for the $(C_6H_5)_2M(mnt)_2{}^{2-}$ complexes is a reasonable proposal.

The tin-carbon asymmetric stretching mode in the $(CH_3)_2Sn(mnt)_2{}^{2-}$ ion is found at 531 cm^{-1}. The region where the symmetric stretching mode would occur (if present) is masked by ligand absorptions.[10] The value of the methyl-tin coupling constant is closer to the value for a cis disposition of methyl groups[20] than that observed for a complex exhibiting the trans configuration.[32] Therefore, as a tentative proposal, a distorted cis geometry is preferred for the $(CH_3)_2Sn(mnt)_2{}^{2-}$ moiety. Further investigations on the stereochemistry of these complexes is in progress.

Registry No. $(CH_3)_2Sn(mnt)$, 16257-02-6; $(C_6H_5)_2Sn(mnt)$, 17250-19-0; $(C_6H_5)_2Pb(mnt)$, 37862-08-1; $[(C_2H_5)_4N]_2Sn(mnt)_2(CH_3)_2$, 37837-96-0; $[(C_2H_5)_4N]_2Sn(mnt)_2(C_6H_5)_2$, 37837-97-1; $[(C_2H_5)N]_2Pb(mnt)_2$, 37862-09-2; $[(C_4H_9)_4N]_2Pb(mnt)_2(C_6H_5)_2$, 37837-98-2; $[(C_4H_9)_4N]_2Sn(mnt)_2(C_6H_5)_2$, 37837-99-3; $[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Cl$, 37837-95-9; $[(C_6H_5)_4As]_2Sn(mnt)_2(CH_3)_2$, 37953-08-5; $[(C_6H_5)_4As]Sn(mnt)(C_6H_5)_2Cl$, 37838-00-9; $[(C_6H_5)_4As]Pb(mnt)_2(C_6H_5)_2Cl$, 37838-55-4; $[(C_6H_5)_4As]_2Pb(mnt)_2$, 37862-10-5; $[(C_6H_5)_4As]Sn(mnt)(CH_3)_2Br$, 37838-01-0; $[(C_6H_5)_4As]Sn(mnt)(CH_3)_2I$, 37838-02-1; $[(C_6H_5)_4P]Sn(mnt)(CH_3)_2Cl$, 37838-03-2.

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(32) M. M. McGrady and R. S. Tobias, *J. Amer. Chem. Soc.*, **87**, 1909 (1965).

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Hydrolysis Kinetics of the *trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) and -cobalt(III) Cations in Acidic Aqueous Solution

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The syntheses of *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ and *trans*-$[Cr(en)(tmd)(OH)(OH_2)](ClO_4)_2$ and a simplified synthesis of *trans*-$[Co(en)(tmd)Cl_2]X$ ($X = Cl \cdot H_2O, ClO_4$) are described. From these, the cations *trans*-$Cr(en)(tmd)Cl_2{}^+$, *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$, *trans*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$, *cis*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$, *trans*-$Co(en)(tmd)Cl_2{}^+$, *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$, and *cis*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ have been isolated and characterized in solution. At 25.0°, the first-order rate constants and kinetic parameters for the primary hydrolysis of *trans*-$M(en)(tmd)Cl_2{}^+$ ($M = Cr, Co$) (corresponding to the formation of *trans*- and predominantly *cis*-$M(en)(tmd)(OH_2)Cl^{2+}$, respectively) are $10^5 k$ (sec^{-1}) = 1.93 ± 0.09 (0.4 *F* HNO_3), 39.6 ± 1.2 (0.3 *F* HNO_3); E_a (kcal mol^{-1}) = 23.4 ± 0.3, 24.2 ± 0.3; log [PZ (sec^{-1})] = 12.43, 14.38; $\Delta S^{\ddagger}{}_{298}$ (cal deg^{-1} mol^{-1}) = −3.6 ± 0.5, +5.1 ± 0.5, respectively. The first-order halide release rate constants and kinetic parameters for *trans*- and *cis*-$M(en)(tmd)(OH_2)Cl^{2+}$ ($M = Cr, Co$, respectively) in 1.0 *F* HNO_3 at 25.0° are (units as above) $10^5 k$ = 0.31 ± 0.05, 10.3 ± 0.2; E_a = 21.9 ± 1, 18.8 ± 0.5; log PZ = 10.54, 9.81; $\Delta S^{\ddagger}{}_{298}$ = −12.3 ± 2, −15.7 ± 1, respectively. The *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$ cation also hydrolyzes *via* Cr–N bond rupture, and $Cr(tmd)(OH_2)_4{}^{3+}$ has been isolated as the major decomposition product.

Introduction

As part of a program to investigate the acid hydrolysis of some analogous Cr(III) and Co(III) complexes,[1] we have studied the rate of halide release and mode of decomposition of the *trans*-$M(en)(tmd)Cl_2{}^+$ cations[2] ($M = Cr, Co$) in acid solution. The rate constants and kinetic parameters allow a comparison with similar data for the *trans*-$M(AA)_2Cl_2{}^+$ ($M = Cr, Co$; AA = en, pn, tmd) systems.

Experimental Section

1,2-Diaminoethane (ethylenediamine) was obtained from Fluka AG Laboratories and 1,3-diaminopropane (trimethylenediamine) from Aldrich Chemical Co.; both were used without further purification. All other chemicals were of reagent grade quality. The ion-exchange material was Zeo-Karb 225, SRC-6 cation-exchange resin in the Na^+ form (52–100 mesh). The dichloro cations were isolated using 6 × 1 cm columns cooled by a jacket of circulating ice water, and all others were isolated using a 10 × 1 cm tap water cooled column. The preparation and analyses of the cationic complexes were repeated at least three times to check the reproducibility of the ion-exchange separations and the visible absorption spectral parameters.

Caution! Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these complexes should be treated as potentially explosive and handled with care.

***trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)-chromium(III) Perchlorate.** This salt was obtained using a modification of the preparation used for *trans*-$[Cr(tmd)_2Cl_2]ClO_4$.[1,3] A solution of green $CrCl_3 \cdot 6H_2O$ (16.2 g) in DMSO[2] (75 ml) was boiled for 10 min. An equimolar mixture of the diamines (9.3 ml) in DMSO (45 ml) was added to the hot solution and boiling was continued 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 and washed with acetone (three 50-ml portions), and the still damp solid was suspended in HCl (60 ml, 12 *F*). This suspension was heated on a steam bath for 10 min, when $HClO_4$ (30 ml, 60%) was added. The solution was cooled slowly and the green crystals that deposited overnight were collected, washed with 2-propanol and then ether, and air-dried. The mother liquors were returned to the steam bath for 15 min. HCl (15 ml, 12 *F*) was added and the solution was cooled slowly. This procedure was repeated several times to give either green or purple crystals. The

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(1) M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972), and references cited therein.

(2) Abbreviations used: en, $NH_2(CH_2)_2NH_2$; pn, $NH_2CH(CH_3)CH_2NH_2$; tmd, $NH_2(CH_2)_3NH_2$; DMSO, dimethyl sulfoxide.

(3) D. A. House, *Inorg. Nucl. Chem. Lett.*, **6**, 741 (1970).

total yield was 6.5 g or 29%. Microscopic examination of all the crystal crops showed them to be mixtures. Those containing the bulk of the green product were recrystallized from hot 0.1 *F* HCl by the addition of equal volumes of 12 *F* HCl and 60% $HClO_4$. Green crystals slowly deposited leaving a red solution and these were collected, washed, and dried as above. *Anal.* Calcd for $[Cr(en)(tmd)Cl_2]ClO_4$: C, 16.83; H, 5.05; N, 15.70; Cr, 14.59; ligand Cl, 19.91. Found: C, 17.37; H, 5.06; N, 15.28; Cr, 14.70; ligand Cl, 19.99.

