constants for anation of Cr(III) by $HgCl^+$, $HgCl_2$, and $HgCl_3^-$ of 9.6×10^{-10}, 3.8×10^{-9}, and 7.9×10^{-8} M^{-1} sec^{-1}, respectively. These rate constants are within the Cr(III) range found by Espenson[34] despite the difference in charge involved in the first two reactions. The present study and the data of Armor and Haim[26] on $CrNCS^{2+}$ yield a range of rate constants for anation of Cr^{3+} by HgX^+ of only $(0.98\text{–}34) \times 10^{-11}$ M^{-1} sec^{-1} (Table V) and a value for anation by HgClI of 7.2×10^{-11} M^{-1} sec^{-1}. This range is narrower than that found by Espenson for the unassisted Cr(III) anations and is comparable to the range found for the Fe(III) anations. Since the LFER for the assisted Cr(III) aquations indicates that this transition state resembles the products of the reaction more than does that for the unassisted reactions, it is reasonable that the anation rates should show a smaller dependence on the entering ligand. The fact that the rate constants for the HgX^+ anations are lower than those found for X^- anations is probably due in part to a difference in ionic strength (0.50 instead of 1.0 M) and charge type as well as the difference in the role played by the incoming ligand in the transition state.

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Hydrolysis Kinetics of the *trans*-Dichloro- and *trans*-Dibromobis(1,3-diaminopropane)chromium(III) Cations in Acidic Aqueous Solution

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The synthesis of *trans*-$[Cr(tmd)_2Cl_2]Br$, *trans*-$[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$, and *trans*-$[Cr(tmd)_2Br_2]X$ (X = Br, ClO_4) is described, and the cations *trans*-$Cr(tmd)_2Cl_2^+$, *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$, *trans*-$Cr(tmd)_2(OH_2)Br^{2+}$, *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$, *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$, and $Cr(tmd)(OH_2)_4^{3+}$ have been isolated and characterized in solution. At 25.0°, the first-order rate constants and kinetic parameters for the primary hydrolysis of *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br) (corresponding to the formation of *trans*-$Cr(tmd)_2(OH_2)X^{2+}$) are 10^5k $(sec^{-1}) = 2.08 \pm 0.06$ (0.1 F HNO_3), 36.2 ± 1.3 (0.3 F HNO_3); E_a (kcal mol^{-1}) $= 24.5 \pm 0.3$, 22.9 ± 0.3; $\log [PZ\ (sec^{-1})] = 13.26$, 13.34; ΔS°_{298} (cal deg^{-1} mol^{-1}) $= +0.1 \pm 0.5$, $+0.5 \pm 0.5$, respectively. The secondary hydrolysis of these cations is complicated by isomerization and concurrent Cr–N bond rupture. The first-order halide release rate constants and kinetic parameters for *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ (X = Cl, Br) in 1.0 F HNO_3 at 45.0° are 10^5k $(sec^{-1}) = 2.88 \pm 0.06$, 13.6 ± 0.8; E_a (kcal mol^{-1}) $= 21.7 \pm 0.5$, 24.2 ± 0.5; $\log [PZ\ (sec^{-1})] = 10.39$, 12.73, respectively.

Introduction

In the past several years, much effort has been focused on the kinetic and mechanistic behavior of octahedral transition metal complexes.[2] In particular, the diacidobis(ethylenediamine)cobalt(III) and, to a lesser extent, the analogous chromium(III) complexes[3] have received considerable attention. More recently, kinetic studies have been concentrated on multidentate[4–6] and macrocyclic[7] polyamine systems. Of considerable interest is the effect of an increase in the ring size on the reaction rate, although only a few such comparative studies have been made. *trans*-$Co(tmd)_2X_2^+$ (X = Cl, Br)[8] is one such system that has recently been investigated.[9]

As part of a program to investigate the mode of acid hydrolysis of some analogous Co(III) and Cr(III) complexes,[10–14] we have studied the rates of halide release from *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br). The rate constants and kinetic parameters allow a comparison with similar data (where available) for the *trans*-$M(AA)_2X_2^+$ (M = Co, Cr; AA = en, pn, tmd; X = Cl, Br) systems.

A preliminary report on the rate of the primary hydrolysis of *trans*-$Cr(tmd)_2Cl_2^+$ at 35.0° has been published.[15]

Experimental Section

The amine, 1,3-diaminopropane, was obtained from Aldrich Chemical Co. and used without further purification. All other chemicals were reagent grade quality. The ion-exchange material used was Zeo-Karb 225, SRC-6 cation-exchange resin in

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(8) Abbreviations used: en = $NH_2(CH_2)_2NH_2$; pn = $NH_2(CH_3)CHCH_2NH_2$; tmd = $NH_2(CH_2)_3NH_2$; *meso*-bn = *meso*-$NH_2(CH(CH_3))_2NH_2$; dan = $NH_2CH_2C(CH_3)_2CH_2NH_2$; dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$; X = Cl, Br; M = Co, Cr; unless otherwise stated.

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the Na^+ form (52–100 mesh) for all preparations except *trans*-$Cr(tmd)_2Cl_2^+$, where Zeo-Karb 225, SRC-13 cation-exchange resin (14–52 mesh) was used. The dichloro and dibromo cations were isolated using 6 × 1 cm columns cooled by a jacket of circulating ice water, and all others using a 10 × 1 cm tap water cooled column. The preparations and analyses of the cationic complexes were repeated at least three times to check the reproducibility of the synthetic methods and the visible absorption spectral parameters. *Caution!* Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these compounds should be treated as potentially explosive and handled with care.

***trans*-Hydroxoaquobis(1,3-diaminopropane)chromium(III) Perchlorate.**—A suspension of 3 g of *trans*-$[Cr(tmd)_2Cl_2]ClO_4$ (prepared as described previously[16]) in 30 ml of water containing 10 ml of pyridine was heated on a steam bath for 10 min to form a red-brown solution. $NaClO_4 \cdot H_2O$ (5 g) was added and the orange-red crystals that deposited from the ice-cooled solution were collected, washed with 2-propanol and ether, and air-dried. The yield was 1.4 g (41%). *Anal.* Calcd for $[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$: C, 16.55; H, 5.30; N, 12.90; Cr, 11.95. Found: C, 16.96; H, 5.24; N, 12.14; Cr, 11.45.

***trans*-Dichlorobis(1,3-diaminopropane)chromium(III) Bromide.**—This salt was prepared using a modification of the method used to prepare the perchlorate salt.[16] $CrCl_3 \cdot 6H_2O$ (16.2 g) in dimethyl sulfoxide (DMSO) (75 ml) was boiled for 10 min. A mixture of tmd (10.2 ml) and DMSO (45 ml) was added and the solution was boiled for a further 2 min. After cooling to 60°, the dull green solution was poured into 900 ml of well-stirred acetone. The purple precipitate that deposited was filtered off and washed with acetone (three 50-ml portions), and the still damp solid was suspended in HBr (60 ml, 48%). This suspension was heated on a steam bath for 10–15 min during which time, green crystals deposited. These were collected from the ice-cooled solution, washed with ethanol (three 25-ml portions) and ether (two 25-ml portions), and air-dried. The yield was 5 g (24%). *Anal.* Calcd for $[Cr(tmd)_2Cl_2]Br$: C, 20.50; H, 5.70; N, 15.90; Cr, 14.8; halide, 43.1. Found: C, 20.38; H, 5.79; N, 15.85; Cr, 14.5; halide, 42.4.

