$
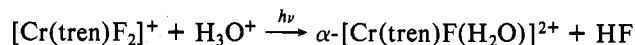
Support for this reaction includes (a) spectral changes identical with those observed upon thermal aquation, (b) a photoinert product with a spectrum previously identified as that of α-$[Cr(tren)F(H_2O)]^{2+}$, (c) release of 1.0 ($\pm$0.1) mol of fluoride/mol of complex, and (d) the similar thermal behavior of the thermally and photochemically produced $[Cr(tren)F(H_2O)]^{2+}$ ions. The photoproduced spectral changes at pH 1–2 are indistinguishable from those observed upon thermal aquation at the same pH, and the final photoproduct spectrum is identical with the spectra of the aquofluoro ions generated upon acid- or base-catalyzed hydrolysis, when the solutions are adjusted to the same pH. On the basis of these results, in addition to the isolation of only one product upon ion-ex-

(23) Parris, M.; Wallace, W. J. *Can. J. Chem.* **1969**, *47*, 2257.
(24) Nozari, M. S.; McLean, J. A., Jr. "Coordination Chemistry", Plenum: New York, 1969.
(25) Jones, T. P.; Phillips, J. K. *J. Chem. Soc. A* **1971**, 1881.

(26) Wilder, R. L.; Kamp, D.; Garner, C. S. *Inorg. Chem.* **1971**, *10*, 1393.
(27) Miller, M. V.; Madan, S. K. *Inorg. Chem.* **1970**, *9*, 2362.
(28) Miller, M. V.; Madan, S. K. *Inorg. Chem.* **1971**, *10*, 1250.

change chromatography of photolyzed solutions and the very sharp isosbestic point observed when photoproduct solutions are heated, we conclude that ligand field photolysis of [Cr-(tren)F$_2$]$^+$ generated the same aquofluoro isomer, tentatively assigned the α configuration, as is generated in the acid- or base-catalyzed thermal reaction.

An additive angular overlap model has been presented[29,30] to account for the ligand field photochemistry of chromium-(III) complexes; interpretation of the photochemistry of Cr(III) fluoride complexes has been of particular interest,[14] as questions have been raised concerning the importance of ground-state vs. excited-state bond energies. Use of this model requires that the unique amine–amine axis in [Cr(tren)F$_2$]$^+$ (Figure 3) be set as the z axis, with the two fluorides considered as equivalent ligands in the xy plane. In this configuration the photoreactive state is $^4B_{2g}$ ($xz, yz, x^2 - y^2$).

To use this model, one calculates the energy of each metal–ligand bond for the complex in the photoreactive excited state. Three interrelated criteria have been proposed to be important: (a) the strength of the bond in the excited state,[29] with the weakest bond predicted to be photolabilized, (b) the strength of the bonds in the ground state,[14] and (c) the change in bond strength upon formation of the excited state.[14] Pursuing the first, and presumably most important criterion, and assuming that the amines of tren have the same σ and π parameters as ammonia, one obtains

$$I^*(Cr-N)_{ax} = 2\sigma_{ax} = 14370 \text{ cm}^{-1}$$

$$I^*(Cr-N)_{eq} = (5/4)\sigma_{eq} = 8980 \text{ cm}^{-1}$$

$$I^*(Cr-F)_{eq} = (5/4)\sigma_{eq} + 3\pi_{eq} = 14640 \text{ cm}^{-1}$$

In the excited state, the bond energies of the equatorial amines are the weakest and hence should be labilized upon formation of the $^4B_{2g}$ state. Of these two ligands, one is a tertiary amine and would be constrained from leaving the primary coordination sphere, while the other is a primary amine and should experience no special constraints which could prevent photoinduced aquation. (Photolabilization of chelated primary amines are well-known.[31]) Photolyses were performed in pH 1–2 solutions, so that instantaneous amine protonation would have trapped any photolabilized amines, preventing rapid ring closure. There is no evidence for such amine labilization, however, so we conclude that the photoinduced aquation of a fluoride from [Cr(tren)F$_2$]$^+$ is not consistent with Vanquickenborne's model.

