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Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. X. Synthesis and Characterization of Some Chromium(III) Complexes of β,β',β''-Triaminotriethylamine and the Kinetics of Primary and Secondary Aquation of the Dichloro(β,β',β''-triaminotriethylamine)chromium(III) Cation[1]

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New complexes of chromium(III) containing β,β',β''-triaminotriethylamine (tren) have been isolated and characterized, including one in which the tren ligand acts as a tridentate chelating agent. The aquation of one of these compounds, $[Cr(tren)Cl_2]Cl$, which occurs in two steps, has been investigated kinetically. The first step is a simple replacement of a chloride ligand by water while, in the second step, a water ligand enters with concurrent Cr–N bond rupture. Rate constants and activation parameters were evaluated for both reactions in 0.1 M $HClO_4$ at 25 °C and are $k_1 = (5.18 \pm 0.27) \times 10^{-2}$ s^{-1}, $\Delta H^{\ddagger} = 12.3 \pm 0.5$ kcal/mol, and $\Delta S^{\ddagger} = -23.0 \pm 1.3$ cal deg^{-1} mol^{-1} for the aquation of $Cr(tren)Cl_2^+$ and $k_2 = (7.15 \pm 0.02) \times 10^{-4}$ s^{-1}, $\Delta H^{\ddagger} = 19.1 \pm 0.4$ kcal/mol, and $\Delta S^{\ddagger} = -8.4 \pm 1.0$ cal deg^{-1} mol^{-1} for the aquation of $Cr(tren)Cl(H_2O)^{2+}$. Comparisons are made with tren complexes of cobalt(III) and rhodium(III).

There has been much recent interest in the syntheses and rates of reaction of chromium(III) complexes containing multidentate polyamine ligands. In particular, many complexes containing the linear polyamine triethylenetetramine (trien)[2] have been prepared,[3,4] and an extensive study of the multistep aquation of *cis*-α-$Cr(trien)Cl_2^+$ has been carried out.[5,6] Since these studies and previous ones of this type have concentrated on the behavior of linear polyamine complexes, it seemed of great interest to investigate the chromium(III) complexes of the nonlinear polyamine β,β',β''-triaminotriethylamine (tren), the tripodal isomer of trien.

Since octahedral tren complexes of cobalt(III) and rhodium(III) have been shown to have abnormally fast aquation rates, due to their unique stereochemistry,[7] we were convinced that the Cr^{III}–tren species would exhibit this unusual behavior. Also of interest was the possibility of ligand "unwrapping" or chromium–nitrogen bond breaking, which is known to occur in many aquations of linear chromium(III)–polyamine complexes[8,9] and might be expected to occur in the tren system. The effect of the tripodal geometry of tren on this process is unknown.

For these reasons it was thought to be instructive to synthesize a number of new Cr^{III}–tren complexes and study the primary and secondary aquation of one of these: $[Cr(tren)Cl_2]Cl$.

Experimental Section

Preparation of Compounds. All inorganic salts, acids, etc. used were reagent grade. Triaminotriethylamine was purchased from Ames Laboratory, Milford, Conn. Unless otherwise mentioned, all compounds were washed with absolute ethanol or acetone and ether and dried in vacuo.

Dichloro(triaminotriethylamine)chromium(III) Chloride, $[Cr(tren)Cl_2]Cl$. $[Cr(H_2O)_4Cl_2]Cl_2 \cdot H_2O$ (7.2 g, 0.027 mol) was added to DMSO (12 ml) and the mixture was boiled until the green color of the initially formed solution turned to rose red (indicative of loss of water). After removal from heat, a solution of tren (4.0 g, 0.027 mol) in DMSO (5 ml) was added slowly with stirring. *Caution*! Heat is given off and splattering may occur. When larger quantities of reactants were used, the chromium(III) solution was immersed in ice during the addition of the amine. The mixture was returned to the hot plate briefly until crystallization occurred. After cooling, the deep purple crystals were filtered and washed successively with DMSO, cold absolute ethanol, and ether and dried in vacuo; yield 3.24 g (70%).

Chloroperchlorato(triaminotriethylamine)chromium(III) Perchlorate Hydrate, $[Cr(tren)ClClO_4]ClO_4 \cdot H_2O$. Seventy percent $HClO_4$ (0.5 ml) was added dropwise, with stirring, to $[Cr(tren)Cl_2]Cl$ (0.5 g, 0.0016 mol). A gas (HCl) was evolved. After 2–3 days in the refrigerator, the rose pink slurry was filtered and washed; yield 0.35 g (48%). *Caution*! Although no difficulty was found here, perchlorates are a potential explosion hazard and should be treated accordingly.

Chlorobisulfato(triaminotriethylamine)chromium(III) Bisulfate Hydrate, $[Cr(tren)ClHSO_4]HSO_4 \cdot H_2O$. Concentrated H_2SO_4 (10–12 drops) was added, with stirring, to $[Cr(tren)Cl_2]Cl$ (1.0 g, 0.0032 mol). After the cessation of gas evolution (HCl), the rose pink slurry was filtered and washed; yield 0.73 g (50%).

Oxalato(triaminotriethylamine)chromium(III) Perchlorate Hydrate, $[Cr(tren)ox]ClO_4 \cdot H_2O$. The compound $[Cr(tren)Cl_2]Cl$ (1.0 g, 0.0032 mol) was dissolved in the minimum amount of water and added to 0.8 g (0.0053 mol) of $Na_2C_2O_4 \cdot H_2O$. After warming, the bright red solution was decanted from the undissolved $Na_2C_2O_4 \cdot H_2O$, and $NaClO_4$ (0.5 g) was added. The red crystals were cooled and washed; yield 0.75 g (60%).

Chlorothiocyanato(triaminotriethylamine)chromium(III) Chloride, $[Cr(tren)ClNCS]Cl$. The compound $[Cr(tren)Cl_2]Cl$ (1.0 g, 0.0032 mol) was dissolved in the minimum amount of water and NaSCN (0.28 g, 0.0034 mol) was added. After warming on a steam bath for 30 minutes, the red crystals were cooled and washed; yield 0.73 g (60%).

Chlorobromo(triaminotriethylamine)chromium(III) Bromide, $[Cr(tren)ClBr]Br$. The compound $[Cr(tren)Cl_2]Cl$ (0.3 g, 0.001 mol) was dissolved in the minimum amount of water and 0.5 g (0.005 mol) of NaBr added. The pink solution was cooled in ice, and absolute ethanol was added drop by drop until a faint cloudiness persisted. After refrigeration for 3–4 days, the lustrous purple crystals were filtered and washed; yield 0.2 g (51%). This compound could also be prepared with satisfactory elemental analysis by dissolving $[Cr(tren)Cl_2]Cl$ in cold 40% HBr and adding an equal volume of cold ethanol after the solution had been standing for 10 min.