***trans*-Dibromobis(1,3-diaminopropane)chromium(III) Perchlorate.**—The mother liquors from the previous preparation were returned to the steam bath for 15 min. $HClO_4$ (15 ml, 60%) was added and the solution allowed to cool slowly. The green crystals (1 g) that deposited overnight were collected, washed with 2-propanol and ether, and air-dried. *Anal.* Calcd for $[Cr(tmd)_2Br_2]ClO_4$: C, 15.67; H, 4.35; N, 12.21; Cr, 11.3; Br, 34.8. Found: C, 17.96; H, 5.11; N, 12.23; Cr, 11.1; Br, 35.6.

***trans*-Dibromobis(1,3-diaminopropane)chromium(III) Bromide.**—This complex was prepared by heating *trans*-$[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$ (2 g) in HBr (20 ml, 48%) on a steam bath for 10 min to form an orange-brown solution containing bright green crystals. After cooling to room temperature, the crystals were collected, washed with 2-propanol and ether, and air-dried. The yield was 1.7 g (80%). *Anal.* Calcd for $[Cr(tmd)_2Br_2]Br$: C, 16.38; H, 4.56; N, 12.76; Cr, 11.8; Br, 54.5. Found: C, 16.13; H, 4.38; N, 11.98; Cr, 11.8; Br, 53.9.

The *trans*-Dichlorobis(1,3-diaminopropane)chromium(III) Cation.—The green *trans*-$Cr(tmd)_2Cl_2^+$ cation was isolated by suspending *ca.* 150 mg of *trans*-$[Cr(tmd)_2Cl_2]ClO_4$ in 0.025 *F* HNO_3 (30 ml). The unreacted solid was filtered from the solution which dripped directly onto the top of an ion-exchange column, prewashed with 1.0 *F* and then 0.025 *F* HNO_3. The green band that formed at the top of the resin column was washed with 30 ml of 0.025 *F* HNO_3 and the green dichloro cation was then eluted with 50 ml of 0.6 *F* HNO_3 into an ice-cooled flask. The absorption spectrum was recorded immediately and analysis of solutions prepared in this manner (*ca.* 2 m*F* in complex) gave Cr:Cl atom ratios of 1:2.08 ± 0.14 (5)[17] in acceptable agreement with the formula $Cr(tmd)_2Cl_2^+$.

The *trans*-Dibromobis(1,3-diaminopropane)chromium(III) Cation.—The green *trans*-$Cr(tmd)_2Br_2^+$ cation was isolated in solution by a method similar to that used for *trans*-$Cr(tmd)_2Cl_2^+$, except that 0.3 *F* HNO_3 was the eluting agent. Analysis of effluent solutions gave Cr:Br atom ratios of 1:2.03 ± 0.04 (7)[17] in agreement with the formula $Cr(tmd)_2Br_2^+$.

The *trans*-Chloroaquobis(1,3-diaminopropane)chromium(III) Cation.—The orange *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$ cation was generated in solution by allowing *trans*-$[Cr(tmd)_2Cl_2]ClO_4$ (*ca.* 150 mg in 50 ml of 0.1 *F* HNO_3) to hydrolyze for 1.5 hr at 45°. The cooled reaction solution was adsorbed on an ion-exchange column which had been prewashed with 2 *F* and then 0.1 *F* HNO_3. Elution with 30 ml of 0.6 *F*, followed by 20 ml of 0.8 *F* HNO_3, removed the unreacted *trans*-$Cr(tmd)_2Cl_2^+$ cation and the orange *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$cation was eluted with 50 ml of 1.0 *F* HNO_3. Absorption spectral parameters were measured immediately and analyses of these solutions (*ca.* 3 m*F* in complex) gave Cr:Cl atom ratios of 1:1.00 ± 0.07 (9)[17] in agreement with the formula $Cr(tmd)_2(OH_2)Cl^{2+}$.

The *trans*-Bromoaquobis(1,3-diaminopropane)chromium(III) Cation.—The green-brown *trans*-$Cr(tmd)_2(OH_2)Br^{2+}$ cation was prepared by a method similar to that used for the chloroaquo analog, except that the heating time was reduced to 20 min before adsorption on an ion-exchange column. Analyses of the effluent solutions (*ca.* 4 m*F* in complex) gave Cr:Br ratios of 1:1.02 ± 0.05 (9)[17] in agreement with the formula $Cr(tmd)_2(OH_2)Br^{2+}$.

The *trans*-Diaquobis(1,3-diaminopropane)chromium(III) Cation.—The orange *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$ cation was synthesized by allowing *ca.* 150 mg of *trans*-$[Cr(tmd)_2Cl_2]ClO_4$ to hydrolyze in 50 ml of distilled water for 6 hr at 35° before cooling. HNO_3 (6 ml, 1.0 *F*) was then added and the resulting orange solution was adsorbed on an ion-exchange column which had been prewashed with 2 and 0.1 *F* HNO_3. The orange band was washed with two 50-ml portions of 1.0 *F* followed by 30 ml of 1.25 *F* HNO_3 and the desired cation was eluted with 1.5 *F* HNO_3 into an ice-cooled 50-ml flask, discarding the first 10 ml. The absorption spectrum was measured immediately. This cation was also obtained by using the same procedure with *trans*-$[Cr(tmd)_2Br_2]Br$.

The same complex was also prepared from *trans*-$[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$, either by dissolving an accurately weighed amount in 0.6 *F* HNO_3 and measuring the absorption spectrum or by taking *ca.* 120 mg in 30 ml of 0.6 *F* HNO_3 and adsorbing this solution on a cation-exchange resin (prewashed with 2 *F* and then 0.6 *F* HNO_3). The orange band was washed with 30 ml of 1.25 *F* HNO_3 and the cation was eluted with 1.5 *F* HNO_3 into a 50-ml ice-cooled flask, the first 15 ml being discarded. All four methods gave absorption spectra which were identical in the positions of the maxima and minima and in molar absorbancy indices.

The *cis*-Diaquobis(1,3-diaminopropane)chromium(III) Cation.—The orange *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$ cation was prepared by dissolving *ca.* 150 mg of *trans*-$[Cr(tmd)_2Cl_2]ClO_4$ (or *trans*-$[Cr(tmd)_2Br_2]Br$) and 500 mg of mercuric acetate in 50 ml of 0.6 *F* HNO_3 and leaving the solution at room temperature in the dark for 3 days. The solution was then adsorbed on an ion-exchange column which had been prewashed with 2 *F* and then 0.6 *F* HNO_3. The orange band that formed was washed with 40 ml of 1.0 F, followed by 20 ml of 1.25 *F* HNO_3 and the desired complex was eluted with 50 ml of 1.5 *F* HNO_3 to give an approximately 4 m*F* solution.