A second consideration[14] is the energy of metal–ligand bonds in the ground state. Because of ground-state isotropy (t_{2g}^3), the calculated bond strengths for the equatorial and axial amines are identical, and one obtains $I(Cr-N) = 14370 \text{ cm}^{-1}$ and $I(Cr-F) = 18760 \text{ cm}^{-1}$. Strong Cr–F bonds have been cited[14] to account for the photoinertness of the Cr–F moiety in *trans*-[Cr(en)$_2$F$_2$]$^+$ and cannot account for the Cr–F photolability in [Cr(tren)F$_2$]$^+$.

Consideration of the bond energy changes resulting from the $^4B_{2g} \leftarrow {}^4B_{1g}$ transition are also inadequate to account for the observed photochemistry. A useful comparison is between [Cr(tren)F$_2$]$^+$ and [Cr(NH$_3$)$_5$F]$^{2+}$ [32] and *trans*-[Cr(en)$_2$NH$_3$(F)]$^{2+}$,[33] as all three complexes have an amine–fluoride axis in the photoreactive regions. In all three cases,

the higher ligand field strength amine is calculated to be the more seriously affected by formation of the $^4B_{2g}$ state. The latter two complexes exhibit the predicted amine loss, while [Cr(tren)F$_2$]$^+$ does not fit the pattern and appears as an exception to the ligand field model.

A serious approximation is necessary to treat [Cr(tren)F$_2$]$^+$ with the angular overlap model, as no distinction is made between the tertiary and primary amines and both are treated as ammonia. This is a poor approximation, as only the primary amines of free tren are protonated, even in strongly acidic solution,[34] so it is more reasonable to assume that the primary amines would be the stronger bases toward Cr(III) (another hard acid). Given that the tertiary amine is the weaker base, a smaller σ_{tert} term would be anticipated and

$$I^*(Cr-N_{tert})_{eq} = (5/4)\sigma_{tert} < 8980 \text{ cm}^{-1}$$

Despite this change, there is no reason to assume that any of the other ligand bonds would be affected by the presence of a tertiary amine. Thus the angular overlap model would still predict loss of the tertiary amine as the primary photochemical step. It is therefore apparent that the available analyses of the angular overlap model does not deal with the problem presented by this compound: what is the anticipated photochemical process in a complex where a presumably photolabile ligand is sterically constrained from leaving the primary coordination sphere?

One approach would be to assume that the next weakest bond would be broken, and hence labilization of the other equatorial amine (an unconstrained primary amine) would be predicted. No evidence of such photoinduced amine loss was observed. A second interpretation would be that in the absence of an efficient reactive pathway, reactionless deactivation would dominate, and an unusually photoinert complex would result. However, the quantum yield for fluoride loss, ϕ_{F^-} = 0.21, is a typical value for the ligand field photolysis of a chromium(III)–haloamine complex. Such an efficiency does not support the idea of suppressed photochemical reactivity.

Thus, it appears that the existing angular model does not account for the observed photochemistry of the [Cr(tren)F$_2$]$^+$ ion. This ion presents an unusual problem, however, in that the ligand predicted to be photoreactive cannot undergo aquation due to the geometry of the tetradentate chelate.

It is interesting to note that the semiempirical photolysis rules[35] can be used for this asymmetric ion, for these rules invoke a photolabile axis, defined by the metal and two trans ligands, along which the excitation energy is concentrated. (The second photolysis rule indicates which of the ligands on that axis would be preferentially labilized.) No such photolabile axis is invoked in the angular overlap model, as each metal–ligand bond is considered individually. On assignment of the tertiary amine to be of lower ligand field strength than the primary amines (vide supra), the photoreactive axis is easily identified as the tertiary amine–fluoride axis. Since the tertiary amine is constrained from leaving and since the excitation energy should be regiospecific along this axis, labilization of the fluoride ion trans to the tertiary amine would be the predicted photoreaction. As discussed earlier, the available information indicates that it is the fluoride trans to the tertiary amine which is photolabilized.