Chloroselenocyanato(triaminotriethylamine)chromium(III) Selenocyanate, $[Cr(tren)ClSeCN]SeCN$. The compounds $[Cr(tren)Cl_2]Cl$ (1.0 g, 0.0032 mol) and KSeCN (1.0 g, 0.007 mol) were dissolved in 5 ml of water and warmed on a steam bath for 30 min. A reddish scum was filtered from the cherry red solution and further evaporation resulted in a red-brown powder, which was washed with ice water, methanol, and ether and dried in vacuo. Extraction with CS_2 verified the absence of elemental selenium; yield 0.6 g (41%).

Difluoro(triaminotriethylamine)chromium(III) Perchlorate, $[Cr(tren)F_2]ClO_4$. This compound was prepared by the literature method[10] except that the reaction mixture was poured into absolute ethanol to induce precipitation. Anal. Calcd: Cr, 15.6; ClO_4, 30.0. Found: Cr, 15.7; ClO_4, 30.2.

Fluoroaquo(triaminotriethylamine)chromium(III) Perchlorate, $[Cr(tren)FH_2O](ClO_4)_2$. This was prepared in a manner similar to that used for $[Cr(tren)ClClO_4]ClO_4 \cdot H_2O$, using $[Cr(tren)F_2]ClO_4$ (2.7 g, 0.0081 mol) as the starting material, however, and allowing the slurry to stand only 5 min before filtration; yield 2.5 g (72%).

Fluorothiocyanato(triaminotriethylamine)chromium(III) Perchlorate, $[Cr(tren)FNCS]ClO_4$. The compound $[Cr(tren)F_2]ClO_4$ (0.67 g, 0.002 mol) was warmed on a steam bath in the minimum amount of water and NaSCN (0.16 g, 0.002 mol) was added. The mixture was warmed for 30 min. After evaporation, the red crystals were washed with ice water, ethanol, and ether and dried in vacuo; yield 0.52 g (60%).

Diazido(triaminotriethylamine)chromium(III) Bromide, [Cr-

(tren)$(N_3)_2$]Br. The compound [Cr(tren)Cl_2]Cl (1.0 g, 0.0032 mol) was warmed for 30 min on a steam bath with excess NaN_3 (1.0 g, 0.013 mol). The salt NaBr (0.309 g, 0.003 mol) was added to precipitate the magenta complex; yield 0.78 g (60%).

Anation of [Cr(tren)F(H_2O)]$(ClO_4)_2$ in Methanol. The following compounds were prepared by shaking [Cr(tren)FH_2O]$(ClO_4)_2$ in 20 ml of anhydrous methanol in a stoppered flask until dissolved, adding the appropriate ammonium or sodium salt, and shaking until the salt dissolved and the desired compound precipitated. Sometimes it was necessary to warm the uncovered flask slightly to aid precipitation. Amounts of starting materials and yields are listed below.

Fluorobromo(triaminotriethylamine)chromium(III) perchlorate, [Cr(tren)FBr]ClO_4: [Cr(tren)FH_2O]$(ClO_4)_2$ (0.4 g, 0.00092 mol); NH_4Br (0.15 g, 0.0015 mol); yield 0.25 g (64%).

Fluorochloro(triaminotriethylamine)chromium(III) perchlorate, [Cr(tren)FCl]ClO_4: [Cr(tren)FH_2O]$(ClO_4)_2$ (0.3 g, 0.00069 mol); NH_4Cl (0.2 g, 0.0037 mol); yield 0.18 g (72%).

Fluoroazido(triaminotriethylamine)chromium(III) perchlorate, [Cr(tren)FN_3]ClO_4: [Cr(tren)FH_2O]$(ClO_4)_2$ (0.25 g, 0.00058 mol); NaN_3 (0.2 g, 0.0025 mol); yield 0.12 g (58%).

Fluoroacetato(triaminotriethylamine)chromium(III) perchlorate, [Cr(tren)F($C_2H_3O_2$)]ClO_4: [Cr(tren)FH_2O]$(ClO_4)_2$ (0.3 g, 0.00069 mol); $NH_4C_2H_3O_2$ (0.2 g, 0.0026 mol); yield 0.18% (70%).

Cr(tren)Cl(H_2O)$^{2+}$ was generated in solution by allowing [Cr(tren)Cl_2]Cl to react in 0.1 M $HClO_4$ for 1.5 min (10 half-lives of the aquation at 25 °C). Spectrophotometric or ion-exchange procedures with this species were carried out at temperatures near 0 °C to retard further aquation.

Cr(trenH)Cl(H_2O)$_2^{3+}$ was generated in solution by allowing [Cr(tren)Cl_2]Cl to aquate in 0.1 M $HClO_4$ until visible spectra were constant (about 1 h at 25 °C). Spectra of this species remained constant for long periods of time (1 or more months).

Analytical Methods. Chromium was determined by spectrophotometric analysis of chromate at 372 nm after decomposition of the complexes and oxidation of chromium(III) with alkaline peroxide. Carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss, Oxford, England. Halogen analyses were performed by gravimetry (AgCl) or by potentiometric titration with 0.01 M $AgNO_3$ after decomposition of the complexes by boiling with 6 M NaOH. Titrations on the complex containing both chloride and bromide were analyzed by the method of Martin.[11] Thiocyanate analyses were performed iodimetrically.[12] Perchlorate was analyzed by precipitation with nitron.[13] Oxalate analysis was carried out by permanganate titration.[14] A qualitative test for the presence of free primary amine was carried out by reaction with sodium nitrite in acid solution.[15]

Ion-Exchange Procedures. Ion-exchange procedures were carried out with Bio-Rad AG-50-W-X8 (100–200 mesh) (H^+ form), which was purified either by alternate washing with dilute ammonium hydroxide and dilute hydrochloric acid or by the method of Kemp and King.[16] Experiments were carried out in a jacketed column of inside dimensions 10 cm × 2 cm. For procedures carried out at low temperature, ice water was circulated through the column jacket.

Elution characteristics of various cations were determined by charging the column with the appropriate aged solution in 0.1 M $HClO_4$ and eluting with increasing concentrations of acid. In all cases, recovery of chromium-containing species from the column was complete within experimental error (2–3%).

The extent of aquation was established by charging the appropriately aged solution onto the column and eluting with 2 M $HClO_4$ for Cr(tren)Cl(H_2O)$^{2+}$ (done near 0 °C) or 3 M $HClO_4$ for Cr(trenH)Cl(H_2O)$_2^{3+}$ and analyzing the effluents for Cr.

Determination of chloride in Cr(trenH)Cl(H_2O)$_2^{3+}$ was carried out by charging a solution of this ion in 0.1 M $HClO_4$ onto the column, eluting with 0.1 M $HClO_4$ until the washing gave a negative test for chloride, and determining chloride in the washings after evaporation. The purple resin containing the complex was removed from the column for chromium determination. Charge determinations on Cr(trenH)Cl(H_2O)$_2^{3+}$ were carried out by the method of Beukenkamp and Herrington[17] as modified by Lin and Garner,[18] using 5 ml of a solution of approximately 0.05 M $HClO_4$, containing 1×10^{-3} g/ml of Cr.