The purple material obtained was *cis*-$[Cr(en)_2Cl_2]Cl\cdot H_2O$. *Anal.* Calcd for $[Cr(en)_2Cl_2]Cl\cdot H_2O$: C, 16.19; H, 6.07; N, 18.90; Cr, 17.54; Cl, 35.92. Found: C, 17.71; H, 5.95; N, 19.48; Cr, 16.60; Cl, 34.90.

***trans*-Hydroxoaquo(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) Perchlorate.** A suspension of *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ (1.1 g) in water (10 ml) containing pyridine (4 ml) was heated on a steam bath for 15 min to form a red-brown solution. $NaClO_4\cdot H_2O$ (2.5 g) was added and the orange-red crystals (0.6 g, 46%) that deposited from the ice-cooled solution were collected, washed with 2-propanol and ether, and air-dried. *Anal.* Calcd for $[Cr(en)(tmd)(OH_2)(OH)](ClO_4)_2$: C, 14.28; H, 5.00; N, 13.33; Cr, 12.38. Found: C, 15.53; H, 5.29; N, 13.28; Cr, 12.10.

***trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Chloride Monohydrate.** A modification of the method of Schlessinger[4] for *trans*-$[Co(en)_2Cl_2]Cl$ was used. A solution of $CoCl_2\cdot 6H_2O$ (30 g) in water (90 ml) was added to an equimolar mixture of the diamines (19.1 ml) in 100 ml of water and a vigorous stream of air was drawn through the liquid for 6 hr. The dark red oxidized solution was placed in an evaporating dish and HCl (66 ml, 12 *F*) was added. The volume was reduced to 100 ml on a steam bath and the green crystals that were obtained on cooling overnight were washed with 2-propanol and ether and air-dried. The mother liquors with added HCl (20 ml, 12 *F*) were returned to the steam bath for 20 min to obtain a second crop. The total yield was 11.6 g (31%). *Anal.* Calcd for $[Co(en)(tmd)Cl_2]Cl\cdot H_2O$: C, 18.90; H, 6.30; N, 17.64; Co, 18.58; Cl, 33.54. Found: C, 18.75; H, 5.98; N, 17.71; Co, 18.30; Cl, 33.20.

***trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Perchlorate.** The mother liquors from the previous preparation were returned to the steam bath for 30 min with 20 ml of 60% $HClO_4$ added. An additional 10 ml of $HClO_4$ (60%) was added and the solution was allowed to cool slowly. The green crystals obtained (12 g) were washed and dried as above. *Anal.* Calcd for $[Co(en)(tmd)Cl_2]ClO_4$: C, 16.50; H, 4.95; Co, 16.23; ligand Cl, 19.53. Found: C, 16.93; H, 5.09; Co, 16.45; ligand Cl, 19.30.

The *trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) Cation. The green *trans*-$Cr(en)(tmd)Cl_2^+$ cation was isolated in solution by suspending *ca.* 150 mg of *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ in 0.025 *F* HNO_3. The unreacted solid was filtered from the solution which dripped directly onto the top of an ion-exchange column, which had been 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 0.4 *F* HNO_3 into an ice-cooled flask. The absorption spectrum was recorded immediately and analysis of solutions prepared in this manner (*ca.* 4 m*F* in complex) gave Cr:Cl atom ratios of 1:1.94 ± 0.05 (11)[5] in acceptable agreement with the formula $Cr(en)(tmd)Cl_2^+$.

The *trans*-Dichloro(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Cation. The green *trans*-$Co(en)(tmd)Cl_2^+$ cation was isolated in solution by methods analogous to those used for the Cr(III) complex, except that 0.3 *F* HNO_3 was used for the elution. Analyses of the effluent solutions (*ca.* 4 m*F* in complex) gave Co:Cl atom ratios of 1:2.03 ± 0.03 (19)[5] in agreement with the formula $Co(en)(tmd)Cl_2^+$.

The *trans*-Chloroaquo(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) Cation. The orange *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$ cation was generated in solution by allowing *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ (*ca.* 150 mg in 50 ml of 0.1 *F* HNO_3) to hydrolyze for 2 hr at 40°. 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*-dichloro cation and the orange chloroaquo cation was eluted with 50 ml of 1.0 *F* HNO_3. Absorption spectral parameters were measured immediately and analyses of the solutions (*ca.* 2 m*F* in complex) gave Cr:Cl atom ratios of 1:0.99 ± 0.09 (6)[5] in agreement with the formula $Cr(en)(tmd)(OH_2)Cl^{2+}$.

The *cis*-Chloroaquo(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Cation. The purple *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$ was isolated in solution by allowing *trans*-$[Co(en)(tmd)Cl_2]ClO_4$ (*ca.* 200 mg in 30 ml of 0.1 *F* HNO_3) to hydrolyze for 5 min at 40°. The cooled solution was treated as outlined for the isolation of *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$. Analysis of the effluent solutions (*ca.* 3 m*F* in complex) gave Co:Cl atom ratios of 1:1.04 ± 0.03 (6)[5] in agreement with the formula $Co(en)(tmd)(OH_2)Cl^{2+}$. Variation in reaction times from 3 to 20 min gave chromatographically isolated solutions with identical absorption spectral parameters, suggesting that the isolated $Co(en)(tmd)(OH_2)Cl^{2+}$ cation is isomerically pure.

The *trans*-Diaquo(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) Cation. The orange *trans*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$ cation was generated by allowing *ca.* 150 mg of *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ to hydrolyze in 50 ml of distilled water for 3.5 hr at 40° 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 of effluent. The absorption spectrum was measured immediately.

The same complex was formed from *trans*-$[Cr(en)(tmd)(OH_2)(OH)](ClO_4)_2$, 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 three methods gave absorption spectra which were identical in the position of the maxima and minima and molar absorbancy indices.

The *cis*-Diaquo(1,2-diaminoethane)(1,3-diaminopropane)chromium(III) Cation. The orange *cis*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$ cation was prepared by dissolving *ca.* 150 mg of *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ 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* and 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 3 m*F* solution.

The *cis*-Diaquo(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Cation. The orange-pink *cis*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ cation was generated by a method similar to that used for the Cr(III) analog. The effluent solutions were *ca.* 2 m*F* in complex.

The *trans*-Dihydroxo(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Cation. The magenta *trans*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ cation was prepared from *trans*-$[Co(en)(tmd)Cl_2]ClO_4$, either by dissolving an accurately weighed amount in 0.5 *F* NaOH and measuring the absorption spectrum or by taking *ca.* 200 mg in 30 ml of 0.025 *F* HNO_3 and adsorbing this solution on a cation-exchange resin (prewashed with 2 *F* and then 0.025 *F* HNO_3). The green band was washed with distilled water until the effluent was neutral. The magenta cation was then eluted with 0.1 *F* NaOH into a 50-ml ice-cooled flask, the first 20 ml being discarded. Both methods gave identical absorption spectral parameters.

The *cis*- ⇌ *trans*-Diaquo(1,2-diaminoethane)(1,3-diaminopropane)cobalt(III) Equilibrium Solution. An accurately weighed amount of *trans*-$[Co(en)(tmd)Cl_2]ClO_4$ was dissolved in 0.5 *F* NaOH (25 ml) and left for 3 min before making up to 50 ml with 1.0 *F* HNO_3. The absorption spectral parameters remained constant after 3 days at room temperature.