The Tetraaquo(1,3-diaminopropane)chromium(III) Cation.—The pink $Cr(tmd)(OH_2)_4^{3+}$ cation was isolated in solution by dissolving *ca.* 150 mg of $[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$ in 50 ml of 0.6 *F* HNO_3 and leaving the solution for 5 days at 35°. The solution was cooled and adsorbed on an ion-exchange column which had been prewashed with 2 *F* and then 0.6 *F* HNO_3. The resulting pink band was washed with 40 ml of 0.8 *F* HNO_3 and then eluted with 50 ml of 1.0 *F* HNO_3, the absorption spectrum being measured immediately. Analysis of this solution (*ca.* 6 m*F* in complex) gave a Cr:N atom ratio of 1:2.08, in acceptable agreement with the formula $Cr(tmd)(OH_2)_4^{3+}$.

Kinetic Measurements.—For the primary hydrolysis studies of *trans*-$Cr(tmd)_2Cl_2^+$, weighed samples of the perchlorate salt were dissolved in the appropriate HNO_3–$NaNO_3$ solutions in glass-stoppered volumetric flasks which were wrapped in Al foil to exclude light[18,19] and immersed in a temperature-controlled water bath. For the primary hydrolysis of *trans*-$Cr(tmd)_2Br_2^+$ and the secondary hydrolysis runs, the cations *trans*-$Cr(tmd)_2Br_2^+$, *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$, and *trans*-$Cr(tmd)_2(OH_2)Br^{2+}$, chromatographically isolated with 0.3, 1.0, and 1.0 *F* HNO_3, respectively, were allowed to react at the appropriate temper-

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ature in glass-stoppered flasks which were wrapped in Al foil. Zero reaction time was taken 5–15 min after the reaction flasks were immersed in the temperature-controlled baths.

In the titrimetric method, 5-ml aliquots of reaction solution, removed at known time intervals, were quenched by delivery into 20 ml of ice-cold water containing 2 ml of concentrated HNO_3. The free halide was determined by potentiometric titration with standard $AgNO_3$, using a silver–silver halide electrode with a saturated calomel reference electrode and a Radiometer pH meter. All titrations were performed in an ice bath.

In the spectrophotometric method, the reaction was followed by leaving the cells containing the reaction solution in the temperature-controlled cell compartment of the spectrophotometer. The visible absorption spectra were scanned at known time intervals, or a constant-wavelength scan was taken over a known time interval.

The cation-exchange chromatographic procedure used was essentially the same as that of MacDonald and Garner[19] with slight modifications. Aliquots (5 ml) were adsorbed (2.8 ml/min) on a 3 × 1 cm cation-exchange resin column cooled by circulating ice water. The complex cations were selectively displaced from the resin by stepwise elution with increasing acid concentrations using the following scheme. Fifty milliliters of 0.3 *F* HNO_3 and then 50 ml of 0.6 *F* HNO_3 removed the *trans*-$Cr(tmd)_2Cl_2^+$ cation, and the *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$ cation was then removed with 50 ml of 1.0 *F* HNO_3 followed by 50 ml of 1.5 *F* HNO_3. Each 50-ml fraction was analyzed for Cr content.

Chemical Analyses.—Cr was analyzed as CrO_4^{2-} by measuring the absorption at 372 nm after decomposition of the complexes with hot alkaline $(NH_4)_2S_2O_8$. Cl and Br were determined by potentiometric titration with standard $AgNO_3$ using a Radiometer pH meter. The complexes were decomposed with hot NaOH and the solutions acidified with HNO_3 prior to titration. N was determined using a micro Kjeldahl apparatus. The complexes were chromatographically isolated with H_2SO_4 instead of HNO_3, and, after the normal Kjeldahl procedure, the released NH_3 was steam distilled into 2% H_3BO_3 and titrated with standard HCl. Professor A. D. Campbell's laboratory at the University of Otago, Otago, New Zealand, performed the C, H, and N analyses of solid complexes. All spectrophotometric measurements were made with a Beckman DBG recording spectrophotometer.

Results

In addition to the previously described[16,20,21] *trans*-$[Cr(tmd)_2Cl_2]ClO_4$, the complexes *trans*-$[Cr(tmd)_2Cl_2]Br$, *trans*-$[Cr(tmd)_2(OH_2)(OH)](ClO_4)_2$, and *trans*-$[Cr(tmd)_2Br_2]X$ ($X = ClO_4$, Br[21]) have been prepared as crystalline solids. From aged solutions of the dihalo complexes, the cations *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ (X = Cl, Br), *cis*- and *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$, and $Cr(tmd)(OH_2)_4^{3+}$ have been isolated by ion-exchange methods and characterized in solution by their visible absorption spectra (Table I, Figures 1–3) and Cr:ligand atom ratios.

Hydrolysis Rates of *trans*-$Cr(tmd)_2X_2^+$.—The hydrolysis of *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br) was followed by halide-release titration, spectrophotometrically and chromatographically (dichloro only). The spectrophotometric data (using both repetitive-scan and fixed-wavelength techniques) were analyzed from the relationship

$$kt = \ln [(A_0 - A_\infty)/(A - A_\infty)]$$

where A_0 is the zero-time absorbance and A_∞ the absorbance assuming 100% aquation to *trans*-$Cr(tmd)_2(OH_2)X^{2+}$. For the dichloro, the wavelengths 387.5 and 600 nm were used, as these correspond to the maximum absorbance difference between parent and daughter. Corresponding wavelengths for the dibromo were 390 and 625 nm (see Figures 1 and 2). Good agreement was observed between the rate constants obtained at the two different wavelengths.

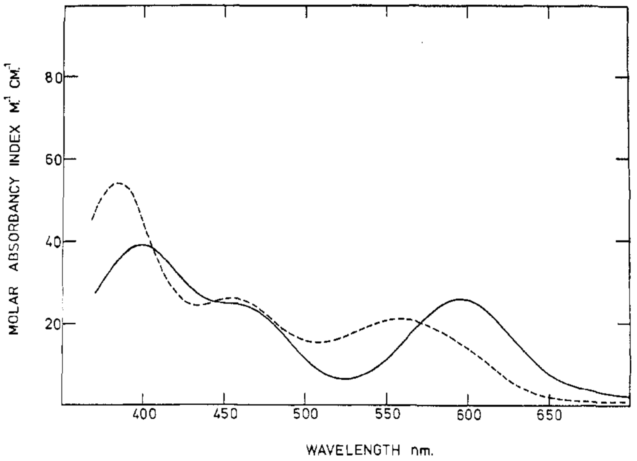

Figure 1.—Visible absorption spectra of *trans*-$Cr(tmd)_2Cl_2^+$ (——) in 0.6 *F* HNO_3 and *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$ (- - - -) in 1.0 *F* HNO_3 at 20–23°.