Infrared Spectra. Infrared spectra were recorded on either a Perkin-Elmer Model IR-457 or a Beckman IR-12 recording spectrophotometer. Samples were examined as Nujol mulls on CsBr plates between 4000 and 300 cm^{-1}. Calibrations were made with polystyrene film.

Electronic Absorption Spectra. Visible spectrophotometric measurements were carried out on a Cary 14-M recording spectrophotometer with a thermostated cell compartment.

Kinetic Measurements. The basic kinetic techniques, i.e., thermostating of cells and calculation of pseudo-first-order rate constants, have been described previously.[7a] Both the first and second aquations were followed by measuring the decrease in absorbance at an appropriate wavelength with a 0.0–0.2 slidewire of the Cary 14-M. The reactions were carried out by either of the following procedures: (1) addition of solid to the thermostated cell containing preheated or precooled acid with a device based on a Drummond micropipet and mixing by compression of the pipet bulb; (2) injecting a known volume of thermostated acid by preheated or cooled syringe into the solid contained in the cell. The average time elapsed before a recording of absorbance was 15 s. There was no difference in rate constants obtained by the two procedures. Infinite-time absorbances were obtained experimentally and duplicate runs generally agreed to better than 3%. Pseudo-first-order rate constants were linear for more than 3 half-lives.

Results

A number of new Cr^{III}–tren complexes have been synthesized, and the first and second aquations of one of these, [Cr(tren)Cl_2]Cl, have been investigated. The compounds were characterized by elemental analysis (Table I),[19] visible spectra (Table II), and infrared spectra (Table III).[19] (See Discussion.)

Aquation of [Cr(tren)Cl_2]Cl. When [Cr(tren)Cl_2]Cl is dissolved in 0.1 M $HClO_4$, the spectra of the initially formed purple solution change rapidly to those of Cr(tren)Cl(H_2O)$^{2+}$ with λ_{max} at 520 and 396 nm. Spectral scans of the absorbance changes during the reaction (measured at 5 °C because of its rapidity) showed three isosbestic points, which were held throughout the reaction and were in good agreement with those predicted from the spectra of [Cr(tren)Cl_2]Cl (in concentrated HCl) and Cr(tren)Cl(H_2O)$^{2+}$: predicted, 527, 458, 380 nm; found, 530, 456, 383 nm.

When solutions of [Cr(tren)Cl_2]Cl in 0.1 M $HClO_4$ were aquated for 1.5 min (10 half-lives of the aquation at 25 °C) and charged onto a cation-exchange column (H^+ form) (see Experimental Section) at 1–2 °C, elution with increasing concentrations of $HClO_4$ showed that all chromium-containing species were present in a single rose pink band, which was eluted quantitatively (98–99%) with 2 M $HClO_4$. This elution behavior is consistent with the behavior of a double-charged cation of this size and type.[20]

The rate of aquation of [Cr(tren)Cl_2]Cl was studied spectrophotometrically by measuring the decrease in absorbance during reaction at a fixed wavelength. The majority of the rate measurements were made at 600 nm, where a large difference in absorption between reactant and product occurs. The effect on the observed aquation rate of acid concentration, ionic strength and temperature was studied (Table IV). Most of the kinetic measurements were carried out at a complex concentration of 3.3 mM, although there was no variation in reaction rate over the range 1.6–5.0 mM. There was also no variation in rate constant within experimental error, over the pH range 2–5 at constant ionic strength, as would be expected for an uncomplicated aquation. From Table IV, it can be seen that within the range studied, ionic strength has no effect on the aquation rate. Similarly, the rate was unchanged in nitric or hydrochloric acids.

Excellent linear Arrhenius plots were obtained by standard methods over the temperature range 12–31 °C from the data in Table IV. The following activation parameters were calculated: $\Delta H^{\ddagger} = 12.3 \pm 0.49$ kcal/mol; $\Delta S^{\ddagger} = 23.0 \pm 1.3$ cal deg^{-1} mol^{-1}.

Aquation of Cr(tren)Cl(H_2O)$^{2+}$. After the conclusion of the primary aquation, further slow spectral changes occur in the solution, along with a color change from rose pink to deep purple. The spectrum of the solution changes to that of

Table II. Electronic Spectral Data of Chromium(III) Complexes of β,β',β''-Triaminotriethylamine (25 °C)

Complex	Medium	Absorption maxima, cm^{-1} × 10^{-3} (ε, M^{-1} cm^{-1})	
		$^4A_{2g} \rightarrow {}^4T_{2g}$	$^4A_{2g} \rightarrow {}^4T_{2g}$ (F)
[Cr(tren)Cl$_2$]Cl	Concd HCl	18.2 (114)	24.5 (95.0)
cis-[Cr(en)$_2$Cl$_2$Cl[a]		18.7 (70.7)	24.9 (68.5)
cis-[Cr(NH$_3$)$_4$Cl$_2$]Cl[b]	0.1 N HCl	18.3 (41.5)	24.9 (39.5)
cis-α-[Cr(trien)Cl$_2$]Cl[b]	0.1 N HCl	18.8 (97.2)	25.2 (96.5)
cis-α-[Cr(trien)Cl$_2$]Cl[c]		18.8 (95.5)	25.2 (86.7)
cis-β-[Cr(trien)Cl$_2$]Cl[b]	Methanol	18.4 (~100)	24.9 (~85)
Cr(tren)Cl(H$_2$O)$^{2+}$	H$_2$O	19.3 (71.0)	25.4 (63.0)
[Cr(tren)ClClO$_4$]ClO$_4$·H$_2$O	H$_2$O	19.7 (83.0)	26.7 (36.3)
[Cr(tren)Cl(NCSe)]NCSe	H$_2$O	19.8 (86.3)	29.3 (194)
[Cr(tren)ClNCS)]Cl	H$_2$O	19.3 (146)	25.0 (72.5)
[Cr(tren)ox]ClO$_4$·H$_2$O	H$_2$O	19.8 (90.0)	27.1 (66.0)
[Cr(tren)ClBr]Br	Concd HCl	18.0 (103)	24.4 (81.5)
[Cr(tren)(N$_3$)$_2$]Br	50% methanol	18.9 (157)	24.9 (90.2)
[Cr(tren)F$_2$]ClO$_4$[d]	H$_2$O	19.0 (116)	26.5 (56.8)
[Cr(tren)F(H$_2$O)](ClO$_4$)$_2$	H$_2$O	19.2 (63.9)	26.7 (32.4)
[Cr(tren)F(NSC)]ClO$_4$	50% methanol	19.5 (132)	27.1 (50.0)
[Cr(tren)F(C$_2$H$_3$O$_2$)]ClO$_4$	50% methanol	19.4 (120)	26.1 (52.0)
[Cr(tren)FBr]ClO$_4$	H$_2$O	18.8 (54.1)	25.4 (29.5)
[Cr(tren)FCl]ClO$_4$	H$_2$O	17.4 (81.9)	26.6 (31.2)
[Cr(tren)F(N$_3$)]ClO$_4$	H$_2$O	18.9 (175)	24.9 (61.6)
[Cr(tren)Cl(HSO$_4$)]HSO$_4$·H$_2$O	H$_2$O	19.1 (112)	25.5 (69.8)
Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$	H$_2$O	18.4 (72.0)	25.1 (45.1)

[a] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4125 (1961). [b] P. S. Sheridan, to be submitted for publication. [c] Reference 5. [d] Reference 10.

