result in a loss of ring strain in the chelate complex. This relaxation of ring strain could in turn lead to a general shift of absorbances to lower fields.

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Stepwise Aquation of 1,2,3- and 1,2,6-Triaquodiethylenetriaminechromium(III) Cations to Hexaaquochromium(III) Cation. Reaction Kinetics and Isolation of the Bidentate and Unidentate Diethylenetriamine Intermediates[1a–c]

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Abstract: Aquation of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ was studied spectrophotometrically in 1–2 *F* $HClO_4$ ($\mu = 1$–$2\ M$, $NaClO_4$) at 50–70°. At $\mu = 2\ M$, the first-order rate constant, k_{1c}, is the same in 1 and 2 *F* $HClO_4$. At 59.80°, $k_{1c} = (5.89 \pm 0.09) \times 10^{-5}$ sec^{-1} in 1 *F* $HClO_4$ ($\mu = 1\ M$); $E_a = 24.3 \pm 0.7$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.72 ± 0.51. By extrapolation, $k_{1c} = (8.1 \pm 0.8) \times 10^{-7}$ sec^{-1} at 25°. The product is the new complex $Cr(dienH)(OH_2)_4^{4+}$, with a singly protonated bidentate dien ligand. Aquation of this isolated pink intermediate was investigated in 0.1–2 *F* $HClO_4$ ($\mu = 1$–$2\ M$) at 60–80°. At 59.80°, the first-order rate constant is $k_2 = (2.16 \pm 0.03) \times 10^{-5}$ sec^{-1} in 1 *F* $HClO_4$ ($\mu = 1\ M$); $E_a = 24.0 \pm 0.6$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.09 ± 0.40, and $k_2 = (3.1 \pm 0.3) \times 10^{-7}$ sec^{-1} at 25° by extrapolation. At 70 and 80°, k_2 is the same in 0.1 and 1 *F* $HClO_4$ ($\mu = 1\ M$). The product is purple $Cr(dienH_2)(OH_2)_5^{5+}$, a new complex with a doubly protonated unidentate dien ligand. Hydrolysis of this isolated second intermediate was studied in 0.1–2 *F* $HClO_4$ ($\mu = 1$–$2\ M$) at 60–80°. In 0.1–1 *F* $HClO_4$ ($\mu = 1\ M$), $k_{3\,\mathrm{obsd}} = k_3 + (k_3'/[H^+])$, where k_3 is the first-order rate constant for aquation of $Cr(dienH_2)(OH_2)_5^{5+}$ to $Cr(OH_2)_6^{3+}$ and k_3' has been interpreted as $k_{3h}K_a$, k_{3h} being the first-order aquation rate constant of $Cr(dienH_2)(OH_2)_4OH^{4+}$ and K_a being the first acid dissociation constant of $Cr(dienH_2)(OH_2)_5^{5+}$. At 59.80°, $k_3 = (2.59 \pm 0.13) \times 10^{-6}$ sec^{-1} and $k_{3h} \sim 2 \times 10^{-3}$ sec^{-1}; for the k_3 path, $E_a = 26.5 \pm 0.8$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 11.81 ± 0.52, and by extrapolation $k_3 = (2 \pm 1) \times 10^{-8}$ sec^{-1} at 25°. Aquation of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ was studied in 0.01–1 *F* $HClO_4$ ($\mu = 0.15$–$1.1\ M$) at 15–30°. At 25.00°, the first-order rate constant is $k_{1t} = (5.34 \pm 0.05) \times 10^{-4}$ sec^{-1} in 0.1–1 *F* $HClO_4$ ($\mu = 1.1\ M$); $E_a = 19.2 \pm 0.6$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 10.80 ± 0.20. Ionic strength dependences of k_{1c}, k_{1t}, k_2, and k_3 are small over the ranges involved. The same intermediates appear to be produced in aquation of 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$. Visible absorption spectra of the complexes are presented.

Recently the aquation of tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$, and of its isolated product, $Cr(enH)(OH_2)_5^{4+}$ with a singly protonated unidentate en ligand, has been studied kinetically.[2] As part of a continuing program of investigating the "unwrapping" of multidentate amine ligands from chromium(III) centers, this paper reports the related isolation and characterization of the intermediates, namely, the new complexes $Cr(dienH)(OH_2)_4^{4+}$ and $Cr(dienH_2)(OH_2)_5^{5+}$ with "partially unwrapped" bidentate and unidentate diethylenetriamine ligands,[3] which form in the stepwise aquation of 1,2,3- and 1,2,6-triaquodiethylenetriaminechromium(III) cations, 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$, to the hexaaquochromium(III) cation. These intermediates appear to be the first metal complexes isolated in which the normally tridentate diethylenetriamine ligand has a denticity of less than three. We report also the kinetics of the stepwise aquation reactions. The possible structures and reaction schemes for these complexes are shown in Figure 1.