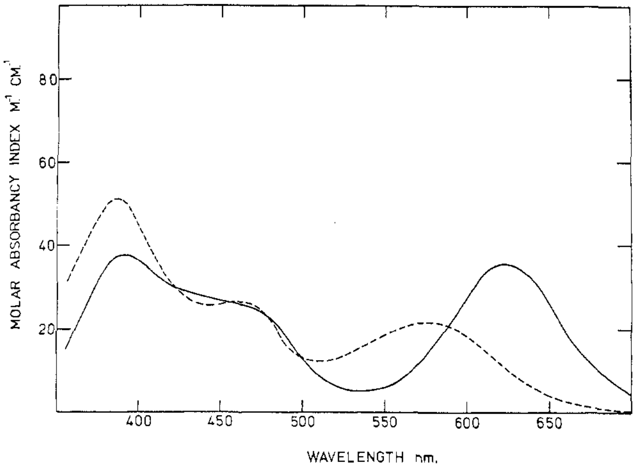

Figure 2.—Visible absorption spectra of *trans*-$Cr(tmd)_2Br_2^+$ (——) in 0.3 *F* HNO_3 at 12–18° and *trans*-$Cr(tmd)_2(OH_2)Br^{2+}$ (- - - -) in 1.0 *F* HNO_3 at 20–23°.

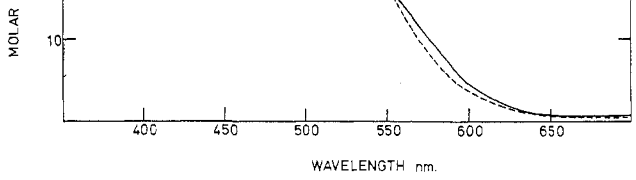

Figure 3.—Visible absorption spectra of *cis*- (- - - -) and *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$ (——) in 0.6–1.5 *F* HNO_3 at 20–23°.

For the halide-release titrations, the data were analyzed using the following equation

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TABLE I

VISIBLE ABSORPTION MAXIMA AND MINIMA (320–650-NM REGION) OF SOME AQUO-, HALOAQUO-, AND DIHALO(DIAMINE)CHROMIUM(III) COMPLEXES IN AQUEOUS ACIDIC SOLUTION AT 12–23°[a]

Cation	Acid (concn, *F*)	Max[b]	Min[b]	Max[b]	Min[b]	Max[b]
trans-$Cr(tmd)_2Cl_2^+$ [d,e]	HNO_3 (0.1–0.6)	398 (38.8 ± 1.3)		457 sh[c] (24.9 ± 1.1)	525 (8.9 ± 1.8)	596 (25.5 ± 0.8)
trans-$Cr(pn)_2Cl_2^+$ [f]	$HClO_4$ (0.1)	395 (38.4)	438 (26.5)	450 (27.3)	515 (10.8)	577 (27.9)
trans-$Cr(en)_2Cl_2^+$ [g]	HNO_3 (0.1)	396 (34.0)	439 (22.3)	453 (22.8)	514 (8.1)	578 (24.5)
trans-$Cr(tmd)_2Br_2^+$ [d]	HNO_3 (0.3)	390 (36.9 ± 0.6)		458 sh (26.7 ± 0.8)	534 (5.8 ± 0.8)	623 (35.5 ± 0.6)
trans-$Cr(pn)_2Br_2^+$ [h]	HNO_3 (0.1)	406 (34.0)		460 sh (27.9)	528 (7.7)	606 (36.9)
trans-$Cr(en)_2Br_2^+$ [i]	$HClO_4$ (0.1)	406 (30.7)		460 sh (24)	530 (5.2	607 (34.9)
trans-$Cr(tmd)_2(OH_2)Cl^{2+}$ [d]	HNO_3 (1.0)	384 (52.5 ± 1.0)	436 (23.3 ± 0.2)	456 (24.9 ± 0.7)	506 (15.7 ± 1.1)	556 (20.6 ± 0.8)
trans-$Cr(pn)_2(OH_2)Cl^{2+}$ [f]	HNO_3 (1.4)	380 (47.2)	427 (22.9)	453 (25.0)	500 (16.0)	546 (20.9)
trans-$Cr(en)_2(OH_2)Cl^{2+}$ [g]	HNO_3 (0.2)	380 (45.5)	428 (23.7)	448 (24.4)	500 (15.4)	546 (20.5)
trans-$Cr(tmd)_2(OH_2)Br^{2+}$ [d]	HNO_3 (1.0)	386 (49.6 ± 0.8)	443 (25.5 ± 0.7)	456 (26.0 ± 0.5)	512 (13.2 ± 1.4)	573 (21.9 ± 0.5)
trans-$Cr(en)_2(OH_2)Br^{2+}$ [i]	HNO_3 (1.4)	384 (44.8)	444 (24.7)	455 (24.9)	504 (14.2)	561 (23.2)
trans-$Cr(tmd)_2(OH_2)_2^{3+}$ [d]	HNO_3 (0.6–1.5)	368 (43.9 ± 0.6)	414 (20.9 ± 0.6)	450 (28.6 ± 0.5)		512 sh (19.6 ± 0.2)
trans-$Cr(en)_2(OH_2)_2^{3+}$ [j]	H^+ (1 *F* $NaNO_3$)	361 (39.2)	404 (20.0)	442 (29.3)		508 sh (22.5)
cis-$Cr(tmd)_2(OH_2)_2^{3+}$ [d]	HNO_3 (1.5)	370 (37.8 ± 0.9)	420 (16.1 ± 1.1)			488 (29.8 ± 0.7)
cis-$Cr(pn)_2(OH_2)_2^{3+}$ [k]	$HClO_4$ (4.0)	369 (48.7)	417 (20.6)			487 (76.0)
cis-$Cr(en)_2(OH_2)_2^{3+}$ [j]	H^+ (1 *F* $NaNO_3$)	367 (42.5)	417 (17.0)			484 (67.0)
$Cr(tmd)(OH_2)_4^{3+}$ [d]	HNO_3 (1.0)	380 (26.6)	438 (8.6)			514 (28.2)
$Cr(pn)(OH_2)_4^{3+}$ [l]	$HClO_4$ (1.0)	383 (24.4)	438 (11.6)			515 (36.0)
$Cr(en)(OH_2)_4^{3+}$ [m]	$HClO_4$ (1.0–3.0)	385 (24.3)	433 (10.7)			512 (41.7)

[a] Values in parentheses are the molar absorbancy indices a_M defined by $A = \log (I_0/I) = a_M cd$ in M^{-1} cm^{-1}. The data in this work are the mean ± the standard deviation of five to nine determinations of the molar absorbancy index. [b] In nanometers (±2 nm for this work). [c] sh = shoulder. [d] This work. [e] References 16, 20, 21. [f] Reference 18. [g] Reference 19. [h] J. A. McLean and R. I. Goorman, *Inorg. Nucl. Chem. Lett.*, **7**, 9 (1971). [i] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964). [j] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958). [k] M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967); **30**, 1984 (1968). [l] D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **6**, 1077 (1967). [m] D. A. House and C. S. Garner, *ibid.*, **5**, 840 (1966).

$$kt = \ln [C_\infty/(C_\infty - C_t)]$$

where C_∞ is the halide ion concentration assuming complete release of one halide ion (equals the initial Cr(III) concentration, C_0) and C_t is the halide ion concentration at time t. Log plots and point-by-point calculations were used for both the spectrophotometric and halide-release methods. The first-order kinetic plots were linear over 2–3 half-lives and the point-by-point calculations showed only random fluctuations over the same period. There was good agreement between the rate constants obtained from both techniques. Analysis of the chromatographic data (Figure 4) followed that of Barona and McLean.[18]