Table IV. Pseudo-First-Order Rate Constants for the Aquation of [Cr(tren)Cl$_2$]Cl in Acid Solution

Temp, °C	[HClO$_4$], M	μ, M	10^{-2}k_1,[a,c] s^{-1}
12.3	0.0975	0.102	2.10 ± 0.06
16.9	0.0975	0.102	3.03 ± 0.16
20.2	0.0975	0.102	3.99 ± 0.09
25.0	0.0975	0.102	5.18 ± 0.27
30.8	0.0975	0.102	8.46 ± 0.08
25.0	0.0975	0.304	5.25 ± 0.06
25.0	0.00975	0.0138	5.11 ± 0.16
25.0	9.75 × 10^{-4}	0.005	5.22 ± 0.12
25.0	0.0962[b]	0.0966	5.02 ± 0.12
25.0	0.100	0.104	5.20 ± 0.16[d]
25.0	0.100	0.204	5.23 ± 0.09[d]
25.0	0.200	0.204	5.31 ± 0.19[d]
25.0	0.0975	0.102	5.23 ± 0.03[e]

[a] Errors given are standard deviations. [b] HNO$_3$. [c] Measurements at 600 nm except where noted. [d] HCl; μ controlled by LiCl; λ 556 nm. [e] λ 580 nm.

Table V. Pseudo-First-Order Rate Constants for the Aquation of Cr(tren)Cl(H$_2$O)$^{2+}$

Temp, °C	[HClO$_4$], M	μ, M	10^{-3}k_2,[a,b] s^{-1}
20.6	0.117	0.117	0.408 ± 0.04
25.0	0.117	0.117	0.715 ± 0.02
30.3	0.117	0.117	1.23 ± 0.03
34.1	0.117	0.117	1.84 ± 0.07
39.8	0.117	0.117	3.21 ± 0.11
39.8	0.117	0.117	3.26 ± 0.03[c]
34.1	0.152	2.00	1.20 ± 0.05[d]
34.1	0.125	2.00	1.17 ± 0.01[d]
34.1	0.100	1.10	1.57 ± 0.07[d]
34.1	0.123[e]	0.123	1.97 ± 0.07
34.1	2.03[e]	2.03	1.84 ± 0.05
34.1	0.0952[e]	2.09	1.77 ± 0.06
34.1	0.118[e]	1.12	1.69 ± 0.01

[a] Measurements made at 510 nm except where noted. [b] Error limits are standard deviations. [c] λ 470 nm. [d] LiClO$_4$ added to maintain μ. [e] HNO$_3$; LiNO$_3$ to maintain μ when needed.

Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$ with a shift of the lowest energy band to higher wavelength (545 nm). Spectrophotometric scans in 0.1 M HClO$_4$ at 25 °C during the course of the reaction show an isosbestic point at 556 nm, which is held throughout and agrees well with the value predicted from the spectra of Cr(tren)Cl(H$_2$O)$^{2+}$ and Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$ (557 nm).

When aged (1–1.5 h at 25 °C) constant-spectra solutions of Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$ in 0.1 M HClO$_4$ were charged onto an ion-exchange column in H$^+$ form (see Experimental Section), one deep purple band was sorbed onto the column. This band was eluted with 3 M HClO$_4$ and contained all of the chromium (98–99%) that was put onto the column. Elution of a 3+ species with 3 M HClO$_4$ is consistent with the behavior of other triply charged ions of this size and type.

When known amounts of aged constant-spectra solutions (usually 0.060 g for Cr(tren)Cl$_2$$^+$) were charged onto an ion-exchange column and the free chloride was eluted with 150–200 ml of 0.1 M HClO$_4$, 66.5 ± 1.0% (three determinations) of the total chloride was eluted. All chromium-containing species remained on the column. This indicated that one of the three chloride ions originally present per mole of [Cr(tren)Cl$_2$]Cl remained in the chromium-containing species, giving a Cr:Cl ratio for the species of 1:1, which is consistent with its identification as Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$.

The presence of free primary amine in Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$ was indicated by the evolution of nitrogen gas upon the addition of sodium nitrite in an acid solution at room temperature. Negative results were obtained when the test was performed on Cr(tren)Cl(H$_2$O)$^{2+}$ and on an acid blank.

The charge per chromium atom for solutions of Cr(trenH)Cl(H$_2$O)$_2$$^{3+}$ was (3.3 ± 0.1)+ (four determinations), which is consistent with elution data. A charge determination on a solution aged for 2 weeks gave identical results.

The kinetics of aquation of Cr(tren)Cl(H$_2$O)$^{2+}$ were measured in HClO$_4$, and the effects on the rate of aquation of varying complex concentration, ionic strength, and acidity were studied. Most of the data were obtained at a complex concentration of 1.0 mM, although there was no effect on the reaction rate over the range of concentrations used (0.8–10 mM). Kinetic data are compiled in Table V. It can be seen that there is no effect of acid strength over the range studied, 0.1–2.0 M HNO$_3$. (At acid concentrations over 0.1 M, it was more convenient to dissolve the complex in HNO$_3$, because of its limited solubility in HClO$_4$.) This has been the case for similar aquations of chromium(III) amines involving metal–nitrogen bond breaking.[8]

In HClO$_4$, there is a 30% decrease in the value of k_2 when the ionic strength is increased from 0.1 to 2.0 M. This effect has been noticed previously[6] and is within the normal range of salt effects at high ionic strengths. It is interesting that only a very small decrease in k_2 at high ionic strength is noticed in nitric acid.

Excellent linear Arrhenius plots were obtained from the temperature dependence of k_2 between 20 and 40 °C, for which the following activation parameters were calculated: $\Delta H^\ddagger = 19.1 \pm 0.4$ kcal/mol; $\Delta S^\ddagger = -8.4 \pm 1.0$ cal deg^{-1} mol^{-1}.

Discussion

Synthesis of New Complexes and Infrared Spectral Studies. $[Cr(tren)Cl_2]Cl$ was synthesized as deep violet crystals of high purity by the in situ dehydration of $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ in DMSO and its subsequent reaction with neat tren. The use of DMF as a solvent resulted in a less pure product. Attempts to replace the chloride anion with perchlorate were unsuccessful, due to the rapid aquation of the complex ($t_{1/2} \approx 12$ s).

When solutions of $[Cr(tren)Cl_2]Cl$ in 0.01 M $HClO_4$ were refluxed for 1–2 h with 2 and 3 equiv of $AgClO_4$, the visible spectra of the two solutions were identical, with λ_{max} at 525 and 390 nm, indicating that the solution in both cases consists mainly of $Cr(tren)Cl(H_2O)^{2+}$. The second chloride ion is quite resistant to removal, as is shown by our kinetic results.