An identical spectrum was obtained by leaving a solution of *trans*-$[Co(en)(tmd)Cl_2]ClO_4$ and excess mercuric acetate in 50 ml of 1.0 *F* HNO_3 for 3 days at room temperature.

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 *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ in 50 ml of 0.6 *F* HNO_3 and leaving the solution for 3 days at 35°. The cooled solution was 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 recorded immediately.

Kinetic Measurements. For all hydrolysis studies, the cations were chromatographically isolated by elution from ion-exchange resins with HNO_3. These solutions were allowed to react at the

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[4] G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, p 237.

[5] The numbers are the mean plus or minus the standard deviation. The number in parentheses is the number of determinations.

appropriate temperature in glass-stoppered flasks which were wrapped in Al foil to exclude light.[6,7] The titrimetric and spectrophotometric procedures followed were the same as those described previously.[1] For both the M(en)(tmd)Cl_2^+ cations, plots of log ($T_\infty - T_t$) *vs.* time (T_∞ = titer for one Cl^-, T_t = titer at time *t*) extrapolated back to T_t = 0 at *t* = 0, indicating that fast-reacting species, such as *trans*-Co(tmd)$_2$-Cl_2^+, were absent.

Chemical Analyses. Co was determined by decomposing the complexes with ammonium peroxodisulfate solution and spectrophotometrically estimating the Co(II) produced as the thiocyanate complex in 50% aqueous acetone at 620 nm.[8] Cr and Cl were determined using the methods described previously.[1] Professor A. D. Campbell's laboratory at the University of Otago, Otago, New Zealand, performed the C, H, and N analyses of the solid complexes. All spectrophotometric measurements were made with a Beckman DBG recording spectrophotometer.

Results

The complexes *trans*-[Cr(en)(tmd)Cl_2]ClO_4 and *trans*-[Cr(en)(tmd)(OH)(OH_2)]$(ClO_4)_2$ have been prepared as crystalline solids and a one-step synthesis of *trans*-[Co(en)-(tmd)Cl_2]X (X = $Cl \cdot H_2O$ and ClO_4) is described. The desired product, *trans*-[Cr(en)(tmd)Cl_2]ClO_4, is unlikely to be contaminated with *trans*-[Cr(en)$_2Cl_2$]ClO_4 as Pedersen[9] has shown that the reaction between ethylenediamine and $CrCl_3 \cdot 6H_2O$ in DMSO or dimethylformamide yields only *cis*-Cr(en)$_2Cl_2^+$. In addition, the X-ray powder photographs of *trans*-[Cr(tmd)$_2Cl_2$]ClO_4 (another possible reaction product), *trans*-[Cr(en)(tmd)Cl_2]ClO_4, and *trans*-[Cr(en)$_2Cl_2$]ClO_4 are distinctly different. This, together with a satisfactory elemental analysis (apart from a high C figure) and unique spectral parameters of the parent and hydrolysis products, serves to characterize *trans*-[Cr(en)(tmd)Cl_2]ClO_4 and distinguish it from other possible reaction products. From acid solutions of *trans*-[Cr(en)(tmd)Cl_2]ClO_4, the *trans*-Cr(en)-(tmd)Cl_2^+ and *trans*-Cr(en)(tmd)(OH_2)Cl^{2+} cations have been isolated by ion-exchange techniques and characterized in solution by their visible absorption spectra and Cr:Cl atom ratios. The *cis*-Cr(en)(tmd)$(OH_2)_2{}^{3+}$ has been isolated and characterized in a similar manner from acidic solutions of *trans*-Cr(en)(tmd)Cl_2^+ containing Hg^{2+}, and the *trans*-diaquo species has been isolated from solutions of *trans*-[Cr(en)-(tmd)(OH)(OH_2)]$(ClO_4)_2$ in acid. The *trans*-Cr(en)(tmd)-(OH_2)Cl^{2+} cation hydrolyzes both *via* chloride release and Cr-N bond rupture and the Cr(tmd)$(OH_2)_4{}^{3+}$ cation has been isolated from aged solutions.

From acidic solutions of *trans*-[Co(en)(tmd)Cl_2]ClO_4, the *trans*-dichloro and *cis*-Co(en)(tmd)(OH_2)Cl^{2+} cations have been isolated. Although we have evidence for the formation of *trans*-Co(en)(tmd)(OH_2)Cl^{2+}, this cation is sufficiently unstable as to preclude its isolation and characterization. Similarly, the *trans*-Co(en)(tmd)$(OH_2)_2{}^{3+}$ cation could not be isolated although the *trans*-Co(en)(tmd)$(OH)_2^+$ and *cis*-Co(en)(tmd)$(OH_2)_2{}^{3+}$ cations have been characterized. Absorption spectral parameters for the isolated cations are presented in Table I along with similar data for related species.

Hydrolysis Rates of *trans*-M(en)(tmd)Cl_2^+. The hydrolysis of chromatographically isolated *trans*-Cr(en)(tmd)Cl_2^+ in 0.4 *F* HNO_3 was followed by chloride-release titration and by spectrophotometry. Rate constants were obtained using the relationships described previously.[1] The spectrophotometric data (using both repetitive-scan and fixed-wavelength techniques) were analyzed at 390 and 600 nm (these wavelengths correspond to the maximum absorbance difference between parent[10] and *trans*-Cr(en)(tmd)(OH_2)Cl^{2+}, Figure 1) with good agreement between the rate constants obtained at both wavelengths and from the chloride-release data.

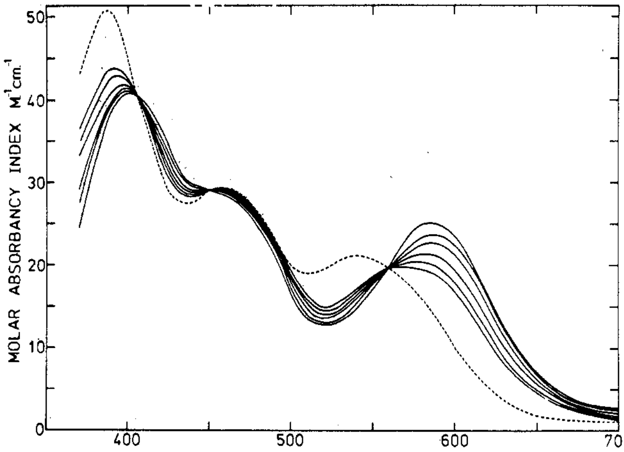

Figure 1. Spectral changes in the primary hydrolysis of *trans*-Cr(en)(tmd)Cl_2^+ (———) in 0.4 *F* HNO_3 at 35°. Reading downward at 585 nm (or upward at 390 nm) the reaction times are 0, 20, 40, 80, 120, and 160 min. The final curve (- - - - -) is that of *trans*-Cr(en)(tmd)(OH_2)Cl^{2+}.

Similar techniques were used to monitor the hydrolysis of *trans*-Co(en)(tmd)Cl_2^+ in 0.3 *F* HNO_3. Repetitive spectrophotometric scans showed the production of two sets of isosbestic points and the second set (at 380 and 580 nm) was used for analysis of the kinetic data, where *cis*-Co(en)(tmd)-(OH_2)Cl^{2+} has a_M values of 62.5 and 34.2 M^{-1} cm^{-1}, respectively (Figure 3).[11] There was good agreement between the rate constants obtained from the two different wavelengths and from the chloride-release data.