The effect on the observed aquation rate of acid concentration (dichloro only), temperature, and complex ion concentration was studied. The kinetic data are presented in Table II. The energies of activation, E_a, and log PZ values were obtained from a least-squares analysis of a plot of log k *vs.* $1000/T$°K and the standard entropies of activation, $\Delta S°_{298}$, were calculated using the equation

$$\Delta S°_{298} = [\Delta H°_{298} + 1000/298] + 4.576[\log k - \log 6.2128 \times 10^{12}]$$

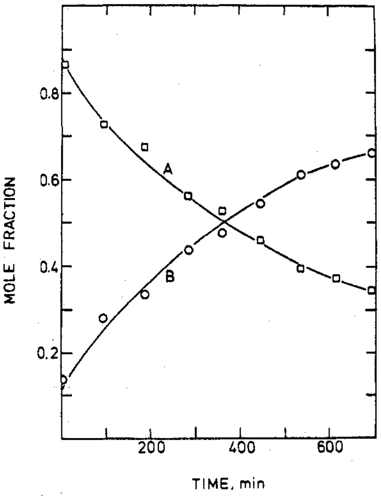

Figure 4.—Concentration–time curves for the hydrolysis of *trans*-$Cr(tmd)_2Cl_2^+$ in 0.1 *F* HNO_3 at 27.5°: (A) *trans*-$Cr(tmd)_2Cl_2^+$; (B) *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$.

where $\Delta H°_{298} = E_a - 0.59$ kcal mol^{-1} and k (in sec^{-1}) is the first-order rate constant at 25°. These data are presented in Table III.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE PRIMARY HYDROLYSIS OF *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br) IN ACIDIC SOLUTION

Temp, °C	$[HNO_3]$, *F*	C_0, m*F*	10^5k,[a] sec^{-1}	10^5k (calcd),[b] sec^{-1}	Method[c]
			(A) *trans*-$Cr(tmd)_2Cl_2^+$		
25.0	0.1			2.08	
27.5	0.1	4.40	2.90 ± 0.15	2.94	C (1)
35.0	0.1	3.54–4.43	7.85 ± 0.17	7.96	H (5), S (3)
40.0	0.1	4.28–4.56	16.0 ± 0.8	15.1	H (2)
45.5	0.1	4.08–4.66	29.2 ± 1.7	29.7	H (3)
50.0	0.1	3.85–5.66	50.1 ± 1.7	50.9	H (3), S (5)
35.0	0.01[d]	3.91–4.24	8.35 ± 0.42		H (2)
35.0	0.001[d]	4.00–4.32	11.6 ± 0.6		H (2)
			(B) *trans*-$Cr(tmd)_2Br_2^+$		
14.0	0.3	1.96–3.72	8.18 ± 0.21	8.16	H (7)
15.0	0.3	2.33–4.44	9.69 ± 0.29	9.39	S (6)
20.0	0.3	1.79–4.12	17.8 ± 0.7	18.6	H (3), S (3)
25.0	0.3	2.72–4.77	36.2 ± 1.3	35.9	H (3), S (4)

[a] The numbers quoted are the mean ± the standard deviation. Where the number of determinations is ≤2, an error of 5% is assumed. [b] Rate constants calculated using the E_a and log *PZ* values in Table III. [c] Method used in monitoring the reaction. C = chromatographic separation; H = halide-release titration; S = spectrophotometric. Numbers in parentheses are the number of individual determinations. [d] Ionic strength 0.1 *M* with $NaNO_3$.

Hydrolysis Rates of *trans*-$Cr(tmd)_2(OH_2)X^{2+}$.—The spectrophotometric scans of hydrolyzing *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ (X = Cl, Br) did not hold isosbestic points, and the rate of loss of parent was followed by halide-release titration only. Product separation of hydrolyzed *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ solutions (or aged acidic solutions of *trans*-$Cr(tmd)_2X_2^+$, which produce *trans*-$Cr(tmd)_2(OH_2)X^{2+}$ as the first formed product) by ion-exchange chromatography showed that *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$, *cis*-$Cr(tmd)_2(OH_2)_2^{3+}$, and $Cr(tmd)(OH_2)_4^{3+}$ were formed.

The first-order rate plots obtained by halide release from *trans*-$Cr(tmd)_2(OH_2)Cl^{2+}$ were linear for 1–2 half-lives, but for the bromo analog, negative deviation from linearity was observed after about 0.5 half-life. The values of the rate constants are given in Table IV and the calculated E_a, log *PZ*, and $\Delta S°_{298}$ values in Table III. As these data are associated with a complex reacting system at high ionic strength, their absolute values should be interpreted with caution.

Discussion

On the basis of much cited information[22-24] that complexes with six-membered rings are "less stable" than those with five-membered rings and the observation[9] that *trans*-$Co(tmd)_2Cl_2^+$ hydrolyzes in acidic solution with a half-life of 13 sec at 25°, we expected rapid hydrolysis reactions for *trans*-$Cr(tmd)_2X_2^+$ (X = Cl, Br) complicated by considerable Cr–N bond rupture. Neither of these expectations were fulfilled. The cations *trans*-$M(en)_2Cl_2^+$ [19,25,26] and *trans*-$M(pn)_2Cl_2^+$ [18,27] (M = Co, Cr) hydrolyze slowly (half-lives of 3–8 hr at 25°) in aqueous acidic solution. In the Cr(III) systems, halide release accounts for about 90% of the reaction and Cr–N bond rupture for the remainder. Some isomerization also occurs in the *trans*-$Cr(pn)_2Cl_2^+$ system. In the Co(III) systems, considerable isomerization occurs (35% *cis*-$Co(en)_2(OH_2)Cl^{2+}$ is observed[28]) but no Co–N bond rupture has been detected. (See, however, ref 29.)

TABLE III

KINETIC PARAMETERS FOR THE PRIMARY AND SECONDARY HYDROLYSIS OF SOME *trans*-$M(AA)_2X_2^+$ CATIONS (M = Co, Cr; AA = en, pn, tmd; X = Cl, Br) IN ACIDIC SOLUTION AT 25°