At room temperature, the reaction of 40% HBr with $[Cr(tren)Cl_2]Cl$ was used to prepare $[Cr(tren)ClBr]Br$. However, attempts to introduce two bromides into the coordination sphere by repeated evaporation with 40% HBr, in a manner similar to the preparation of *cis*-$[Cr(en)_2Br_2]Br$,[21] gave a green crystalline solid, which contained both Cl and Br and gave C, H, N, and Cr analyses within 1% of the values expected for the species $trenH_3CrCl_3Br_3$. Evaporation of $[Cr(tren)Cl_2]Cl$ with concentrated HCl gave a similar green precipitate which was identified by analysis and electronic spectra as a slightly impure $trenH_3CrCl_6$. Hexachlorochromate(III) is known[22] and the triammoniotriethylamine cation is likely to be an effective precipitant for the triply negative halo anion, as it is for similar halo anions of rhodium(III) and iridium(III).[23]

The reaction of 70% perchloric acid with $[Cr(tren)F_2]ClO_4$ resulted in the replacement of one fluoride ligand with water. This method has been used previously to prepare fluoroaquo salts of chromium ammines.[24] The reaction of 70% perchloric acid with $[Cr(tren)Cl_2]Cl$, however, results in the formation of a pink solid whose visible spectrum is similar to that of $Cr(tren)Cl(H_2O)^{2+}$ (Table II), as would be expected for an N_4ClO chromophore. The infrared spectrum of the compound shows splitting of the antisymmetric stretching vibration of the perchlorate ion near 1000 cm^{-1} into two components (1135, 1100 cm^{-1}) and also of the antisymmetric bend near 625 cm^{-1} (625, 618 cm^{-1}). This splitting indicates monodentate coordination of the perchlorate ion in this species,[25] which is best formulated as $[Cr(tren)ClClO_4]ClO_4\cdot H_2O$. If coordination did not occur, these bands would not be split but rather would have the appearance of those observed in the fluoroaquo complex, i.e., single, broad peaks.

The complex $[Cr(tren)ClHSO_4]HSO_4\cdot H_2O$ was prepared by the action of 18 M H_2SO_4 on $[Cr(tren)Cl_2]Cl$. Comparison of the spectrum of this compound with spectra of sulfate and bisulfate in the region 1350–850 cm^{-1} [26] clearly indicates that this compound contains bisulfate, not sulfate. Monodentate sulfate is well-known[27] and an intermediate containing coordinated bisulfate has been proposed recently in the decomposition of cobalt(III) hexaammine.[28] The bisulfate ion has the symmetry C_{3v}, which is lowered to C_{2v} upon monodentate coordination. This should result in further splitting of the infrared-active vibrations in the 1200–1000-cm^{-1} region. Any splitting would be difficult to detect, however, because of the superposition of the absorbance of ionic bisulfate and also because of the bands in this region being broad and ill defined, even in thin mulls. No major differences were seen between the spectra of $KHSO_4$ and $[Cr(tren)ClHSO_4]HSO_4\cdot H_2O$ in this region. However, since the primary species in 18 M H_2SO_4 is the bisulfate ion, with little or no sulfate present, it seems extremely likely that the complex prepared in this manner contains both ionic and coordinated bisulfate, despite the lack of definite infrared evidence of coordination.

The complex $Cr(trenH)Cl(H_2O)_2{}^{3+}$, which has been isolated in solution, contains tridentate tren, with one of the primary nitrogens uncoordinated. Tren compounds of this type have not been previously isolated, although chromium(III) complexes of tren with the tertiary amine group uncoordinated have been recently prepared,[29] and there is indirect evidence for a complex of silver(I) in solution in which only the two primary amine groups of tren are coordinated.[30] It is extremely unlikely that any complex of tren with only the tertiary amine group coordinated would exist, even though the basicity of triethylamine, for example, is similar to that of ethylamine.[31] The tertiary amine group is a poor coordinating agent for steric reasons. It has been suggested[32] (and seems reasonable on the basis of molecular models) that when the three primary nitrogens of tren coordinate, the tertiary amine group is put into a favorable position for coordination to occur. When $[Cr(tren)Cl_2]Cl$ is evaporated with concentrated HCl or HBr, all three primary amines uncoordinate and are protonated, due to the high $[H^+]$, and the tertiary amine unhooks, allowing the $trenH_3{}^{3+}$ to act as a cation. (See previous discussion.)

The infrared spectra of complexes containing thiocyanate, azide, and oxalate were very similar to those of the analogous Co^{III}–tren complexes and indicated coordination of the ligand. These absorptions have been tabulated previously.[33] The carbon–nitrogen stretching vibrations in the selenocyanate complex were in the region expected for coordination through nitrogen (ν(C–N) 2080, 2075 cm^{-1}), as has been found for other complexes of first-row transition elements.[27,34]

The infrared absorptions in the regions 3300, 1600, and 800 cm^{-1} of Cr^{III}–tren complexes were very similar to those found for Co^{III}–tren complexes and have been discussed and assigned previously.[35]

In the region 600–380 cm^{-1}, Cr^{III}–tren complexes show a pattern of five absorption bands at 570–550 (I), 510 (II), 470 (III), 450–440 (IV), and 410–395 cm^{-1} (V), several of these showing splitting. A typical spectrum in this region is shown in Figure 1. A similar pattern, consisting of four bands with slightly shifted wavenumbers, has been found in this region for *cis*-bis(ethylenediamine) complexes of chromium(III).[36] For these complexes, there existed no one absorption corresponding to a pure chromium–nitrogen stretching vibration, all Cr–N vibrations being strongly coupled to vibrations of the ethylenediamine ring. This coupling was attributed to the low symmetry of the cis complexes, and the situation is likely to be similar in the necessarily cis tren complexes.[37]

Absorptions in the 3550–3200- and 1650–1620-cm^{-1} regions in the complexes containing water of hydration were attributed to the antisymmetric and symmetric O–H stretching modes and to the H–O–H bending mode, respectively.[27]

Electronic Spectral Studies. The electronic spectral data of the Cr^{III}–tren complexes are given in Table II. Chromium(III) is a d^3 cation with a ^4F ground state. Upon the application of an octahedral field, it will split into a $^4A_{2g}$ ground state and two excited states, $^4T_{2g}$ and $^4T_{1g}$ (F). In general, for chromium(III) complexes experiencing a pseudooctahedral ligand field environment,[38] the transitions can be interpreted as $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ (F). The ^2G state transitions are either not observed or are very weak, since they are spin forbidden.