For the Cr(III) complex, the first-order kinetic plots were linear over 2-3 half-lives, but for the Co(III) complex, negative deviation from linearity was observed after 2 half-lives. Point-by-point calculations showed only random fluctuations over the period where linearity was observed. For both complexes, the observed rate constants were independent of the complex ion concentration over a twofold variation in initial concentration. The kinetic data are presented in Table II.

The spectrophotometric scans for the hydrolysis of both *trans*- and *cis*-M(en)(tmd)(OH_2)Cl^{2+} (M = Cr, Co, respectively) (chromatographically isolated in 1.0 *F* HNO_3) did not hold isosbestic points, and the rate of loss of parent was followed by chloride release only. The first-order rate plots obtained showed negative deviation from linearity after 0.5 half-life and initial slope values were used to obtain the rate constants presented in Table III. As these data are associated with complex reacting systems at high ionic strength, their absolute values should be interpreted with caution.

The energies of activation, E_a, log *PZ* values and entropies of activation, $\Delta S^{\ddagger}_{298}$, were calculated using the methods described previously.[1] These data are presented in Table IV along with similar data for related systems.

Discussion

Syntheses. The reaction between $CrCl_3 \cdot 6H_2O$, dehydrated

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[6] R. R. Barona and J. A. McLean, *Inorg. Chem.*, 10, 286 (1971).

[7] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, 83, 4152 (1961).

[8] R. G. Hughes, J. F. Endicott, M. Z. Hoffman, and D. A. House, *J. Chem. Educ.*, 46, 440 (1969).

[9] E. Pedersen, *Acta Chem. Scand.*, 24, 3362 (1970).

[10] At 390 nm, the parent and daughter have a_M values of 38.2 and 50.4 M^{-1} cm^{-1}, respectively, while at 600 nm the corresponding values are 22.7 and 11.0 M^{-1} cm^{-1}.

[11] At 380 and 580 nm, the a_M values for *trans*-Co(en)(tmd)-Cl_2^+ are 45.3 and 19.2 M^{-1} cm^{-1}, respectively.

Table I. Visible Absorption Maxima and Minima (320–650 nm) of Some Aquo, Chloroaquo-, and Dichloro(diamine)chromium(III) and -cobalt(III) Complexes in Aqueous Acidic Solution at 12–23°

Cation	Acid and concn, *F*	Min[a]	Max[a]	Min[a]	Max[a]	Min[a]	Max[a]
trans-$Cr(en)_2Cl_2^+$ [b]	HNO_3		396	439	453	514	578
	0.1		(34.0)	(22.3)	(22.8)	(8.1)	(24.5)
trans-$Cr(en)(tmd)Cl_2^+$ [c]	HNO_3		402		450 sh[e]	523	588
	0.4 (16)[d]		(41.3 ± 1.2)		(29.6 ± 1.0)	(10.3 ± 1.6)	(24.8 ± 0.7)
trans-$Cr(tmd)_2Cl_2^+$ [f]	HNO_3		398		457 sh	525	596
	0.1–0.6		(38.8)		(24.9)	(8.9)	(25.5)
trans-$Co(en)_2Cl_2^+$ [g]	MeOH–H_2O		385		450		625
			(43.7)		(25.2)		(34.7)
trans-$Co(en)(tmd)Cl_2^+$ [c]	HNO_3	394	422		450 sh	536	625
	0.3 (10)[d]	(43.9 ± 0.9)	(46.8 ± 0.8)		(43.1 ± 0.7)	(7.7 ± 0.6)	(38.2 ± 0.6)
trans-$Co(tmd)_2Cl_2^+$ [g]	MeOH–H_2O		398		475		650
			(54.8)		(29.0)		(38.3)
trans-$Cr(en)_2(OH_2)Cl^{2+}$ [b]	HNO_3		380	428	448	500	546
	0.2		(45.5)	(23.7)	(24.4)	(15.4)	(20.5)
trans-$Cr(en)(tmd)(OH_2)Cl^{2+}$ [c]	HNO_3		387	434	456	509	545
	1.0 (7)[d]		(51.3 ± 1.3)	(26.8 ± 0.8)	(28.7 ± 0.8)	(18.7 ± 1.0)	(21.1 ± 0.8)
trans-$Cr(tmd)_2(OH_2)Cl^{2+}$ [f]	HNO_3		384	436	456	506	556
	1.0		(52.5)	(23.3)	(24.9)	(15.7)	(20.6)
trans-$Co(en)_2(OH_2)Cl^{2+}$ [b]	$HClO_4$	440	442	510			590
	0.012	(34)	(35)	(14)			(35)
cis-$Co(en)_2(OH_2)Cl^{2+}$ [b]	$HClO_4$		373	435			515
	0.012		(67)	(15)			(84)
cis-$Co(en)(tmd)(OH_2)Cl^{2+}$ [c]	HNO_3	358	376	440			522
	1.0 (6)[d]	(62.0 ± 0.7)	(67.5 ± 0.6)	(26.9 ± 0.6)			(52.3 ± 0.5)
trans-$Cr(en)_2(OH_2)_2^{3+}$ [h]	H^+		361	404	442		508 sh
	1 *F* $NaNO_3$		(39.2)	(20.0)	(29.3)		(22.5)
trans-$Cr(en)(tmd)(OH_2)_2^{3+}$ [c]	HNO_3		370	412	449		508 sh
	0.6–1.5 (4)[d]		(46.1 ± 0.8)	(23.6 ± 0.9)	(33.4 ± 0.9)		(21.6 ± 1.6)
trans-$Cr(tmd)_2(OH_2)_2^{3+}$ [f]	HNO_3		368	414	450		512 sh
	0.6–1.5		(43.9)	(20.9)	(28.6)		(19.6)
cis-$Cr(en)_2(OH_2)_2^{3+}$ [h]	H^+		367	417			484
	1 *F* $NaNO_3$		(42.5)	(17.0)			(67.0)
cis-$Cr(en)(tmd)(OH_2)_2^{3+}$ [c]	HNO_3		370	415			480
	1.5 (3)[d]		(42.0 ± 0.4)	(18.9 ± 0.5)			(32.2 ± 0.5)
cis-$Cr(tmd)_2(OH_2)_2^{3+}$ [f]	HNO_3		370	420			488
	1.5		(37.8)	(16.1)			(29.8)
trans-$Co(en)_2(OH_2)_2^{3+}$ [i]	HNO_3, 0.05		∿340	410	444	492	550
	1 *F* $NaNO_3$		(∿55)	(32.0)	(35.1)	(19.2)	(32.8)
cis-$Co(en)_2(OH_2)_2^{3+}$ [i]	HNO_3, 0.05		355	410			492
	1 *F* $NaNO_3$		(60)	(14.3)			(80.9)
cis-$Co(en)(tmd)(OH_2)_2^{3+}$ [c]	HNO_3		358 sh	418			498
	1.5 (5)[d]		(75.7 ± 0.9)	(15.9 ± 2.0)			(73.9 ± 0.6)
cis- $\rightleftharpoons$ *trans*-$Co(en)(tmd)(OH_2)_2^{3+}$ [c]	HNO_3		358	418			500
	1.0 (7)[d]		(70.2 ± 0.9)	(15.4 ± 0.5)			(72.4 ± 0.6)
trans-$Co(en)(tmd)(OH)_2^+$ [c]	NaOH	324	375	438			522
	0.1–0.5 (4)[d]	(24.0 ± 1.0)	(87.9 ± 1.3)	(19.1 ± 1.1)			(79.5 ± 1.2)
$Cr(tmd)(OH_2)_4^{3+}$ [f]	HNO_3		380	438			514
	1.0		(26.6)	(8.6)			(28.2)
$Cr(tmd)(OH_2)_4^{3+}$ [c]	HNO_3		382	438			514
	1.0 (4)[d]		(26.4 ± 1.0)	(8.4 ± 2.6)			(28.0 ± 0.1)
$Cr(en)(OH_2)_4^{3+}$ [j]	$HClO_4$		385	433			512
	1.0–3.0		(24.3)	(10.7)			(41.7)