Experimental Section

1,2,3-Triaquodiethylenetriaminechromium(III) Cation. This complex was first reportedly prepared by reaction of $[Cr(dien)(O_2)_2]\cdot H_2O$[4] with warm 1 *F* $HClO_4$.[5,6] Subsequently we found that the complex prepared in this way is contaminated with large amounts of its tetraaquo aquation product, and that pure 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ can be chromatographed out of this mixture, as described in the section on synthesis of the tetraaquo aquation product. Usually, however, we prepared 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ from green 1,2,3-$Cr(dien)Cl_3$[7,8] by the method of Caldwell and House,[8] modified by

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[1] (a) Work partly supported by Contract AT(11-1)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-3 to the AEC. (b) Based upon the Ph.D. dissertation of D. K. Lin, UCLA, March 1969. (c) Abbreviations: en = ethylenediamine, $H_2N(CH_2)_2NH_2$; enH = 2-aminoethylammonium unidentate ligand, $H_2N(CH_2)_2NH_3^+$; dien = diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; dien H = bidentate dien ligand with one amino group protonated; dienH₂ = unidentate dien ligand with two amino groups protonated; trien = triethylenetetraamine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$.

[2] R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 7, 749, 2678 (1968).

[3] See D. K. Lin and C. S. Garner, *Inorg. Nucl. Chem. Lett.*, 5, 481 (1969), for an earlier brief description of these complexes.

[4] D. A. House and C. S. Garner, *Nature*, 208, 776 (1965).

[5] D. A. House and C. S. Garner, *Inorg. Nucl. Chem. Lett.*, 1, 137 (1965).

[6] D. A. House and C. S. Garner, *Inorg. Chem.*, 5, 840 (1966).

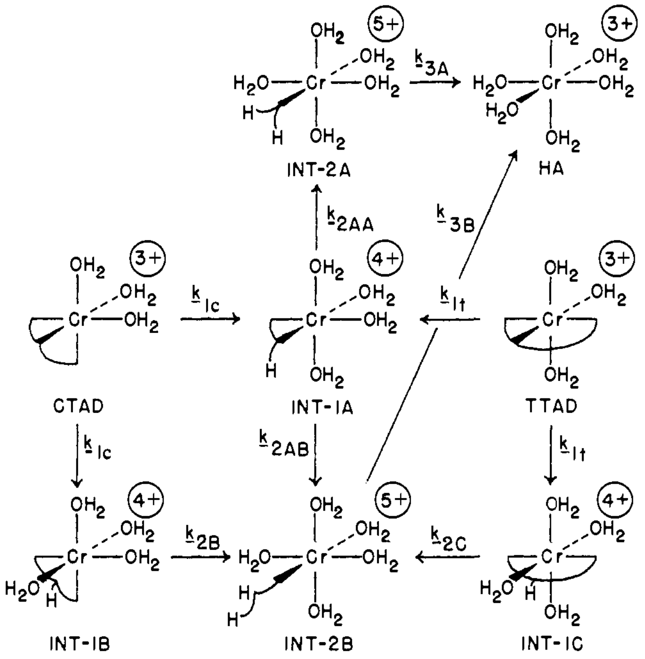

Figure 1. Possible paths for aquation of 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ to $Cr(OH_2)_6{}^{3+}$.

increasing the scale to 1 g of 1,2,3-$Cr(dien)Cl_3$, dissolving in *ca.* 25 ml of a solution 1 *F* in $HClO_4$ and 0.4 *F* in $Hg(NO_3)_2$ (in place of $Hg(OAc)_2$), and letting the solution stand at 20–25° for *ca.* 1 hr (instead of 16 hr, which we found by chromatography to allow formation of small amounts of $Cr(OH_2)_6{}^{3+}$). In order to remove Hg^{2+}, which we found catalyzes the aquation of 1,2,3-$Cr(dien)(OH_2)_3{}^{3+}$, the resulting solution was charged onto a 20 cm by 1 cm diameter column of H^+ Dowex AG50W-X4 (200–400 mesh); the Hg^{2+} and $HgCl_2$ were removed with ~300 ml of 1 *F* $HClO_4$ (until a test for Hg(II) with $SnCl_6{}^{4-}$ and Cl^- gave negative results); then the pink-to-red 1,2,3-$Cr(dien)(OH_2)_3{}^{3+}$ was eluted with *ca.* 150–200 ml of 3 *F* $HClO_4$, taking the center cut for spectral and kinetic run purposes. The visible absorption spectrum was the same as reported by Caldwell and House.[8] The 1,2,3 or *cis* configuration (see CTAD, Figure 1) of this triaquo complex now seems well established, since the 1,2,3 configuration of the green $Cr(dien)Cl_3$ from which this triaquo species is made has recently been confirmed by an X-ray structure study;[9] the purple 1,2,6-$Cr(dien)Cl_3$ generates the other (1,2,6) isomer of $Cr(dien)(OH_2)_3{}^{3+}$.

1,2,6-Triaquodiethylenetriaminechromium(III) Cation. This orange complex was synthesized by shaking purple 1,2,6-$Cr(dien)Cl_3$[5,6] with excess 0.1 *F* NaOH for 10 min at 20–25°, then acidifying with $HClO_4$.[8] The visible absorption spectrum of 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ prepared in this way agreed with the spectrum reported by Caldwell and House.[8] An earlier report[10] that this complex can be made by the action of $Hg(ClO_4)_2$ on 1,2,6-$Cr(dien)Cl_3$ in 1 *F* $HClO_4$ has been found to be incorrect; we have found that Hg^{2+} catalyzes the aquation of 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ and that the method gives largely the tetraaquo aquation product described below.