In summary, [Cr(tren)F$_2$]$^+$ in aqueous solution is susceptible to fluoride loss via an acid-catalyzed aquation, a base-catalyzed hydrolysis, and a photoinduced aquation. All three reactions generate the same [Cr(tren)F(H$_2$O)]$^{2+}$ species, which has been assigned the α configuration on the basis of electronic spectra and mechanistic considerations. Aquation of this aquofluoro

(29) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977,** *99,* 2208.

(30) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978,** *100,* 475.

(31) See, for example: Pyke, S. G.; Linck, R. G. *J. Am. Chem. Soc.* **1971,** *93,* 5281. Manfrin, M. F.; Sandrini, D.; Juris, A.; Gandolfi, M. T. *Inorg. Chem.* **1978,** *17,* 90.

(32) Wright, R. E.; Adamson, A. W. *Inorg. Chem.* **1977,** *16,* 3360.

(33) Wong, C. F. C.; Kirk, A. D. *Inorg. Chem.* **1977,** *16,* 3148.

(34) Zipp, S. G.; Zipp, A. P.; Madan, S. K. *Coord. Chem. Rev.* **1974,** *14,* 29.

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

ion in acidic solution causes the labilization of one arm of the tren ligand, generating $[Cr(trenH)F(H_2O)_2]^{3+}$ with a tridentate tren ligand. The photochemical reaction of $[Cr(tren)F_2]^+$ does not fit the pattern predicted by the currently available theoretical models of ligand field photochemistry of

d^3 centers but is consistent with the semiempirical photolysis rules.

Registry No. $[Cr(tren)F_2]ClO_4$, 28650-58-0; $[Cr(tren)F-(H_2O)](ClO_4)_2$, 73068-68-5; $[Cr(trenH)F(H_2O)_2]^{3+}$, 73017-55-7; $[Cr(tren)F_2]^+$, 46140-83-4; $[Cr(tren)F(H_2O)]^{2+}$, 73068-67-4.

Contribution from the Department of Chemistry, The University of North Carolina,
Chapel Hill, North Carolina 27514

Ferromagnetism in Copper(II) Oxydiacetate Hemihydrate

PETER J. CORVAN, WILLIAM E. ESTES, ROBERT R. WELLER, and WILLIAM E. HATFIELD*

Magnetic susceptibility and isothermal magnetization studies on powdered samples of the layer compound copper(II) oxydiacetate hemihydrate have revealed that the substance undergoes a transition to a ferromagnetic state at 3.3 K. The copper(II) ions within a given layer are exchange coupled, and an exchange coupling constant $J = +4.66$ cm^{-1} resulted from a fit of a series expansion for a Heisenberg two-dimensional system to the magnetic susceptibility data. The out-of-plane anisotropy field was estimated to be 250 Oe, and the ratio of interplanar to intraplanar exchange was estimated to be 1.3 $\times$ 10^{-3}.

Introduction

Although ferromagnetic interactions leading to ferromagnetism are known in a limited number of ionic, insulating, layered solids[1] such as bis(benzylammonium) tetrachlorocuprate(II) and bis(methylammonium) tetrachlorochromate-(II),[2] there are very few chelated coordination compounds which are ferromagnets. These include $K_2Cu(CO_3)_2$,[3] Fe-$(detc)_2Cl_3$ (detc$^-$ = diethyldithiocarbamate),[4-6] and manganese(II) phthalocyanine.[7] The absence of ferromagnets in this wide range of compounds has stimulated much unpublished discussion and conjecture concerning the structural and electronic features which may be required for the realization of ferromagnetism in typical coordination compounds. As a starting point for subsequent discussions on this topic, we summarize here the guidelines which have been developed up to this time for the selection of good candidates for study. Structurally, the systems should be highly symmetrical so that superexchange pathways can be readily identified and controlled, and the bridging ligands should promote ferromagnetic interactions between neighboring paramagnetic ions. Toward this end, low-dimensional systems, especially layered structures, are good candidates, because the absence of tightly bonding networks between layers moderates the importance of superexchange interactions between the layers. Thus, if ferromagnetic interactions can be assured, then the problem is reduced to the determination of the factors which control the nature of the three-dimensional ordering. Furthermore, because of the more simple mathematical models, there exist a