[a] In nanometers (±2 nm for this work). 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 plus or minus the standard deviation (see footnote *d*). [b] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961). [c] This work. [d] The number of individual determinations used to obtain the mean. [e] sh = shoulder. [f] M. C. Couldwell and D. A. House, *Inorg. Chem.*, **11**, 2024 (1972). [g] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956); H. Kawaguchi, N. Yano, and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **42**, 136 (1969). [h] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958). [i] C. K. Poon and M. L. Tobe, *J. Chem. Soc.*, 1549 (1968); J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952). [j] D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).

in DMSO,[2] and an equimolar mixture of 1,2-diaminoethane and 1,3-diaminopropane produces (after the subsequent work-up) *trans*-$[Cr(en)(tmd)Cl_2]ClO_4$ and *cis*-$[Cr(en)_2Cl_2]Cl{\cdot}H_2O$, the former being the less soluble. The yields of the *trans*-dichloro perchlorate are low, but sufficient material was isolated for the present kinetic study. Conversion of this to the *trans*-hydroxoaquo parallels the bis(1,3-diaminopropane) system.[1] The Co(III) analog has previously[12] been prepared by reacting $Co(en)(NH_3)(NO_2)_3$ with 1,3-diaminopropane, and material from this source was used in a previous kinetic study.[13] In this work, the direct air oxidation of an aqueous solution of a Co(II) salt, together with an equimolar mixture of the diamines, followed by subsequent reaction with HCl–$HClO_4$ was successful in producing *trans*-$[Co(en)(tmd)Cl_2]Cl{\cdot}H_2O$ and the perchlorate salt.[14] The good agreement between the kinetic data found here and that reported

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(12) J. C. Bailar and J. B. Work, *J. Amer. Chem. Soc.*, **68**, 232 (1946).

(13) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 3089 (1953).

(14) We have also succeeded in preparing the *trans*-dichloro complexes $[Co(en)(pn)Cl_2]ClO_4$ and $[Co(pn)(tmd)Cl_2]ClO_4$ by this method.

Table II. First-Order Rate Constants for the Primary Hydrolysis of *trans*-M(en)(tmd)Cl_2^+ (M = Cr, Co) in Acidic Solution

Temp, °C	C_0,[a] m*F*	10^5k,[b] sec^{-1}	10^5k(calcd),[c] sec^{-1}	Method[d]
		(A) *trans*-Cr(en)(tmd)Cl_2^+ in 0.4 *F* HNO_3 [e]		
25.0			1.93	
30.0	2.78–3.88	3.58 ± 0.18	3.69	H(2)
35.0	2.41–4.17	7.04 ± 0.15	6.94	H(2), S(2)
40.0	2.89–5.32	13.3 ± 0.2	12.8	H(3)
45.0	3.38–5.92	23.0 ± 1.6	23.0	H(4)
50.0	3.85–7.39	39.7 ± 1.7	40.8	H(4), S(2)
		(B) *trans*-Co(en)(tmd)Cl_2^+ in 0.3 *F* HNO_3 [f]		
13.8	3.52–5.18	8.31 ± 0.13	8.20	H(5)
15.0[g]		9.85[g]		S
15.5	3.52–4.70	10.5 ± 0.2	10.53	S(3)
17.0	3.20	13.3 ± 0.7	13.1	H(1)
20.0	3.02–4.72	19.8 ± 1.4	20.1	H(7)
22.0	4.02	26.9 ± 1.3	26.7	H(1)
25.0	2.56–7.10	39.6 ± 1.2	40.5	H(8), S(2)
25.0[g]		43.3[g]		S
30.0	4.40	79.9 ± 4.0	79.5	S(1)
35.0[g]		150[g]		S

[a] Initial complex ion concentration. [b] The numbers quoted are the mean plus or minus the standard deviation. Where the number of determinations is ≤2, an error of 5% is assumed. [c] Rate constants calculated using the E_a and log *PZ* values in Table IV. [d] Method used in monitoring the reaction. H = halide-release titration; S = spectrophotometric. Numbers in parentheses are the number of individual determinations. [e] Corresponding to eq 1. [f] Corresponding to eq 3. [g] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, 75, 3089 (1953), in 0.1 *F* HNO_3.

Table III. First-Order Rate Constants for the Formation of Cl^- in the Hydrolysis of M(en)(tmd)$(OH_2)Cl^{2+}$ (M = Cr, Co) in 1.0 *F* HNO_3

Temp, °C	C_0,[a] m*F*	10^5k,[b] sec^{-1}	10^5k(calcd),[c] sec^{-1}	Method[d]
		(A) *trans*-Cr(en)(tmd)$(OH_2)Cl^{2+}$		
25.0			0.31 ± 0.05	
45.0	1.94–2.61	3.15 ± 0.18	3.15	H(2)
55.0	1.91–3.00	9.07 ± 0.16	9.06	H(3)
		(B) *cis*-Co(en)(tmd)$(OH_2)Cl^{2+}$		
25.0	3.24–6.15	10.3 ± 0.2	10.2	H(3)
30.0	3.01–3.02	17.2 ± 0.9	17.3	H(2)
36.0	3.26–4.04	31.8 ± 1.6	31.8	H(2)

[a] See footnotes *a–d* in Table II.

Table IV. Kinetic Parameters for the Primary and Secondary Hydrolysis of Some $M(AA)_2Cl_2^+$ Cations (M = Cr, Co) in Acidic Solution at 25°

Complex[a]	Acidity,[b] *F*	10^5k, sec^{-1}	E_a, kcal mol^{-1}	log [*PZ*, (sec^{-1})]	$\Delta S^{\ddagger}_{298}$, 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-$Cr(pn)_2Cl_2^+$ [f]	0.1	8.14 (35°)			
t-Cr(en)(tmd)Cl_2^+ [g]	0.4	1.93 7.04 (35°)	23.4 ± 0.3	12.43	−3.6 ± 0.5
t-$Cr(tmd)_2Cl_2^+$ [h]	0.1	2.08 7.85 (35°)	24.5	13.26	+0.1
t-$Co(en)_2Cl_2^+$ [i–k]	0.1	3.2	26.2	15.9	+14
t-$Co(pn)_2Cl_2^+$ [k]	0.1	6.2	28	(16.3)[l]	(+14)[l]
t-Co(en)(tmd)Cl_2^+ [k]	0.1	43.3	26 (24.0)[l]		
t-Co(en)(tmd)Cl_2^+ [g]	0.3	39.6	24.2 ± 0.3	14.38	+5.1 ± 0.5
t-$Co(tmd)_2Cl_2^+$ [k,m]	H^+ ?	5330	21.3	(14.3)[l]	+6.9
t-$Cr(en)_2(OH_2)Cl^{2+}$ [n]	0.1	∿0.08[d]			
t-Cr(en)(tmd)$(OH_2)Cl^{2+}$ [g]	1.0	0.31[d]	21.9 ± 1	10.54	−12.3 ± 2
t-$Cr(tmd)_2(OH_2)Cl^{2+}$ [h]	1.0	0.29[d]	21.7	10.39	−13.1
t-$Co(en)_2(OH_2)Cl^{2+}$ [o]	0.01	0.28			
c-$Co(en)_2(OH_2)Cl^{2+}$ [o]	0.01	0.19			
c-Co(en)(tmd)$(OH_2)Cl^{2+}$ [g]	1.0	10.3[d]	18.8 ± 0.5	9.81	−15.7 ± 1