Tetraaquo(1-azonia-4,7-diazaheptane)chromium(III) Cation. Originally we prepared this new pink complex, which we believe to have the configuration of the species labeled INT-1A in Figure 1 (see Results and Discussion), by a tedious chromatographic separation, developed only after considerable research. A solution of $[Cr(dien)(O_2)_2]\cdot H_2O$[4] in 1 *F* $HClO_4$ (25 ml, *ca.* 30–50 m*F* in total Cr) was aged in the dark at 40° for *ca.* 2 hr, then cooled to 20–25° and charged onto a 30 cm × 1 cm diameter column of H^+ Dowex AG50W-X4 (200–400 mesh) cation-exchange resin. Small amounts of $Cr(OH_2)_6{}^{3+}$ (identified by its known electronic spectrum[2]) were removed with *ca.* 350 ml of 1.0 *F* $HClO_4$, then 1,2,3-$Cr(dien)(OH_2)_3{}^{3+}$ was eluted with *ca.* 350 ml of 1.5 *F* $HClO_4$ (center cuts of this fraction were used in some kinetic runs made with this substrate), and finally *ca.* 250 ml of 2.0 *F* $HClO_4$ was used to elute $Cr(dienH)(OH_2)_4{}^{4+}$, free of other Cr complexes (the pentaaquo aquation product remains on the column). All elutions were made at 20–25°, with a flow rate of *ca.* 4 ml/min, the entire procedure taking some 5–8 hr. Some aquation kinetic runs were made with the tetraaquo complex prepared in this way.

Later we found that $Cr(dienH)(OH_2)_4{}^{4+}$ could be synthesized more conveniently simply by aging 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ in 0.1–1 *F* $HClO_4$ for 10 half-lives (*ca.* 5 hr) at 20–25° in the dark. This was the method used to prepare the tetraaquo complex for most kinetic runs.

Pentaaquo(1,7-diazonia-4-azaheptane)chromium(III) Cation or Pentaaquo(1,4-diazonia-7-azaheptane)chromium(III) Cation. This new purple complex (either INT-2A or INT-2B of Figure 1) was synthesized and isolated in solution by aging a 2 *F* $HClO_4$ solution of $Cr(dienH)(OH_2)_4{}^{4+}$ for *ca.* 3 hr in the dark at 60° and pouring onto a 10 cm × 1 cm diameter column of H^+ Dowex AG50W-X4 (200–400 mesh) resin, then eluting $Cr(OH_2)_6{}^{3+}$ and unreacted $Cr(dienH)(OH_2)_4{}^{4+}$ with 350 ml of 2 *F* $HClO_4$, and finally eluting $Cr(dienH_2)(OH_2)_5{}^{5+}$ with 50 ml of 3 *F* $HClO_4$. This last effluent was *ca.* 1 m*F* in the pentaaquo complex.

Charge Determination. The charge per Cr atom for each of the two isolated intermediates was determined by a modification of method 1 used by Beukenkamp and Herrington.[11] Instead of using a resin column, we used 0.1 g of H^+ Dowex AG50W-X4 (100–200 mesh) resin in a centrifuge cone, separating the resin and solution by centrifugation and drawing off the centrifugate with a micropipet, since we were unable to get solutions of $Cr(dienH_2)(OH_2)_5{}^{5+}$ in high concentration and low acidity except in small volumes. Such solutions were made by eluting this complex from a cation-exchange resin with 10 ml of 6 *F* $HClO_4$ and lowering the acid concentration to 0.05 *F* by titration with OH^- Dowex AG1-X8 (100–200 mesh) at 0°[12,13] or KOH at 0°, then determining the Cr content before adding to a weighed amount of resin for the charge determination.

ORD Experiment. The method of Turner and Harris[14] was used in an attempt to learn whether the $Cr(dienH)(OH_2)_4{}^{4+}$ produced in aquation of 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ has the configuration of INT-1B (which has a plane of symmetry) or INT-1A (capable of existence in optically active forms if proton exchange with the solvent is slow enough) (see Figure 1). The method is based on the principle that a change in optical activity occurs when a configurationally unstable racemate *dl*-A is added to a stable optically active substance *d*- or *l*-B. Two solutions were prepared: one was 8 m*F* in $Cr(dienH)(OH_2)_4{}^{4+}$, 10 m*F* in *l*-malic acid, and 0.2 *F* in $HClO_4$; the other was identical except for absence of the Cr complex. The optical rotatory dispersion (ORD) curve of each solution was recorded from 210 to 270 nm with a Cary Model 60 spectropolarimeter. No difference was found, probably because INT-1A can exchange the extra proton on the free amino N atom with the solvent rapidly relative to the time (*ca.* 5 min) needed to prepare and measure the solution.