Complex[a]	Acidity,[b] *F*	10^5k, sec^{-1}	E_a, kcal kcal mol^{-1}	Log [*PZ* (sec^{-1})]	$\Delta S°_{298}$, cal deg^{-1} mol^{-1}
t-$Cr(en)_2Cl_2^+$ [c]	0.1	2.25[d] 7.2 (35°)[e]	23.2	12.37	−4
t-$Co(en)_2Cl_2^+$ [f-h]	0.1	3.2	26.2	15.9	+14
t-$Cr(pn)_2Cl_2^+$ [i]	0.1	8.14 (35°)			
t-$Co(pn)_2Cl_2^+$ [f]	0.1	6.2	28	(16.3)[j]	(+14.1)[j]
t-$Cr(tmd)_2Cl_2^+$ [k]	0.1	2.08 7.85 (35°)	24.5	13.26	+0.1
t-$Co(tmd)_2Cl_2^+$ [l,f]	?H^+	5330	21.3	(14.3)[j]	+6.9
t-$Cr(en)_2Br_2^+$ [m,n]	0.1	32.6[d]	22.4	(12.9)[j]	−1
t-$Co(en)_2Br_2^+$ [g]	0.01	13.9	25.6	14.9	(+7.5)[j]
t-$Cr(tmd)_2Br_2^+$ [k]	0.3	36.2	22.9	13.34	+0.5
t-$Co(tmd)_2Br_2^+$ [l]	?H^+	9490	18.3	(12.4)[j]	−2.2
t-$Cr(en)_2(OH_2)Cl^{2+}$ [o]	0.1	~0.08[d] 0.28 (35°)			
t-$Co(en)_2(OH_2)Cl^{2+}$ [p]	0.01	0.28			
t-$Cr(tmd)_2(OH_2)Cl^{2+}$ [k]	1.0	0.29[d]	21.7	10.39	−13.1
t-$Cr(en)_2(OH_2)Br^{2+}$ [n]	1.4	0.3[d]			
t-$Cr(tmd)_2(OH_2)Br^{2+}$ [k]	1.0	1.04[d]	24.2	12.73	−2.2

[a] *t* = *trans*. [b] HNO_3 unless stated otherwise. [c] Reference 25. [d] Rate determined by halide release only. [e] Reference 19. [f] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953). [g] S. Chan and M. Tobe, *J. Chem. Soc.*, 5700 (1963). [h] S. C. Chan, *Aust. J. Chem.*, **20**, 595 (1967). [i] Reference 18. [j] Numbers in parentheses are log *PZ* or $\Delta S°_{298}$ values calculated from data in the original literature. [k] This research. [l] Reference 9. [m] A. M. Weiner and J. A. McLean, *Inorg. Chem.*, **3**, 1469 (1964). [n] L. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964). [o] D. J. MacDonald and C. S. Garner, *ibid.*, **1**, 20 (1962). [p] S. C. Chan, *J. Chem. Soc.*, 5137 (1963).

Thus the primary step in the hydrolysis of *trans*-$Cr(tmd)_2X_2^+$ could conceivably involve three reaction

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TABLE IV

FIRST-ORDER RATE CONSTANTS FOR THE FORMATION OF X^- IN THE HYDROLYSIS OF *trans*-$\mathrm{Cr(tmd)_2(OH_2)X^{2+}}$ (X = Cl, Br) IN 1.0 *F* $\mathrm{HNO_3}$[a]

Temp, °C	C_0, m*F*	10^5k,[a] $\mathrm{sec^{-1}}$	Method[c]
	(A) *trans*-$\mathrm{Cr(tmd)_2(OH_2)Cl^{2+}}$		
25.0		0.29 ± 0.05[b]	
45.0	2.61–4.32	2.88 ± 0.06	H (3)
55.0	2.78–3.81	8.20 ± 0.23	H (4)
	(B) *trans*-$\mathrm{Cr(tmd)_2(OH_2)Br^{2+}}$		
25.0		1.04 ± 0.25[b]	
35.0	2.34–3.66	3.91 ± 0.12	H (3)
45.0	2.82	13.6 ± 0.8	H (1)

[a] See footnotes *a–c* in Table II.

pathways—Cr–X bond rupture, Cr–N bond rupture, or isomerization to the cis form, followed by either of the two postulated bond-rupture processes. The characterization of *trans*-$\mathrm{Cr(tmd)_2(OH_2)X^{2+}}$ as the only (>98%[30]) reaction product is convincing evidence that the latter two pathways have a negligible contribution in the loss of the parent. Nevertheless, a slow preisomerization, followed by rapid Cr–X bond rupture and rapid isomerization of the resulting haloaquo, would also account for the observed product. Such a reaction scheme would be highly fortuitous and the observation[20] that *cis*-$\mathrm{Cr(tmd)_2Cl_2^+}$ readily isomerizes to the trans form is contrary to this proposed pathway.

All the evidence we have points to a single pathway for the primary hydrolysis of the dihalo ions in acidic solution according to the equation

$$trans\text{-}\mathrm{Cr(tmd)_2X_2^+ + H_2O \longrightarrow}\ trans\text{-}\mathrm{Cr(tmd)_2(OH_2)X^{2+} + X^-} \qquad (1)$$

Thus, the spectrophotometric scans hold sharp isosbestic points (see figure in ref 15) for 2–3 half-lives and the observed positions and intensities are in good agreement with those predicted from the spectra of the two pure components (Figures 1 and 2). For the dichloro species, the experimentally observed points are at 571 (19.0), 445 (24.3), and 407 nm (37.4 $M^{-1}\ \mathrm{cm^{-1}}$), while those predicted from Figure 1 are at 570 (19.8), 445 (25.0), and 407 nm (37.5 $M^{-1}\ \mathrm{cm^{-1}}$). For the dibromo species, five isosbestic points are predicted (Figure 2) at 588 (20.7), 498 (13.4), 479 (22.7), 456 (26.4), and 423 nm (29.9 $M^{-1}\ \mathrm{cm^{-1}}$) and five are experimentally observed at 590 (21.1), 498 (13.8), 479 (22.9), 453 (27.0), and 423 nm (29.8 $M^{-1}\ \mathrm{cm^{-1}}$).

These data suggest that the reaction proceeds as in (1), as sharp isosbestic points are usually indicative of a reaction giving a single product or two products in a constant ratio (see, however, ref 31). This latter alternative is unlikely, as only one daughter product, *trans*-$\mathrm{Cr(tmd)_2(OH_2)X^{2+}}$, was detected by ion-exchange chromatography from parent solutions aged for 3–5 half-lives. The good agreement between the chromatographically determined rate constant and that calculated from the spectral and halide-release data also indicates only one daughter.

The daughter products, *trans*-$\mathrm{Cr(tmd)_2(OH_2)X^{2+}}$, have been characterized in solution by satisfactory Cr:X atom ratios, ion-exchange behavior characteristic of a 2+ charged ion, and constant visible absorption spectral parameters. The positions of the maxima and minima, the values of the molar absorbancy indices, and the shapes of the spectral curves are very similar to those of the *trans*-$\mathrm{Cr(AA)_2(OH_2)X^{2+}}$ (AA = en, pn) analogs and we feel confident of our assignment of a trans configuration to the isolated $\mathrm{Cr(tmd)_2(OH_2)X^{2+}}$ ions.