[a] *t* = *trans*; *c* = *cis*. [b] HNO_3 unless otherwise stated. [c] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, 18, 219 (1961). [d] Rate determined by chloride release only. [e] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, 83, 4152 (1961). [f] R. R. Barona and J. A. McLean, *Inorg. Chem.*, 10, 286 (1971). [g] This research. [h] M. C. Couldwell and D. A. House, *Inorg. Chem.*, 11, 2024 (1972); *Inorg. Nucl. Chem. Lett.*, 7, 947 (1971). [i] S. C. Chan, *Aust. J. Chem.*, 20, 595 (1967). [j] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963). [k] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Amer. Chem. Soc.*, 75, 3089 (1953). [l] Numbers in parentheses are log *PZ* or $\Delta S^{\ddagger}_{298}$ values calculated from data in the original literature. [m] I. R. Jonasson, R. S. Murray, D. R. Stranks, and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem.*, 12, 32 (1969). [n] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, 1, 20 (1962). [o] S. C. Chan, *J. Chem. Soc.*, 5137 (1963).

arlier[13] (Tables II and IV) suggests that the two different outes give the same material.

Chromium(III) Cations. The green *trans*-[Cr(en)(tmd)Cl_2]-ClO_4 is soluble in dilute HNO_3 at room temperature to give a green solution which slowly changes to orange-pink. The absorption spectral parameters and ion-exchange properties of the green $Cr(en)(tmd)Cl_2^+$ cation are typical of a *trans*-dichloro complex of this type (Table I). The daughter product, *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$, was isolated from aged (*ca.* 2 half-lives) solutions and characterized by its absorption spectral parameters (which are similar to related cations) and Cr:Cl atom ratios. Spectrophotometric scans during the hydrolysis of acidic solutions of *trans*-$Cr(en)(tmd)Cl_2^+$ held sharp isosbestic points at 405 (40.7), 454 (29.2), and 560 nm (19.1 M^{-1} cm^{-1}) over 3 half-lives, in good agreement with those predicted if *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$ is the sole product, namely, at 406 (40.5), 454 (29.4), and 562 nm (19.4 M^{-1} cm^{-1}) (Figure 1). This suggests that the primary hydrolysis of *trans*-$Cr(en)(tmd)Cl_2^+$ is similar to that of *trans*-$Cr(tmd)_2Cl_2^+$ and takes place according to the equation

$$\textit{trans}\text{-Cr(en)(tmd)Cl}_2^+ + H_2O \rightarrow \textit{trans}\text{-Cr(en)(tmd)(OH}_2\text{)Cl}^{2+} + Cl^- \tag{1}$$

with no evidence for any Cr-N bond rupture paths such as occur during the hydrolysis of *trans*-$Cr(AA)_2Cl_2^+$ (AA = en,[7] AA = pn[6]).

However, the secondary hydrolysis step does appear to be complicated by concurrent Cr-N bond rupture and/or isomerization as isosbestic points were not observed for hydrolyzing solutions of *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$ in 1.0 *F* HNO_3. Due to the difficulty of working with low concentrations of the *trans*-chloroaquo cation, the characterization of the products of this reaction was not attempted. Rather, the *cis*- and *trans*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$ and $Cr(tmd)(OH_2)_4{}^{3+}$ cations were generated directly from the *trans*-dichloro or *trans*-hydroxoaquo salts.

Hydrolysis of *trans*-$Cr(en)(tmd)Cl_2^+$ in water, followed by acidification and ion-exchange separation, produced the *trans*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$ cation, presumably *via* the labile *trans*-$Cr(en)(tmd)(OH)Cl^+$ intermediate. The use of neutral solutions apparently avoids the competing Cr-N bond rupture paths observed in the secondary hydrolysis. An identical species (Figure 2) was produced by preparing solutions of *trans*-$[Cr(en)(tmd)(OH)(OH_2)](ClO_4)_2$ in acid, and the spectral parameters are similar to those of related *trans*-$Cr(AA)_2(OH_2)_2{}^{3+}$ cations (Table I).

Treatment of acid solutions of the *trans*-dichloro species with excess Hg^{2+} produces a Cr(III) cation with ion-exchange properties compatible with a 3+ charge but with an absorption spectrum different from that of the *trans*-diaquo species. The positions of the absorption maxima and minima are similar to those of *cis*-$Cr(en)_2(OH_2)_2{}^{3+}$ (Table I) and we tentatively assign the *cis*-diaquo configuration to the isolated species (Figure 2). The Hg^{2+} ion not only assists in removing the coordinated chloride but also appears to catalyze the *trans*- → *cis*-diaquo isomerization.

Of considerable interest is the nature of the Cr-N bond ruptured intermediate in the reaction

$$Cr(en)(tmd)(OH_2)_2{}^{3+} + 4H_3O^+ \rightarrow Cr(OH_2)_6{}^{3+} + enH_2{}^{2+} + tmdH_2{}^{2+} \tag{2}$$

as this may provide some information as to the kinetic stability of five- or six-membered rings attached to Cr(III). Solutions of *trans*-$Cr(en)(tmd)Cl_2^+$ in 0.6 *F* HNO_3 were allowed to hydrolyze at 35° for 3 days (approximately 4 half-lives for the reaction corresponding to chloride release from *trans*-$Cr(en)(tmd)(OH_2)Cl^{2+}$) and the color changed from green through orange to pink. The major component isolated by ion-exchange separation had absorption spectral parameters corresponding to $Cr(tmd)(OH_2)_4{}^{3+}$ (previously[1] isolated from *trans*-$Cr(tmd)_2(OH_2)_2{}^{3+}$) and considerably different from $Cr(en)(OH_2)_4{}^{3+}$ (Table I). Thus, in *trans*(?)-$Cr(en)(tmd)(OH_2)_2{}^{3+}$, the five-membered ethylenediamine ring is the kinetically less stable with respect to Cr-N bond rupture, despite the much cited information[15] that complexes with six-membered rings are normally "less stable" than those with five-membered rings.[1]

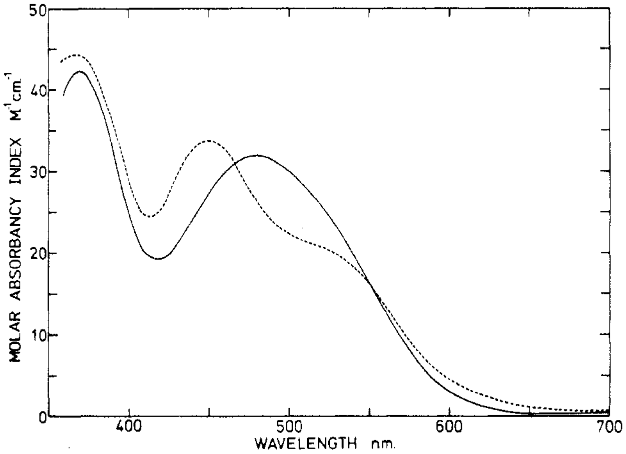

Figure 2. Visible absorption spectra of *cis*- (———) and *trans*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$ (- - - - -) in 0.6-1.5 *F* HNO_3 at 20-23°.