Other Materials and Procedures. The preparation of all other chemicals, and the analytical methods, kinetic run procedures, spectrophotometry, calculation of rate constants from absorbance data, and the "five-variable" computer program used have been described earlier.[2]

Results

Characterization of $Cr(dienH)(OH_2)_4{}^{4+}$ and $Cr(dienH_2)(OH_2)_5{}^{5+}$. These two new complexes were characterized by their mode of formation (aquation of $Cr(dien)(OH_2)_3{}^{3+}$ and $Cr(dienH)(OH_2)_4{}^{4+}$, respectively), by their aquation product ($Cr(dienH_2)(OH_2)_5{}^{5+}$ and $Cr(OH_2)_6{}^{3+}$, respectively), by their chromatographic behavior (the latter more difficultly eluted from a cation-exchange resin than the former, and each more difficultly eluted than $Cr(OH_2)_6{}^{3+}$ or $Cr(dien)(OH_2)_3{}^{3+}$), by charge per Cr atom determinations (+4.1–4.4, and +5.4, respectively), and by their visible absorption

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spectra (Figure 2). These properties and the aquation kinetic behavior were the same within experimental error for each complex whether it was generated from 1,2,3- or 1,2,6-Cr(dien)$(OH_2)_3^{3+}$, suggesting that Cr(dienH)$(OH_2)_4^{4+}$ so obtained has the configuration of INT-1A (Figure 1), which is the only one of the three possible geometric isomers of the tetraaquo complex which can be directly formed by aquation of both 1,2,3- and 1,2,6-Cr(dien)$(OH_2)_3^{3+}$. Moreover, examination of Fisher–Hirschfelder models indicates that rupture of a Cr–N bond to the secondary amino group (required to give INT-1B or INT-1C) should be much more difficult than rupture of a Cr–N bond to a primary amino group (giving INT-1A), especially when the steric requirements are taken into consideration for the proton which must be taken up by the freed amino N atom to stabilize the intermediate. The possibility of direct formation of INT-1B or INT-1C, followed by a relatively fast isomerization to INT-1A, seems remote since we expect such isomerizations to be very slow. Consequently, we assign the configuration of INT-1A, tetraaquo(1-azonia-4,7-diazaheptane)chromium(III)cation, to the Cr(dienH)$(OH_2)_4^{4+}$ isomer involved in this research. The configuration of the Cr(dienH$_2$)$(OH_2)_5^{5+}$ species isolated can be that of either INT-2A or INT-2B; in the absence of pure solid salts of this complex which could be subjected to an X-ray structure determination, we have been unable to think of an operational means of distinguishing between the two isomeric possibilities.

The d–d absorption bands of the tetraaquo complex are at 388 (ϵ 27.7) and 520 nm (ϵ 48.9 M^{-1} cm^{-1}), similar to the band wavelengths of Cr(en)$(OH_2)_4^{3+}$, namely, 385 (ϵ 24.3) and 512 nm (ϵ 41.7 M^{-1} cm^{-1}),[2] as expected since both complexes have essentially the same chromophores and symmetry. The pentaaquo complex has d–d bands at 396 (ϵ 23.4) and 551 nm (ϵ 22.4 M^{-1} cm^{-1}), which, as expected, are nearly the same as for Cr(enH)$(OH_2)_5^{4+}$, namely, 396 (ϵ 21.5) and 549 nm (ϵ 22.2 M^{-1} cm^{-1}),[2] and for Cr(NH$_3$)$(OH_2)_5^{3+}$, namely, 397 (ϵ 21.8) and 545 nm (ϵ 22.1 M^{-1} cm^{-1}).[15]

Aquation of 1,2,3- and 1,2,6-Cr(dien)$(OH_2)_3^{3+}$, Cr(dienH)$(OH_2)_4^{4+}$, and Cr(dienH$_2$)$(OH_2)_5^{5+}$. At 50–80° the rates of the successive aquations

$$\text{1,2,3-Cr(dien)}(OH_2)_3^{3+} + H_3O^+ = \text{Cr(dienH)}(OH_2)_4^{4+} \quad (1)$$

$$\text{Cr(dienH)}(OH_2)_4^{4+} + H_3O^+ = \text{Cr(dienH}_2)(OH_2)_5^{5+} \quad (2)$$

$$\text{Cr(dienH}_2)(OH_2)_5^{5+} + H_2O = \text{Cr}(OH_2)_6^{3+} + H_2\text{dien}^{2+} \quad (3)$$

are sufficiently similar to require the use of consecutive first-order kinetics, at least to evaluate the rate constants k_{1c} and k_2, all first-order rate constants k_n being defined by

$$-dC_n/dt = k_nC_n \quad (4)$$

where C_n is the molar concentration of the unaquated parent complex in the nth aquation step. Aquation of 1,2,6-Cr(dien)$(OH_2)_3^{3+}$ is so much faster than reaction 2 that simple first-order kinetics is adequate. The molar absorptivities, ϵ, of the successive products needed in the kinetic analyses were obtained from the spectra of the chromatographically isolated products (Figure 2). The values for the several rate constants determined under a variety of conditions are given in Tables I–IV.