In the case of the mixed tren–Cr^{III} complexes shown in Table II, the bands in the regions 17.4×10^3–19.8×10^3 cm^{-1}

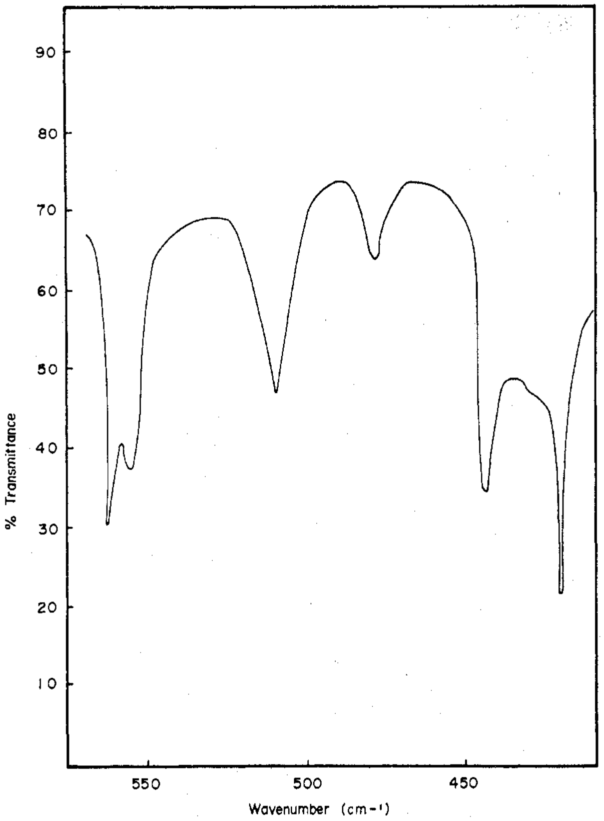

Figure 1. Infrared absorption bands in the region 600–380 cm^{-1} for a typical chromium(III)–triaminotriethylamine complex.

and 24.4 × 10^3–29.3 × 10^3 cm^{-1} are accordingly assigned (O_h) to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ (F) transitions, respectively ($^4A_{2g} \rightarrow {}^4T_{2g}$ representing the ligand field splitting parameter $10Dq$ for the mixed tren–Cr^{III} complexes).

Furthermore, according to theoretical arguments,[39] the intensity of a d–d transition should be enhanced by increasing the asymmetry of the ligand field, and this has been shown to be the case by Belford and Yeranos.[40] It appears reasonable, then, that the increase in the molar absorbancy value (ϵ in M^{-1} cm^{-1}) accompanying rigid tetraamine ligands is produced by increased distortion of the O_h field. Therefore, one would expect that the molar absorbance intensities in the case of the $Cr(tren)Cl_2^+$ complex, for example, would have a higher value than that of the corresponding trien–Cr^{III} complexes, since trien in the α or β form is more flexible than the tripodal-branched tren. A comparison (Table II) of the intensities of a series of amine complexes for a given dichloro complex shows that the absorption intensities are in the order $\epsilon_{tren} > \epsilon_{\beta\text{-trien}} > \epsilon_{\alpha\text{-trien}} > \epsilon_{(en)_2} > \epsilon_{(NH_3)_4}$. This order is in agreement with the theoretical prediction, and an identical order was also observed in the case of the same amines for the cobalt(III) complexes.[35]

Primary and Secondary Aquation Reactions of $Cr(tren)Cl_2^+$. The successive spectral changes which solutions of $Cr(tren)Cl_2^+$ undergo in acid solution correspond to primary and secondary aquation, the latter occurring with concurrent chromium–nitrogen bond breakage.

The very rapid initial spectral changes in these solutions result from an uncomplicated aquation proceeding as

$$Cr(tren)Cl_2^+ + H_2O \xrightarrow{k_1} Cr(tren)Cl(H_2O)^{2+} + Cl^-$$

on the basis of the following evidence: (1) three isosbestic points held throughout the aquation, which agree well with the predicted values (see Results); (2) the movement of d–d bands in the spectrum of the product species to shorter wavelengths, as would be expected from the replacement of chloride by water and the similarity of the spectra of this product to other chromium(III)–chloroaquotetraamine species; (3) formation of only one product during ion-exchange chromatography of suitably aged solutions; (4) the linearity of pseudo-first-order rate plots for the reaction at several wavelengths for over 3 half-lives. Rate constants were identical, within experimental error.

The following evidence indicates that the slow reaction after the primary aquation of $Cr(tren)Cl_2^+$ can be attributed to the aquation of $Cr(tren)ClH_2O^{2+}$ by a single pathway according to

$$Cr(tren)Cl(H_2O)^{2+} + H_3O^+ \xrightarrow{k_2} Cr(trenH)Cl(H_2O)_2^{3+}$$

(1) The isosbestic point observed is maintained throughout the entire aquation and agrees well with the value predicted from the spectra of $Cr(tren)Cl(H_2O)^{2+}$ and $Cr(trenH)Cl(H_2O)_2^{3+}$ (see Results). (2) There is linearity of the pseudo-first-order kinetic plots for over 3 half-lives and agreement of k_2 values measured at several different wavelengths. (3) During cation-exchange chromatography of aged reaction mixtures, only one product was detected, which had a Cr:Cl ratio of 1:1 and a charge of 3+ and contained an uncoordinated primary amine function. (4) The longest wavelength absorption maximum is shifted to a longer wavelength in the spectrum of the product. Such behavior can be used to differentiate between several reaction pathways when the relative positions of the ligands in the spectrochemical series are known. A shift toward longer wavelength indicates breakage of a chromium–nitrogen bond in this case, as replacement of chloride by water would occur with a shift to a shorter wavelength. The possibility of dimer formation in these solutions was eliminated by the good agreement between the charge per species obtained from elution experiments and the charge per chromium atom determined quantitatively by ion exchange and also by the stability of the final product in acid solution. This stability is in contrast to the behavior observed in dimers formed from similar amine complexes.[41] (5) Rechelation of the partially unwrapped complex $Cr(trenH)Cl(H_2O)_2^{3+}$ occurs when solutions of this species (in 0.1 M $HClO_4$) were adjusted to pH 7 with $NaHCO_3$ and reacidified. The spectra of these solutions returned to those of $Cr(tren)Cl(H_2O)^{2+}$. Rechelation should occur easily because of the inability of the dechelated protonated "arm" of the tren molecule to escape from the vicinity of the metal ion.

Inspection of the k_1 values for the first aquation at 25 °C of $Cr(tren)Cl_2^+$ (5.18 × 10^{-2} s^{-1}), *cis*-$Cr(en)_2Cl_2^+$ (3.3 × 10^{-4} s^{-1}),[42] and *cis*-α-$Cr(trien)Cl_2^+$ (1.92 × 10^{-4} s^{-1}) shows that $Cr(tren)Cl_2^+$ aquates much faster than chromium(III) complexes of linear polyamines containing the same or a lesser number of chelate rings. The labilization of one chloride ion which occurs in $Co(tren)Cl_2^+$ is seen to persist in the case of $Cr(tren)Cl_2^+$ and it is likely that a similar explanation can be given.[37]

Attempts to compare the k_2 value for the aquation of $Cr(tren)Cl(H_2O)^{2+}$ at 25 °C (7.15 × 10^{-4} s^{-1}) with rate constants for some similar processes involving chromium–nitrogen bond breaking[4,5,9] reveal that most of the complexes whose aquation rates have been determined are sufficiently different to make good comparisons difficult. An approximate rate constant of 0.5 × 10^{-4} s^{-1} has been measured for the aquation of a complex identified as *cis*-β- or *cis*-β'-$Cr(trien)Cl(H_2O)^{2+}$.[5] This aquation occurs by two different paths and is not completely understood.