Cobalt(III) Cations. In agreement with previous workers[13] we find that acidic solutions of green *trans*-$Co(en)(tmd)Cl_2^+$ quite rapidly ($t_{1/2}$ = *ca.* 30 min at 25°) turn purple. The spectral parameters of the chromatographically isolated chloroaquo product did not correspond to those expected[13] for a trans isomer and the formation of an early and later set of isosbestic points in the spectrophotometric scans suggest that the reaction is proceeding according to

$$\textit{trans}\text{-Co(en)(tmd)Cl}_2^+ \begin{array}{l} \nearrow \textit{trans}\text{-Co(en)(tmd)(OH}_2\text{)Cl}^{2+} + Cl^- \\ \qquad\qquad\qquad\downarrow \\ \searrow \textit{cis}\text{-Co(en)(tmd)(OH}_2\text{)Cl}^{2+} + Cl^- \end{array} \tag{3}$$

At 25°, the first set of isosbestic points at 407 (45.6), 481 (32.9), and 602 nm (30.8 M^{-1} cm^{-1}) was maintained from 0 to 24 min (almost 1 chloride-release half-life) and a second set at 380 (59.5), 453 (29.0), and 580 nm (31.2 M^{-1} cm^{-1}) was stable from 60 to 360 min.

Attempts to isolate *trans*-$Co(en)(tmd)(OH_2)Cl^{2+}$ by ion-exchange chromatography were unsuccessful and only the cis isomer was obtained. Also unsuccessful were attempts to isolate salts of *trans*-$Co(en)(tmd)(OH)Cl^+$ using the literature methods[16,17] for the synthesis of the bis(ethylenediamine) analog.

The spectral parameters of the first formed product(s) of hydrolyzing *trans*-$Co(en)(tmd)Cl_2^+$ were estimated at 12, 20, 28, and 36 min at 25° by subtracting out from the observed spectrum the contribution from the *trans*-dichloro species remaining (80, 65, 50, and 38%, respectively). The mean spectrum is shown in Figure 3 and the product(s)-*trans*-dichloro isosbestic points so obtained [405 (45), 481 (33) and 602 nm (31 M^{-1} cm^{-1})] are in satisfactory agreement with the first formed set. The product(s) spectrum is similar in shape to that of *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$, which suggests

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(15) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 29, 163; (b) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1968, p 156.

(16) J. Meisenheimer, *Justus Liebigs Ann. Chem.*, 438, 217 (1924).

(17) C. G. Barraclough, R. W. Boschen, W. W. Fee, W. G. Jackson, and P. T. McTigue, *Inorg. Chem.*, 10, 1944 (1971).

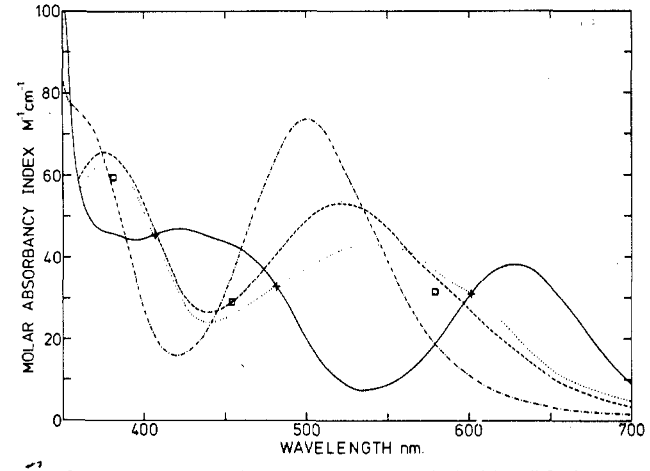

Figure 3. Visible absorption spectra of *trans*-$Co(en)(tmd)Cl_2^+$ (———) (0.3 *F* HNO_3), *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$ (- - - - -) (1.0 *F* HNO_3), *cis*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ (— · — · —) (1.5 *F* HNO_3), and first formed product(s) (· · · · · · · ·) (0.3 *F* HNO_3) of hydrolyzing *trans*-$Co(en)(tmd)Cl_2^+$ at 25°. Observed isosbestic points in this hydrolysis are marked + (first set) and ▫ (second set).

that, like the *trans*-$Co(en)_2Cl_2^+$ system,[18] the parent hydrolyzes directly to form a mixture of the *cis*- and *trans*-chloroaquo products.

As there is general similarity between the spectral parameters of *trans*-$Co(en)_2Cl_2^+$ and *trans*-$Co(en)(tmd)Cl_2^+$ (Table I), we would expect a parallel behavior for the related *trans*-chloroaquo ions. Assuming that *trans*-$Co(en)(tmd)(OH_2)Cl^{2+}$ has a minimum near 510 nm with a molar absorbancy index of 14 ± 5 M^{-1} cm^{-1}, we calculate from the molar absorbancy indices of *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$ and the product(s) spectrum (52.0 and 39.5 M^{-1} cm^{-1}, respectively, at 510 nm) that about 66 ± 5% *cis*-chloroaquo is produced in the primary hydrolysis step.

The second set of isosbestic points is probably composite and due to a combination of reactions 4 as these are maintained for approximately 3 half-lives for the chloride-

$$\begin{tikzcd}
\textit{trans}\text{-Co(en)(tmd)(OH}_2\text{)Cl}^{2+} \arrow[r] \arrow[d, rightleftharpoons] \arrow[dr] & \textit{trans}\text{-Co(en)(tmd)(OH}_2\text{)}_2{}^{3+} \arrow[d, rightleftharpoons] \\
\textit{cis}\text{-Co(en)(tmd)(OH}_2\text{)Cl}^{2+} \arrow[r] \arrow[ur] & \textit{cis}\text{-Co(en)(tmd)(OH}_2\text{)}_2{}^{3+}
\end{tikzcd} \qquad (4)$$

release path from *cis*-$Co(en)(tmd)(OH_2)Cl^{2+}$ and do not correspond to intersections of any of the spectral curves shown in Figure 3. Nevertheless, the rate constants for hydrolyzing *trans*-$Co(en)(tmd)Cl_2^+$ obtained spectrophotometrically at the wavelengths defined by this second set are in good agreement with those obtained from chloride-release titrations.

Treatment of *trans*-$Co(en)(tmd)Cl_2^+$ with excess Hg^{2+} in acidic solution and subsequent ion-exchange separation of the products produced a 3+-charged cation with spectral parameters compatible with those expected for *cis*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ (Figure 3). Attempts to prepare *trans*-$Co(en)(tmd)(OH_2)_2{}^{3+}$ by base hydrolysis of the *trans*-dichloro species (to produce *trans*-$Co(en)(tmd)(OH)_2^+$) and acidification gave solutions with spectral parameters differing from those of the *cis*-diaquo species, probably corresponding to nearly *trans*-$Co(en)(tmd)(OH_2)_2{}^{3+}$. These changed (within 15 min at 35°) to those corresponding to the *cis*- ⇌ *trans*-diaquo equilibrium mixture obtained from the *trans*-dichloro species and excess Hg^{2+}, prior to ion-exchange separation. From the absorption spectral parameters of nearly *trans*-diaquo species and those of the *cis*-diaquo and the *cis* ⇌ *trans*-diaquo equilibrium mixture, we calculate using expression 5[19] that there is 5 ± 3% (mean of seven wavelengths) *trans*-diaquo species in the equilibrium mixture. This is comparable to the <2% *trans*-diaquo species observed in the *cis*- ⇌ *trans*-diaquobis(ethylenediamine)cobalt(III) equilibrium mixture.[20]

$$A_{c+t}/d = \epsilon_c(C_0 - [t]) + \epsilon_t[t] \qquad (5)$$

The relative stability of the *trans*-dihydroxo and the rapid isomerization of the *trans*-diaquo species are in agreement with the observations that the *trans*- → *cis*-$Co(tmd)_2(OH_2)_2{}^{3+}$ isomerization has a half-life of *ca.* 1 min at 25° (*i.e.*, 1450 times faster than that of the corresponding bis(ethylenediamine) system), whereas the related *trans*- → *cis*-$Co(tmd)_2(OH)_2^+$ isomerization is only 13 times faster than that of the bis(ethylenediamine) system.[21]