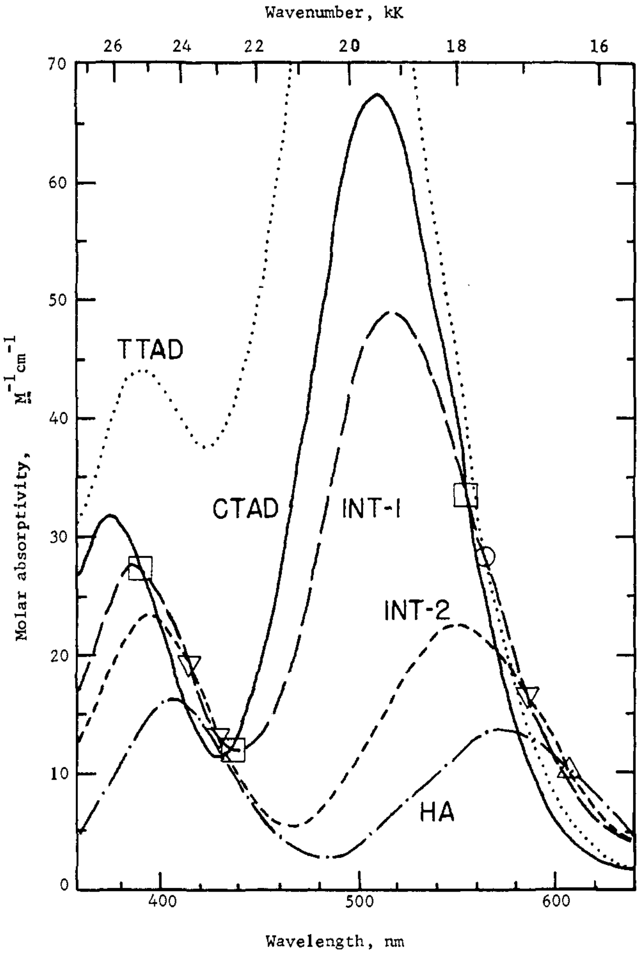

Figure 2. Visible absorption spectra of aquodiethylenetriaminechromium(III) complexes at 20–25°: TTAD, *trans* or 1,2,6 isomer of Cr(dien)$(OH_2)_3^{3+}$ in 1 F HClO$_4$ (the main band has its maximum at 493 nm and 89.6 M^{-1} cm^{-1}); CTAD, *cis* or 1,2,3 isomer of Cr(dien)$(OH_2)_3^{3+}$ in 1 F HClO$_4$; INT-1, Cr(dienH)$(OH_2)_4^{4+}$ in 1 F HClO$_4$; INT-2, Cr(dienH$_2$)$(OH_2)_5^{5+}$ in 3 F HClO$_4$; HA, Cr$(OH_2)_6^{3+}$ 1 F HClO$_4$; the molar absorptivity or molar extinction coefficient, ϵ, is defined by the relation $\log(I_0/I) = A = \epsilon cl$, where c is the molarity of the absorbing complex and l is the optical path in centimeters.

Figure 2 shows that the successive aquations should result in three isosbestic points each in the aquation of 1,2,3-Cr(dien)$(OH_2)_3^{3+}$ and Cr(dienH)$(OH_2)_4^{4+}$ during early reaction times, and one each in the aquation of 1,2,6-Cr(dien)$(OH_2)_3^{3+}$ and Cr(dienH$_2$)$(OH_2)_5^{5+}$; the values predicted for each substrate and its immediate aquation product are presented in Table V, together with the experimentally observed values, which agree well with the predicted values. Spectral changes with time for two typical runs, showing these isosbestic points, are shown in Figure 3; in scans B the isosbestic points at early stages of the reactions can be seen readily only as the first several scans are recorded experimentally, since at later stages the isosbestic points shift due to kinetic overlap of the reactions.

Excellent Arrhenius plots were obtained from the temperature dependences of k_{1t}, k_{1c}, k_2, and k_3 at 1 F HClO$_4$ (μ = 1 M), from which least-squares activation parameters were calculated as follows: 1,2,6-Cr(dien)$(OH_2)_3^{3+}$ aquation, E_a = 19.2 ± 0.6 kcal mol^{-1}, log PZ (sec^{-1}) = 10.80 ± 0.20, $\Delta S^\circ_{298}{}^* = -11 \pm 2$ cal deg^{-1} mol^{-1}, and $k_{1t} = (5.34 \pm 0.05) \times 10^{-4}$ sec^{-1} at 25.00°: 1,2,3-Cr(dien)$(OH_2)_3^{3+}$ aquation, E_a = 24.3 ±

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(15) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