Although the exact amount of the difference in rate constants for the two species is in doubt, because of the uncertainty of the rate constant for the trien species, it is clear that there is some acceleration of rate for the tren complex. All of the factors responsible for the rates of the processes involving

Cr–N bond breakage are not understood, but relief of ring strain has been recognized as an important contributing factor.[9]

Considerable strain is present in tren complexes with all four nitrogen atoms coordinated, as evidenced by abnormal C–C or C–N bond distances in two out of the three chelate rings in $Ni(tren)(NCS)_2$.[43]

Comparison of the ϵ_m value for the lowest energy visible absorption band of $Cr(trenH)Cl(H_2O)_2^{3+}$ (ϵ_m 72) in Table II, with corresponding values for CrN_3O_3 complexes of both 1,2,3 (facial) and 1,2,6 (meridional) configurations[4] shows that it is extremely likely that $Cr(trenH)Cl(H_2O)_2^{3+}$ has the 1,2,3 (facial) configuration, the least strained. [The CrN_3O_2Cl structure of the tren complexes does not contradict this argument, as the ϵ_m values for 1,2,3-$Cr(dien)(H_2O)_2Cl^{2+}$ (λ_{max} 535 nm, ϵ_m 72.0; λ_{max} 394 nm, ϵ_m 38.5)[44] are not much different from those for 1,2,3-$Cr(dien)(H_2O)_3^{3+}$ (λ_{max} 510 nm, ϵ_m 67.0; λ_{max} 375 nm, ϵ_m 32.2).[4,45]] It seems, therefore, that some relief of strain occurs as a result of the unhooking of the primary amine group of tren and that this contributes to the faster reaction rate of the tren species.

It is extremely interesting that the process of metal–nitrogen bond rupture in the Cr^{III}–tren system stops after the unhooking of one primary amine group of the tren ligand. This is in contrast to the behavior of chromium(III) complexes of the linear polyamines trien,[4] tetren,[9] and dien,[18] which continue the unhooking process until the polyamine is eventually removed from the coordination sphere. The complex $Cr(trenH)Cl(H_2O)_2^{3+}$ contains a coordinated tertiary amine with a coordinated primary amine on either side. Secondary amine groups in this condition do not undergo Cr–N bond rupture,[9] and since the tertiary nitrogen has an additional steric requirement of the dangling uncoordinated ethylamine group, it would certainly not be expected to unhook. The resistance to rupture of the two remaining coordinated primary nitrogens is unexplained. However, this may indicate that linear polyamines unwrap successively from one end of the molecule only and not from the coordinated primary amine groups on opposite ends of the molecule.

The k_1 values for the aquation of $M(tren)Cl_2^+$ species at 25 °C are for Rh $k_1 = 1.97 \times 10^{-5}\ s^{-1}$,[7c] for Co $k_1 = 2.96 \times 10^{-3}\ s^{-1}$,[7a] and for Cr $k_1 = 5.18 \times 10^{-2}\ s^{-1}$, given in Table IV. These reaction rates are in the order Cr > Co > Rh, as has been found for other aquations of complexes containing these metal ions. The ratios of these rate constants to those of the *cis*-(en)$_2$ and *cis*-α-trien complexes are for Co $k_{tren}/k_{cis\text{-}(en)_2} = 12$ and $k_{tren}/k_{cis\text{-}\alpha\text{-trien}} = 20$,[7b] for Rh $k_{tren}/k_{cis\text{-}(en)_2} = 50$ and $k_{tren}/k_{cis\text{-}\alpha\text{-trien}} = 60$,[7c] and from this work for Cr $k_{tren}/k_{cis\text{-}(en)_2} = 200$ and $k_{tren}/k_{cis\text{-}\alpha\text{-trien}} = 250$. These ratios can be interpreted by considering the factors which may affect the reaction rates in these systems.

(1) Size of Central Metal Ion. In some labile octahedral complexes it has been found[46] that a larger central metal ion enhances the effects of strain which may be already present in the ligand. A model based on values of the ionic radii for the three metal ions [Co(III), 0.53 Å; Cr(III), 0.62 Å; Rh(III), 0.67 Å] would correctly predict the above rate constant ratios to be higher for rhodium(III) than for cobalt(III). However, the rate ratio for chromium(III) would also be expected to be similar to or smaller than that for rhodium(III). This is not true, however, and the high rate constant ratios observed experimentally for chromium(III) systems indicate that other factors also are affecting these relative rates.

(2) Mechanism of Reaction. The most recent view of chromium(III)-substitution reactions[47] is that of an associative interchange (I_a) process. Reactions of rhodium(III) are thought to be also basically associative,[47–49] although less so than those of chromium(III). This might be expected from its d^6 electronic configuration, which would tend to repel the attack of the incoming ligand. Linear free energy relationship (LFER) plots for some reactions of these two ions reflect this, with slopes of 0.6 for the aquation of $Cr(NH_3)_5X^{2+}$ [8] and 0.9 for the same reaction of rhodium(III).[49] The reactions of cobalt(III) are basically dissociative (I_d), with a LFER slope of 1 for the aquation of $Co(NH_3)_5X^{2+}$ [8] indicating them to be dissociatively activated.

It must be concluded that the peculiar geometric properties of tren affect I_a processes even more than those of a dissociative nature. The geometry of coordinated tren, with the primary nitrogens drawn back toward the tertiary nitrogen,[43] may allow the entering water molecule easier access for attack, thus enhancing the rate of associative processes. It can be seen that the increased rate of tren reactions over that of *cis*-(en)$_2$ or *cis*-α-trien reactions can be correlated with an increase of the I_a character of the reaction, Cr > Rh > Co.

Although there is kinetic evidence for the presence of isomers of $Co(tren)Cl(H_2O)^{2+}$ [50] and isomers of other Co^{III}–tren complexes have been isolated,[51,52] an investigation of the aquation of $Cr(tren)Cl(H_2O)^{2+}$ at 13.5 °C revealed no deviation from first-order kinetics. These kinetic results are consistent with the observed sharpness of the isosbestic point seen for this reaction, and it may be that the aquation of $Cr(tren)Cl_2^+$ is stereospecific, producing only one isomer, or that the amount of any second isomer present is so small as not to be detectable spectrophotometrically.

Furthermore, preliminary spectrophotometric studies of the aquation of $Cr(tren)F_2^+$ in dilute acid indicate that chromium–nitrogen bond breaking occurs in the secondary aquation of this complex and this phenomenon may be a general one in the aquation of Cr^{III}–tren species. Further study of this system is in progress.