Despite a careful search for Cr–N bond rupture products in the primary hydrolysis of *trans*-$\mathrm{Cr(tmd)_2X_2^+}$, none were detected. This contrasts with the *trans*-$\mathrm{Cr(AA)_2X_2^+}$ (AA = en, pn), where about 10% of Cr–N bond rupture occurs in competition with halide release.[18,19] An even greater amount of bond rupture occurs in the acid hydrolysis of Cr(III) complexes with more chelated ring systems.[32,33]

Thus, we conclude that for Cr(III) at least, *the tmd complexes are more robust than the en complexes*, with respect to Cr–N rupture, despite an increase in ring size. Additional support for this hypothesis comes from the observations that $\mathrm{Cr(tmd)_3^{3+}}$ hydrolyzes more slowly than $\mathrm{Cr(en)_3^{3+}}$ in acid solution[34] and that in the acid hydrolysis of *trans*-$\mathrm{Cr(en)(tmd)(OH_2)_2^{3+}}$, the ethylenediamine ring is lost first to give $\mathrm{Cr(tmd)(OH_2)_4^{3+}}$.[35]

Table III lists the kinetic parameters for a number of Co(III) and Cr(III) complexes pertinent to this discussion. For the primary acid hydrolysis of *trans*-$\mathrm{Co(AA)_2Cl_2^+}$ complexes, the rate constant increases dramatically in the order AA = en, pn, *meso*-bn, and tmd[8] with 10^5k = 3.2, 6.2, 420, and 5330 $\mathrm{sec^{-1}}$, respectively, at 25°. The increase in rate with increasing methyl substituents on the ring carbon atoms has been interpreted[36] as a result of steric strain. Similarly, a conventional explanation of the labilization of the tmd complex relative to the en complex would be "release of steric strain in forming a dissociated transition state,[9] as the six-membered rings are "more crowded"! A peculiar result is a decrease in observed rate constant (to 10^5k = 300 $\mathrm{sec^{-1}}$ at 25°) relative to tmd, when the *gem*-dimethyl-substituted ligand with a six-membered ring, dan,[8] is used.[27,37] The ring strain in *trans*-$\mathrm{Co(AA)_2Cl_2^+}$ (AA = tmd, dan) will, presumably, be similar (it is difficult to see how it could be less for dan) and increasing methyl substitution should cause a rate increase if the arguments used in the five-membered ring systems are still valid.

For reaction 1 in the *trans*-$\mathrm{Cr(AA)_2Cl_2^+}$ systems, 10^5k has values of 7.2 ± 0.6, 8.14 ± 0.18, and 7.85 ± 0.17 $\mathrm{sec^{-1}}$ for AA = en, pn, and tmd at 35° in 0.1 *F* $\mathrm{HNO_3}$. These nearly equal rate constants do not reflect the considerable changes observed in the analogous Co(III) systems although Barona and McLean ascribed the possible rate increase from en to pn as a steric effect.[18]

The structures of *trans*-$\mathrm{[M(en)_2Cl_2]Cl\cdot HCl\cdot 2H_2O}$

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(30) Our experimental uncertainty could allow up to 2% of other plausible Cr(III) species to be present.

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(M = Co, Cr) have been determined[38,39] by single-crystal X-ray analysis and the salts are isomorphous. Also, the *trans*-[M(tmd)$_2$Cl$_2$]ClO$_4$ (M = Co, Cr) are known to be isomorphous,[16] and, as *trans*-[Co(tmd)$_2$Cl$_2$]Cl·HCl·2H$_2$O has both tmd rings in the chair configuration,[40] the rings in the Cr(III) complexes will have similar configurations and thus similar ring strain. Consequently, the ring strain differences between *trans*-M(en)$_2$Cl$_2^+$ and *trans*-M(tmd)$_2$Cl$_2^+$ (M = Co, Cr) will be of similar magnitudes. It is thus apparent that ring strain alone cannot account for the rate increase observed in the hydrolysis of *trans*-Co(tmd)$_2$Cl$_2^+$, as on this basis, the Co(III) and Cr(III) complexes should behave similarly.

We believe that the increased reaction rate for *trans*-Co(tmd)$_2$Cl$_2^+$ relative to *trans*-Cr(tmd)$_2$Cl$_2^+$ is due to the greater flexibility inherent in cobalt(III)–polyamine systems, relative to those of Cr(III). Well-characterized geometric isomerization is rare in mono- or dihalochromium(III)–polyamine systems[41] and where isomerization has been reported,[18] it is usually accompanied by Cr–N bond rupture. On the other hand, geometric and proton inversion isomerizations are common in analogous Co(III) systems[42] and Co–N bond rupture is usually[29] negligible.

In Co(III) complexes with isolated six-membered rings, *e.g.*, in *trans*-[Co(tmd)$_2$Cl$_2$]Cl·HCl·2H$_2$O,[40] *trans*-[Co(tmd)$_2$(NO$_3$)$_2$]NO$_3$,[43] *cis*-(−)$_{589}$-[Co(tmd)$_2$(NCS)$_2$][Sb-(+)-tart]·2H$_2$O,[44] and (−)-[Co(tmd)$_3$]Br$_3$·H$_2$O,[45] the chair ring conformation has been shown by single-crystal X-ray analysis. However, with fused six-membered ring systems, *e.g.*, in α-[Co(en)(dpt)Cl]I$_2$·H$_2$O[46] and β-[Co(en)(dpt)Cl]ZnCl$_4$,[8,47] a chair–twist-boat peripheral dpt configuration is adopted in the solid state.

We suggest that, in solution, the tmd rings of *trans*-Co(tmd)$_2$Cl$_2^+$ can adopt the twist-boat configuration.[15] Such distortions would lead to considerable steric interaction between the central methylene protons and the axial chloro ligands and so to a considerably enhanced reaction rate. It then follows that the decrease in the hydrolysis rate of *trans*-Co(dan)$_2$Cl$_2^+$ relative to *trans*-Co(tmd)$_2$Cl$_2^+$ is due to the bulky *gem*-dimethyl substituents restricting the distortion from the favored chair six-membered ring configuration.

Unexpected support for this hypothesis has come from a recent study[48] of (+)-Co(tmd)$_3^{3+}$, where, from the temperature dependence of the circular dichroism spectra, it is calculated that 30% of this complex is in the twist-boat form in aqueous solution at 20°. The conclusion from this present work that Cr(tmd)$_3^{3+}$ would not exhibit these distortions awaits experimental verification.

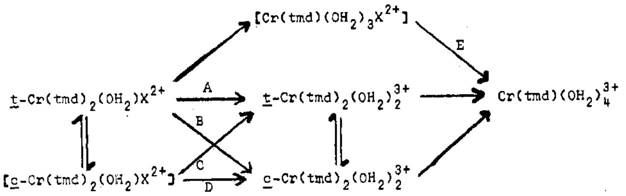

Figure 5.—A possible reaction scheme for the hydrolysis of *trans*-Cr(tmd)$_2$(OH$_2$)X^{2+} in 1.0 *F* HNO$_3$ at 45.0°. t = *trans;* c = *cis;* species in brackets have not been characterized.

A similar situation occurs in the *trans*-M(AA)$_2$Br$_2^+$ systems. The 10^5k values are 13.9 and 9490 sec^{-1} at 25° when M = Co and AA = en and tmd, respectively. Corresponding data for M = Cr are 32.6 and 36.2 sec^{-1}. Again we attribute the enhanced rate in the *trans*-Co(tmd)$_2$Br$_2^+$ case to the formation of twist-boat tmd rings in solution.