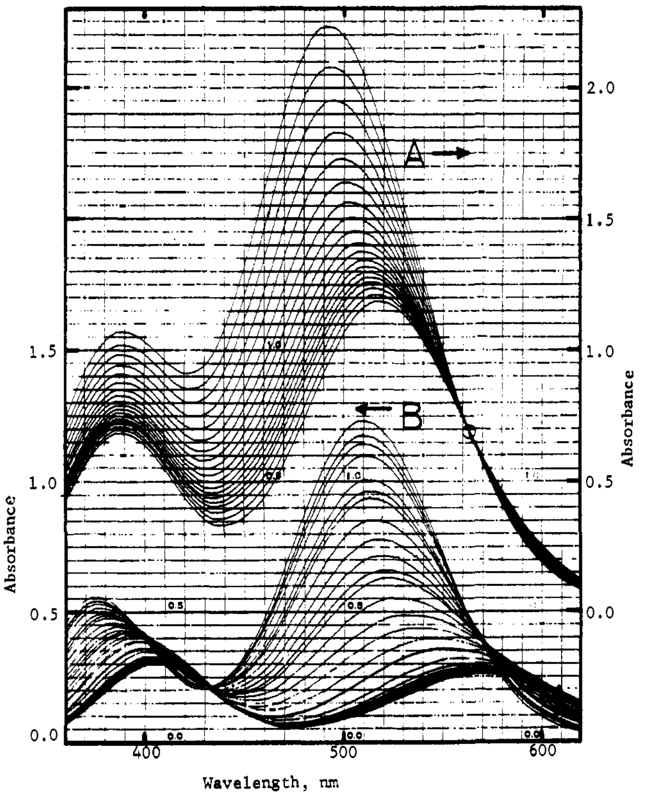

Figure 3. Change in absorption spectra during hydrolysis: A, 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ (C_0 = 2.43 mF) in 0.1 F $HClO_4$ (μ = 0.15 M) at 20.04°; reading downward at 480 nm, reaction time is 3, 8, 13, 18, 23, 28, 33, 38, 43, 48, 53, 58, 63, 68, 73, 78, 88, 102, and 124 min, respectively; B, 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ (C_0 = 1.91 mF) in 0.75 F $HClO_4$ (μ = 2 M) at 59.80°, aquating through $Cr(dienH)(OH_2)_4^{4+}$ and $Cr(dienH_2)(OH_2)_5^{5+}$ to give $Cr(OH_2)_6^{3+}$; reading downward at 490 nm, reaction time is 0, 0.5, 1, 1.5, 2.8, 3.5, 4, 5.5, 7, 8.5, 10, 11, 14, 18, 21, 28, 35, 70, 96.7, 120, 140, 163, 187, 211, and 235 hr, respectively.

Table I. First-Order Rate Constants for Aquation of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ in Aqueous $HClO_4$ in the Dark

Temp,[a] °C	[$HClO_4$], F	C_0, mM	μ,[b] M	10^4k_{1t},[c] sec^{-1}
14.74	0.10	2.08	0.15	2.59 ± 0.05
14.74	0.10	1.96	1.05	2.03 ± 0.03
14.74	1.00	1.67	1.05	1.92 ± 0.02
20.04	0.10	2.03	0.15	4.64 ± 0.09
20.04	0.10	2.28	0.15	4.79 ± 0.07
20.04	0.10	2.43	0.15	4.41 ± 0.07
20.04	0.10	1.42	0.55	4.14 ± 0.06
20.04	0.50	1.48	0.55	4.02 ± 0.07
20.04	0.50	1.53	0.55	3.86 ± 0.06
20.04	0.50	1.96	0.55	4.38 ± 0.07
20.04	0.010	2.20	1.05	3.54 ± 0.05
20.04	0.10	1.98	1.00	3.71 ± 0.06
20.04	0.10	2.00	1.05	3.84 ± 0.06
20.04	0.10	2.35	1.05	3.69 ± 0.05
20.04	0.50	1.69	1.00	3.50 ± 0.05
20.04	0.50	2.38	1.05	3.31 ± 0.04
20.04	0.50	2.49	1.05	3.63 ± 0.06
20.04	0.50	2.71	1.05	3.47 ± 0.05
20.04	1.00	2.20	1.05	3.69 ± 0.06
20.04	1.00	2.45	1.05	3.54 ± 0.05
25.00	0.10	2.22	0.55	5.77 ± 0.09
25.00	1.00	2.21	1.05	5.34 ± 0.05
29.79	0.10	2.33	0.15	13.0 ± 0.2
29.79	0.10	2.45	1.05	10.2 ± 0.2
29.79	1.00	2.42	1.05	10.2 ± 0.2

[a] ±0.01° at 15 and 25°; ±0.02° at 20 and 30°. [b] Ionic strength, controlled with $NaClO_4$. [c] Analyzed at 480 nm; errors are standard deviations; individual rate plots were linear over 3–4 half-times.

Table II. First-Order Rate Constants for Aquation of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ in Aqueous $HClO_4$ in the Dark

Temp,[a] °C	[$HClO_4$], F	C_0, mM	μ,[b] M	10^5k_{1c},[c] sec^{-1}
50.00	1.0	3.41	1.0	1.93 ± 0.03
50.00	1.0	2.03	2.0	1.69 ± 0.03
50.00	2.0	2.65	2.0	1.54 ± 0.02
59.80	1.0	3.21	1.0	5.89 ± 0.09
59.80	1.0	2.03	2.0	4.97 ± 0.08
59.80	1.5	1.79	2.0	4.98 ± 0.08
59.80	2.0	1.75	2.0	4.96 ± 0.08
59.80	2.0	3.40	2.0	4.89 ± 0.08
70.20	1.0	1.32	1.0	18.6 ± 0.3
70.20	1.0	2.03	2.0	14.2 ± 0.2
70.20	2.0	2.65	2.0	14.5 ± 0.2

[a] ±0.05°. [b] Ionic strength, controlled with $NaClO_4$. [c] Analyzed at 490 nm by "five-variable" computer program; errors are standard deviations.