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Registry No. $[Cr(tren)Cl_2]Cl$, 57718-97-5; $[Cr(tren)ClClO_4]ClO_4$, 57718-99-7; $[Cr(tren)ClHSO_4]HSO_4$, 57719-33-2; $[Cr(tren)ox]ClO_4$, 57719-01-4; $[Cr(tren)ClNCS]Cl$, 57719-02-5; $[Cr(tren)ClBr]Br$, 57719-03-6; $[Cr(tren)ClSeCN]SeCN$, 57719-05-8; $[Cr(tren)FH_2O](ClO_4)_2$, 57719-07-0; $[Cr(tren)FNCS]ClO_4$, 57719-09-2; $[Cr(tren)(N_3)_2]Br$, 57719-21-8; $[Cr(tren)FBr]ClO_4$, 57719-23-0; $[Cr(tren)FCl]ClO_4$, 57719-25-2; $[Cr(tren)FN_3]ClO_4$, 57719-27-4; $[Cr(tren)F(C_2H_3O_2)]ClO_4$, 57719-29-6; $Cr(tren)Cl(H_2O)^{2+}$, 57719-30-9; $Cr(trenH)Cl(H_2O)_2^{3+}$, 57719-31-0; *cis*-$[Cr(NH_3)_4Cl_2]Cl$, 19706-96-8; *cis*-α-$[Cr(trien)Cl_2]Cl$, 14883-60-4; *cis*-β-$[Cr(trien)Cl_2]Cl$, 57793-29-0; $[Cr(tren)F_2]ClO_4$, 28650-58-0.

Supplementary Material Available: Table I, containing elemental analyses and color of chromium(III)–triaminotriethylamine complexes, and Table III, giving the infrared spectra between 600 and 380 cm^{-1} of the chromium(III)–triaminotriethylamine complexes (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 169th National Meeting of American Chemical Society, Philadelphia, Pa., April 1975. Work done by S.G.Z. in partial fulfillment of the requirements of the Ph.D. degree at the State University of New York at Binghamton, 1975.
(2) Abbreviations used: tren, β,β',β'' triaminotriethylamine; trien, triethylenetetramine; tetren, tetraethylenepentamine; en, ethylenediamine; DMSO, dimethyl sulfoxide; DMF, *N,N*-dimethylformamide; ox, oxalate; dien, diethylenetriamine; LFER, linear free energy relationship.
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(45) These conclusions hold regardless of whether the chloride in Cr(tren)ClH$_2$O^{2+} is cis or trans to the tertiary nitrogen of tren. It is not clear at the present time which chloride is extremely labilized in aquation reactions. Conflicting views exist in the literature: the x-ray study of Ni(tren)(NCS)$_2$[43] and some recent NMR studies [R. J. West and S. F. Lincoln, *Inorg. Chem.*, **12**, 494 (1973); S. F. Lincoln and R. J. West, *J. Am. Chem. Soc.*, **96**, 400 (1974)] support the labilization of the cis chloride, and other NMR and infrared studies support that of the trans.[51] X-ray studies of some of these tren complexes would clarify the situation.

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Relaxation Pathways of Chromium(III) Quartet Excited States

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The photoracemization of (+)D-Cr(en)$_3^{3+}$ in aqueous solution at 25 °C has been examined under ligand field excitation in the presence and absence of OH$^-$ ion as a specific ^2E_g doublet-state quencher. For excitation wavelengths between 436 and 496.5 nm essentially constant percent reaction quenching by OH$^-$ ion was observed (57%). In contrast, a marked decrease in quenching occurred for irradiations at 514.5 nm (38%) yielding a percent quenching ratio of 0.65 for 514.5 nm vs. 436 nm. The overall racemization quantum yield (ϕ_{rac}) at 25 °C remained constant (0.4) over this wavelength region and was identical with that observed for hydrolysis. These racemization results are interpreted on the basis of a model which indicates that $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing competes successfully with $^4T_{2g}$ vibrational equilibration. Independent support for this analysis comes from the relative phosphorescence yields (P) on 514 nm vs. 436 nm excitation ($P_{514}/P_{436} = 0.63$), a value in close agreement with the percent reaction quenching ratio (0.65).

Introduction

It has been recently found that a limited number of Cr(III) complexes display readily observable phosphorescence in room-temperature fluid solution.[1,2] This knowledge has been subsequently applied with marked success[3-6] to photoreactive excited-state identification, by comparing phosphorescence and photolysis quenching in the presence of specific doublet (^2E_g) excited-state quenchers. Analysis of these quenching data for the O_h and D_3 systems so far examined strongly supports the contention that photoreaction originates solely out of the quartet ($^4T_{2g}$) excited level.

We explore in this report a promising extension of this quenching technique which provides a clearer insight into the details of $^4T_{2g}$ excited state relaxation in aqueous solution (see Figure 1). Up to the present it has been generally assumed that subsequent to $^4A_{2g} \rightarrow {}^4T_{2g}$ excitation, vibrational equilibration of the $^4T_{2g}$ state is very rapid ($<10^{-10}$ s).[7] The implication has been that chemical reaction and $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing (ISC) are competitive processes out of the vibrationally equilibrated (Thexi) quartet.[8] Adamson et al.[9,10] have commented, however, on the possibility of ISC occurring prior to complete quartet relaxation—but except for very low-temperature studies on the Reinecke's salt system,[9] strong experimental support has been lacking.

We have chosen to examine this question for the complex Cr(en)$_3^{3+}$, in view of the extensive photochemical and emission data already available on this system. The experimental probe used was the wavelength dependence of (+)D-Cr(en)$_3^{3+}$ photoracemization, in the presence of hydroxide ion as a specific doublet quencher. The reaction quenching results are interpreted on the basis of a model developed in the Discussion. The relative phosphorescence quantum yields in aqueous solution over this wavelength region have also been determined, to provide supportive data for the reaction quenching results. The evidence to be presented is consistent with ISC competing successfully with $^4T_{2g}$ vibrational equilibration.

Experimental Section

Materials. Racemic and optically active [Cr(en)$_3$]Cl$_3$·2H$_2$O were prepared according to literature procedures[11,12] with samples in each case recrystallized at least twice. Tris(bipyridine)ruthenium(II) chloride ([Ru(bpy)$_3$]Cl$_2$) was purchased from G. F. Smith Chemical Co. and used without further purification. All other reagents were of reagent grade quality.

Apparatus. A modified Aminco-Bowman spectrophotofluorimeter (vide infra) was employed for 365- and 436-nm irradiations, the excitation monochromator being followed by Corning 7-51 and 5-60 band-pass filters, respectively. An argon ion laser (Coherent Radiation, Model 52) was used for photolysis studies at 457.9, 476.5, 488.0, 496.5, 501.7, and 514.5 nm. Optical rotation measurements were obtained at 589 nm using a Bendix automatic polarimeter (Model 1144) with digital readout to 0.0002°. Relative phosphorescence intensity data