The hydrolysis rate ratio for the dibromo relative to the dichloro species of 17.4 at 25° is normal for *trans*-dihalochromium(III) systems (see Table II of ref 14), and the slightly increased rate of *trans*-Cr(tmd)$_2$Br$_2^+$ relative to *trans*-Cr(en)$_2$Br$_2^+$ is probably not significant. The almost zero $\Delta S°_{298}$ values for the primary hydrolysis of the *trans*-Cr(tmd)$_2$X$_2^+$ (X = Cl, Br) ions are in agreement with Tobe's suggestion[49] that steric change is associated with a higher (and positive) $\Delta S°_{298}$ than is retention of configuration, as no isomerization is observed.

Variation of the initial *trans*-Cr(tmd)$_2$X$_2^+$ concentration produced no variation in rate constant outside experimental error, but decreasing the acidity (at ionic strength of 0.1 *F*) caused an increase in hydrolysis rate (Table II). In 0.001 *F* HNO$_3$ (where the change in *k* is significant), the log plots for the chloride-release data showed a positive deviation from linearity at less than 1 half-life, suggesting an increase in secondary hydrolysis, probably due to the formation of the more labile *trans*-Cr(tmd)$_2$(OH)Cl$^+$. The data we have are insufficient to consider this effect in more detail.

The hydrolysis of the *trans*-Cr(tmd)$_2$(OH$_2$)X^{2+} ions has also been investigated. Preliminary spectroscopic studies showed that a complex reaction was taking place and the rate was followed by halide release only. The isolation of *cis*- (by Hg^{2+} catalysis) and *trans*-Cr(tmd)$_2$(OH$_2$)$_2^{3+}$ and Cr(tmd)(OH$_2$)$_4^{3+}$ from aged solutions indicates that these secondary hydrolyses are complicated by concurrent Cr–N bond rupture and isomerization of either parent or daughter although no *cis*-Cr(tmd)$_2$(OH$_2$)Cl^{2+} was detected. This complex situation is similar to that observed in the hydrolysis of *trans*-Cr(en)$_2$(OH$_2$)X^{2+} [50] and 1,2,6-Cr(dien)(OH$_2$)Cl$_2^+$.[10] The hydrolysis products mentioned above were characterized in solution by the similarity of their visible absorption spectra with those of the known en and pn analogs (Table I and Figure 3) and ion-exchange behavior compatible with a 3+ charge. Satisfactory Cr:N atom ratios were also obtained for Cr(tmd)(OH$_2$)$_4^{3+}$.

The nonlinearity of the first-order rate plots for the hydrolysis of *trans*-Cr(tmd)$_2$(OH$_2$)Br^{2+} in 1.0 *F* NHO$_3$ at 45.0° also suggests a complex reaction. However,

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we have preliminary evidence[35] that the nitrate ion may be having a catalytic influence. Rate plots for this system in 1.0 F $HClO_4$ or 0.5 F H_2SO_4 also exhibit negative deviation from linearity, but the values of the rate constants calculated from the initial slopes are about 60% lower.

A possible reaction scheme consistent with the above observations is outlined in Figure 5. Paths A–E all contribute to the formation of halide ion and our qualitative observations suggest that A, B, and E predominate. It is not possible from the present data to analyze this scheme more completely but the mode of hydrolysis and/or isomerization of *trans*-$Cr(tmd)_2(OH_2)_2^{3+}$ is under investigation.

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The Formation Constant of Bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine]iron(II). Evidence for Formation of a Protonated Bis Complex

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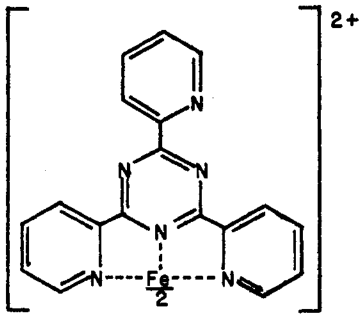
A value of (2.8 ± 1.2) × 10^{11} for the formation constant of bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine]iron(II), $Fe(TPTZ)_2^{2+}$, was determined from the pH dependence of the conditional formation constant which was spectrophotometrically evaluated. Spectroscopic evidence for the formation of a protonated bis complex, $Fe(TPTZ)_2H^{3+}$, was observed at high hydrogen ion concentrations (pH 1.3–2.0) and at a ligand-to-metal mole ratio of 25. Inclusion of the formation of $Fe(TPTZ)_2H^{3+}$ was necessary to rationalize the pH dependence of the conditional formation constant of $Fe(TPTZ)_2^{2+}$. A value of (2.5 ± 1.1) × 10^2 for the formation constant of $Fe(TPTZ)_2H^{3+}$ was determined.

Introduction

The tridentate ligand 2,4,6-tri(2-pyridyl)-1,3,5-triazine, TPTZ, which resembles terpyridine, was first synthesized by Case and Koft.[2] Diehl, *et al.*,[3] first characterized the bis complex of this ligand with iron(II). The high molar absorptivity in aqueous solution at 593 nm has led to the utilization of the complex formation in iron(II) determinations.[3–6] Kratochvil and White[7] made use of the rapid reaction between EDTA and $Fe(TPTZ)_2^{2+}$ in determining trace amounts of EDTA, and Pagenkopf and Margerum[8] utilized the same reaction to characterize the formation and dissociation kinetics of $Fe(TPTZ)_2^{2+}$. The formation equilibrium was first studied by Buchanan, *et al.*[9] Evidence for any appreciable formation of the mono complex, $Fe(TPTZ)^{2+}$, has not been observed.[3,8,9]



$Fe(TPTZ)_2^{2+}$

Buchanan, *et al.*,[9] assuming TPTZ to be weakly monobasic ($K_H = 1.3 \times 10^3\ M^{-1}$), determined the formation constant of $Fe(TPTZ)_2^{2+}$ over the pH range of 1.9–2.2 to be 1.75 × 10^{10}. Pagenkopf and Margerum[8] assumed TPTZ to be weakly dibasic ($K_H = 3.4 \times 10^3$, $K_{2H} = 5.4 \times 10^2\ M^{-1}$) and reevaluated the formation constant, $\beta_2 = (3.0 \pm 1.8) \times 10^{12}$, over a pH range of 2.9–4.5. Prasad and Peterson[10] in the course of a study of the stability of $Co(TPTZ)_2^{2+}$ also reevaluated the basicity of TPTZ and concluded that $K_H = (8 \pm 5) \times 10^2$ and $K_{2H} = (6.58 \pm 0.01) \times 10^2$. Pagenkopf and Margerum[8] discounted the formation of a protonated bis complex on the basis of measured dissociation rates at high hydrogen ion concentrations (pH <2.0). The present study was undertaken to accurately determine the formation constant for $Fe(TPTZ)_2^{2+}$. The evidence for the formation of $Fe(TPTZ)_2H^{3+}$ was somewhat unexpected; its existence would indicate, however, that the mechanism for the acid dissociation of $Fe(TPTZ)_2^{2+}$ is more involved than that originally put forth by Pagenkopf and Margerum.[8]

Experimental Section

Solutions of the ligand TPTZ (G. Frederick Smith Chemical Co.) were prepared by dissolving in a few drops of concentrated sulfuric acid accurately weighed quantities of the trihydrate (mol wt 366.3), which had been purified twice by recrystallization

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