Kinetic Data. The first-order rate constants for the reaction

$$\textit{trans}\text{-Co(AA)(BB)Cl}_2^+ + H_2O \rightarrow \textit{cis}\text{- + }\textit{trans}\text{-Co(AA)(BB)(OH}_2\text{)Cl}^{2+} + Cl^- \qquad (6)$$

increase in the order AA = BB = en; AA = BB = pn; AA = en, BB = tmd; AA = BB = tmd, with 10^5k = 3.2, 6.2, 39.6, and 5330 sec^{-1}, respectively, at 25° (Table IV). The corresponding data for the Cr(III) analogs, hydrolyzing according to eq 1, are 10^5k = 7.2 ± 0.6, 8.14 ± 0.18, 7.04 ± 0.15, and 7.85 ± 0.17 sec^{-1}, respectively, at 35°. The rate constants for the Cr(III) systems appear to be almost independent of the nature of the coordinated diamine and the reactions are much more stereoretentive than those of the Co(III) analogs. Only with AA = BB = en (or pn), where Cr-N bond rupture is observed, is the direct production of *cis*-$Cr(AA)(BB)(OH_2)Cl^{2+}$ detected.[1,6,7]

cis- and *trans*-diacidocobalt(III) complexes of the above type are believed to aquate primarily *via* a dissociative mechanism and the stereochemical changes produced reflect the generation of two different configurations of the pentacoordinated intermediate.[22,23] For cis complexes, the trigonal-bipyramidal intermediate is stabilized directly, the entropy of activation is low, and little stereochemical change is observed. For trans complexes, however, the trigonal bipyramid can only be achieved by rearrangement from the square pyramid; the rate of reaction is slower and the entropy of activation higher than observed for their cis analogs, and considerable stereochemical change can occur.[24]

The present data suggest that the *trans*-$Cr(AA)(BB)Cl_2^+$ complexes (Table IV) aquate *via* a dissociative mechanism with little rearrangement of the square-pyramidal intermediate as the rate constants are similar, the stereochemical change is small, and the entropies of activation are negative or almost zero.[25]

The driving force causing the rate increase of Co(III) complexes containing methyl-substituted diamines has been cor-

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related with steric interaction between the released chloride and the number of axial methyl groups,[26] while the rate increase due to ring expansion has been attributed to steric interaction of boat or twist-boat ring conformations.[1,27] The rate increase in the primary hydrolysis of *trans*-Co(en)(tmd)Cl_2^+ relative to *trans*-$Co(en)_2Cl_2^+$ can also be accounted for on this basis and the positive value for the entropy of activation supports Tobe's theory,[24] as considerable stereochemical change is observed.

Registry No. [Cr(en)(tmd)Cl_2]ClO_4, 36904-25-3; *cis*-[Cr(en)$_2Cl_2$]Cl·H_2O, 20713-30-8; [Cr(en)(tmd)(OH_2)OH]ClO_4, 36904-26-4; [Co(en)(tmd)Cl_2]Cl·H_2O, 36900-74-0; [Co(en)(tmd)Cl_2]ClO_4, 36904-27-5; *trans*-Cr(en)(tmd)(OH_2)Cl^{2+}, 36904-28-6; *cis*-Co(en)(tmd)(OH_2)Cl^{2+}, 36904-29-7; *trans*-Cr(en)(tmd)$(OH_2)_2{}^{3+}$, 36904-30-0; *cis*-Cr(en)(tmd)$(OH_2)_2{}^{3+}$, 36904-31-1; *cis*-Co(en)(tmd)$(OH_2)_2{}^{3+}$, 36904-32-2; *trans*-Co(en)(tmd)$(OH_2)_2{}^{3+}$, 36904-33-3; *trans*-Co(en)(tmd)$(OH)_2{}^+$, 36904-34-4; Cr(tmd)$(OH_2)_4{}^{3+}$, 36965-94-3.

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Trigonal Field Splitting in Tris(ethylenediamine) Complexes. Evidence from the Electron Paramagnetic Resonance Spectrum of $Ru(en)_3{}^{3+}$

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The epr spectrum of the tris(ethylenediamine)ruthenium(III) complex, $Ru(en)_3{}^{3+}$, was measured at 4°K, diluted in single crystals of $[Rh(en)_3Cl_3]_2\cdot NaCl\cdot 6H_2O$ and in powders of $[Co(en)_3]Br_3\cdot 3H_2O$, and employing K-band and X-band frequencies, respectively. The spectrum in both media can be described by an axial spin Hamiltonian with $g_\perp = 2.640 \pm 0.022$ and $g_\parallel = 0.330 \pm 0.007$, defined with respect to the threefold symmetry axis of the complex. Interpretation of these g factors in terms of the theory of axial distortions for a low-spin d^5 electronic configuration shows the ground electronic state to be $E'(^2A_1)$ and yields a value of the trigonal field splitting parameter, K, of -413 cm^{-1}. The observed magnitude and sign of this latter quantity are discussed in terms of the known structure of the complex, crystal field theory predictions, and a comparison with the value for the same quantity in other tris(ethylenediamine) complexes.

Introduction

For a transition metal ion immersed in a crystal field of predominantly octahedral symmetry, but with a superimposed component of trigonal (D_3) symmetry, the lower lying, triply degenerate (t_{2g}) set of d orbitals is expected to split into a nondegenerate a_1 orbital and a doubly degenerate set of e orbitals. Neglecting mixing with the higher energy set of e (e_g) orbitals, the energies of the split t_{2g} orbitals can be parametrized *via* crystal field theory as $E(e) = K$ and $E(a_1) = -2K$, where K, the trigonal field splitting parameter, characterizes the strength of the field.[1] For K positive, the a_1 orbital lies lowest.

For a number of trigonal complexes[2] and trigonal sites in ionic crystals[3] the magnitude and sign of K can be estimated from the splitting of excited electronic states as measured by polarized crystal spectra. However for the tris(ethylenediamine) complexes thus far examined,[4-7] the observed broadband splittings have been so slight, and their direct interpretation complicated by the apparent additional presence of vibronic contributions to band intensities, that estimates of the magnitude of K obtained therefrom may still have a high degree of uncertainty attached to them. Moreover the sign of K for these complexes, determined in this manner, even seems to be controversial by comparison with the sign deduced from circular dichroism studies, both natural and magnetically induced.[8,9]

In favorable cases, such as for metal ions with degenerate ground states in octahedral fields, electron paramagnetic resonance is an additional method which can provide a direct, and precise, determination of the strengths of axial components of a crystal field. The low-spin d^5 Ru^{3+} ion has been shown to be an excellent probe in this regard and has been used extensively to characterize the axial field strengths in a number of well-known type complexes and ionic crystals including the tris(acetylacetonate) complex,[10] corundum,[11] the hexaammine[12] and halopentaammine complexes,[13] several garnets,[14,15] several phosphine complexes,[16] some tris-

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