Table III. First-Order Rate Constants for Aquation of $Cr(dienH)(OH_2)_4^{4+}$ in Aqueous $HClO_4$ in the Dark

Temp,[a] °C	[$HClO_4$], F	C_0, mM	μ,[b] M	10^5k_2,[c] sec^{-1}
59.80	1.0	4.16	1.0	2.16 ± 0.03
70.20	0.10	3.29	1.0	6.53 ± 0.09
70.20	1.0	3.75	1.0	6.57 ± 0.08
80.80	0.10	3.47	1.0	18.4 ± 0.3
80.80	1.0	3.45	1.0	18.9 ± 0.3
80.80	1.0	3.49	1.0	18.7 ± 0.2
80.80	1.0	3.77	1.0	18.6 ± 0.4
80.80	1.0	4.01	1.0	18.6 ± 0.2
80.80	0.97	3.18	2.0	17.3 ± 0.3
80.80	2.0	1.86	2.0	17.0 ± 0.2
80.80	2.0	3.58	2.0	17.2 ± 0.3

[a] ±0.05° at 60 and 70°; ±0.10° at 81°. [b] Ionic strength, controlled with $NaClO_4$. [c] Analyzed at 510 nm; errors are standard deviations; individual rate plots were linear to *ca.* 55% reaction.

Table IV. Observed First-Order Rate Constants for Hydrolysis of $Cr(dienH_2)(OH_2)_5^{5+}$ in Aqueous $HClO_4$ in the Dark

Temp,[a] °C	[$HClO_4$], F	C_0, mM	μ,[b] M	$10^6k_{3\ obsd}$,[c] sec^{-1}
59.80	0.100	4.27	1.03	2.77 ± 0.08
59.80	0.300	3.41	1.03	2.64 ± 0.03
59.80	1.00	4.16	1.03	2.61 ± 0.07
70.20	0.100	3.29	1.03	10.2 ± 0.3
70.20	0.300	3.41	1.03	9.12 ± 0.18
70.20	1.00	3.75	1.03	8.74 ± 0.13
80.80	0.100	3.47	1.03	55.0 ± 1.6
80.80	0.300	3.41	1.03	36.1 ± 1.2
80.80	1.00	3.45	1.03	30.1 ± 1.0
80.80	1.00	3.49	1.03	29.6 ± 1.0
80.80	1.00	3.66	1.03	30.6 ± 1.2
80.80	1.00	3.77	1.03	30.1 ± 0.8
80.80	0.970	3.18	2.03	30.0 ± 0.7
80.80	2.00	2.20	2.03	28.7 ± 0.6[d]
80.80	2.00	3.58	2.03	28.7 ± 0.8

[a,b] See footnotes *a* and *b*, Table III. [c] Analyzed at 510 nm by "five-variable" computer program; errors are standard deviations. [d] Substrate is $Cr(dienH_2)(OH_2)_5^{5+}$ chromatographed from an aged 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ solution, and rate was analyzed at 540 nm; rate plot was linear to 75% reaction.

0.7 kcal mol^{-1}, log PZ (sec^{-1}) = 11.72 ± 0.51, $\Delta S°_{298}{}^*$ = −7 ± 3 cal deg^{-1} mol^{-1}, and by extrapolation k_{1c} = (8.1 ± 0.8) × 10^{-7} sec^{-1} at 25.0°; $Cr(dienH)(OH_2)_4^{4+}$ aquation, E_a = 24.0 ± 0.6 kcal mol^{-1}, log PZ (sec^{-1}) = 11.09 ± 0.40, $\Delta S°_{298}{}^*$ = −10 ± 2 cal deg^{-1} mol^{-1}, and by extrapolation k_2 = (3.1 ± 0.3) × 10^{-7} sec^{-1} at

Table V. Isosbestic Points in 640–360-nm Region in Successive Aquations of 1,2,6- and 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ to $Cr(OH_2)_6^{3+}$

Substrate	Experimental λ, nm	Experimental ε, M^{-1} cm^{-1}	Predicted[a] λ, nm	Predicted[a] ε, M^{-1} cm^{-1}
1,2,6-$Cr(dien)(OH_2)_3^{3+}$	564 ± 1	28.3 ± 0.2	564 ± 1	28.3 ± 0.7
1,2,3-$Cr(dien)(OH_2)_3^{3+}$	390 ± 1	26.4 ± 0.5	390 ± 2	27.8 ± 1.0
	432 ± 1	11.7 ± 0.4	436 ± 2	12.1 ± 0.6
	556 ± 1	31.4 ± 0.8	554 ± 2	34.5 ± 2.3
$Cr(dienH)(OH_2)_4^{4+}$	415 ± 1	19.6 ± 0.4	415 ± 1	19.3 ± 0.6
	431 ± 3	13.1 ± 0.8	429 ± 1	13.5 ± 0.4
	584 ± 2	17.5 ± 0.9	585 ± 2	16.4 ± 0.5
$Cr(dienH_2)(OH_2)_5^{5+}$	608 ± 1	10.0 ± 0.1	607 ± 2	10.1 ± 0.6

[a] From spectra (Figure 2) of substrate and its immediate aquation product.