larger body of theoretical results for low-dimensional systems than for complex structures,[1] and, as a result, properties of these substances may be more easily systematized and understood. The metal ions should have a low total spin to eliminate complications from single ion anisotropy, and of course, systems containing such ions are more reflective of a quantum solid than those with ions having large, approaching classical, spins. These guidelines point to chelate compounds of low total spin metal ions in which the ligands are multidentate and capable of forming a polymeric two-dimensional layer. Fortunately, Whitlow and Davey[8] have provided us with structural data for such an example. We describe here the results of our measurements on copper(II) oxydiacetate hemihydrate which show that the compound is ferromagnetic and suggest that additional substances with this magnetic classification may be identified.

Experimental Section

Samples of copper(II) oxydiacetate were prepared by the procedure given by Whitlow and Davey.[8] Excess oxydiacetic acid (diglycolic acid, obtained from Aldrich Chemical Co.) was added to basic copper carbonate (Fischer Scientific Co.), and the resultant royal blue compound was recrystallized from water to give rectangular platelets, which were twinned along the direction perpendicular to the plate. Analytical data for carbon and hydrogen obtained from Integral Microanalytical Laboratories, Inc., Raleigh, N.C., differed less than 0.3% from that calculated for $[Cu\{O(CH_2CO_2)_2\}]\cdot0.5H_2O$.

Magnetic Measurements. Magnetic susceptibility and magnetization data were collected by using either a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) or a superconducting quantum interference device susceptometer, SQUID (Model A-401 SQUID sensor, and Model A-201 magnetometer electronics console: Superconducting Technology, Inc. (SCT), Mountain View, CA). The vibrating sample magnetometer was operated from zero field to 10 kOe. The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lusch Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^{1}H and ^{3}Li) over the field range 0.35–10 kOe and found to be linear to within better than 1% over the entire range. The field set accuracy is within ±0.3% at 300 G and better than 0.15% at 10 000 G. Fields below 0.35 kOe

(1) de Jongh, L. J.; Miedema, A. R. *Adv. Phys.* **1974,** *23,* 1–260.
(2) Estes, W. E.; Losee, D. B.; Hatfield, W. E. *J. Chem. Phys.* **1980,** *72,* 630–8.
(3) Gregson, A. K.; Moxon, N. T., unpublished observations.
(4) Chapps, G. E.; McCann, S. W.; Wickman, H. H. *J. Chem. Phys.* **1974,** *60,* 990–7.
(5) DeFotis, G. C.; Palacio, F.; O'Connor, C. J.; Bhatia, S. N.; Carlin, R. L. *J. Am. Chem. Soc.* **1977,** *99,* 8314–5.
(6) Arai, N.; Sorai, M.; Suga, H.; Seki, S. *J. Phys. Chem. Solids* **1977,** *38.*
(7) (a) Barraclough, C. G.; Martin, R. L.; Mitra, S.; Sherwood, R. C. *J. Chem. Phys.* **1970,** *53,* 1638–42. (b) Barraclough, C. G.; Gregson, A. L.; Mitra, S. *J. Chem. Phys.* **1974,** *60,* 962–8. (c) Miyoshi, H.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973,** *46,* 2724–8. (d) Miyoshi, H. *J. Phys. Soc. Jpn.* **1974,** *37,* 50–6.

(8) Whitlow, S. H.; Davey, G. *J. Chem. Soc., Dalton Trans.* **1975,** 1228–32.