25.0°; $Cr(dienH_2)(OH_2)_5^{5+}$ aquation (acid-independent path only), $E_a = 26.5 \pm 0.8$ kcal mol^{-1}, log PZ (sec^{-1}) $= 11.81 \pm 0.52$, $\Delta S^{\circ}_{298}{}^{*} = -6 \pm 3$ cal deg^{-1} mol^{-1}, and by extrapolation $k_3 = (2 \pm 1) \times 10^{-8}$ sec^{-1} at 25.0°.

Discussion

From Tables I–III, it is seen that within experimental error there is no hydrogen ion dependence of k_{1t}, k_{1c}, and k_2 at constant ionic strength under the conditions involved. Table IV, however, indicates that the apparent first-order rate constant, $k_{3\,\mathrm{obsd}}$, for hydrolysis of $Cr(dienH_2)(OH_2)_5^{5+}$ is dependent upon the hydrogen ion concentration. Figure 4 presents plots of $k_{3\,\mathrm{obsd}}$ *vs.* 1/[H$^+$], where [H$^+$] is taken as the formality of $HClO_4$ in the reaction solution. Over the range 0.1–1 F $HClO_4$ (μ = 1 M), $k_{3\,\mathrm{obsd}}$ obeys a relation of the form

$$k_{3\,\mathrm{obsd}} = k_3 + (k_3'/[\mathrm{H}^+]) \qquad (5)$$

where k_3 is the first-order rate constant for the aquation of $Cr(dienH_2)(OH_2)_5^{5+}$ itself

$$\mathrm{Cr(dienH_2)(OH_2)_5^{5+} + H_2O \xrightarrow{k_3} Cr(OH_2)_6^{3+} +} \\ \mathrm{H_2dien^{2+}} \text{ (path 1)} \qquad (6)$$

and the second term implies either a contribution from base hydrolysis of the substrate (path 2)

$$\left.\begin{array}{ll} \mathrm{Cr(dienH_2)(OH_2)_5^{5+} + OH^- \xrightarrow{k_{3b}}} & \\ \qquad \mathrm{Cr(OH_2)_5OH^{4+} + H_2dien^{2+}} & (7a) \\ \mathrm{Cr(OH_2)_5OH^{4+} + H^+ \xrightarrow{fast} Cr(OH_2)_6^{3+}} & (7b) \end{array}\right\} \text{(path 2)}$$

for which $k_3'/[\mathrm{H}^+] = (k_3'/K_w)[\mathrm{OH}^-] = k_{3b}[\mathrm{OH}^-]$, where K_w is the ion-product constant for water in the reaction solutions and/or a rapid acid-dissociation preequilibrium followed by a rate-controlling aquation of the hydroxotetraaquo complex (path 3)

$$\left.\begin{array}{ll} \mathrm{Cr(dienH_2)(OH_2)_5^{5+} \overset{K_a}{\rightleftharpoons}} & \\ \qquad \mathrm{Cr(dienH_2)(OH_2)_4OH^{4+} + H^+} & (8a) \\ \qquad \text{(fast equilibrium, far to left)} & \\ \mathrm{Cr(dienH_2)(OH_2)_4OH^{4+} + H_2O \xrightarrow{k_{3h}}} & \\ \qquad \mathrm{Cr(OH_2)_5OH^{2+} + H_2dien^{2+}} & (8b) \\ \text{Reaction 7b} & \end{array}\right\} \text{(path 3)}$$

for which $k_3'/[\mathrm{H}^+] = k_{3h}K_a/[\mathrm{H}^+]$, where K_a is the first acid-dissociation constant of $Cr(dienH_2)(OH_2)_5^{5+}$. An alternative path in which OH^- attacks one of the amino protons of the substrate, or in which it is such a proton that it is dissociated in the acid preequilibrium, may be ruled out since the free nonprotonated amino group would be expected to rechelate and give rise to a back reaction, for which there is no kinetic evidence even after 4 half-times of $Cr(dienH_2)(OH_2)_5^{5+}$ aquation. Table VI gives the values of k_3 and k_3' obtained from the y intercepts and slopes of the plots in Figure 4, together with values of k_{3b} and k_{3h} calculated on the assumption that the [H$^+$]-dependent term arises wholly from path 2 and path 3, respectively. The values of k_{3b} are abnormally large for a Cr(III) complex, and we may exclude any appreciable contribution from path 2. The values of k_{3h}, on the other hand, are reasonable for aquation of $Cr(dienH_2)(OH_2)_4OH^{4+}$ relative to k_3 for aquation of $Cr(dienH_2)(OH_2)_5^{5+}$, based on aquation rate comparisons of Cr(III) and Co(III) hydroxo and aquo complexes. This explanation of the [H$^+$] dependence of $k_{3\,\mathrm{obsd}}$ is compatible with the observed isosbestic points (Table V), since at the lowest [H$^+$], namely, 0.1 M, only *ca.* 0.1% of the complex would be in the hydroxotetraaquo form if $K_a \sim 10^{-4}$. The activation parameters given earlier were for the acid-independent path (path 1); because of the large uncertainty in K_a and, hence, k_{3h} values, activation parameters for $Cr(dienH_2)(OH_2)_4OH^{4+}$ aquation are not worth being calculated.

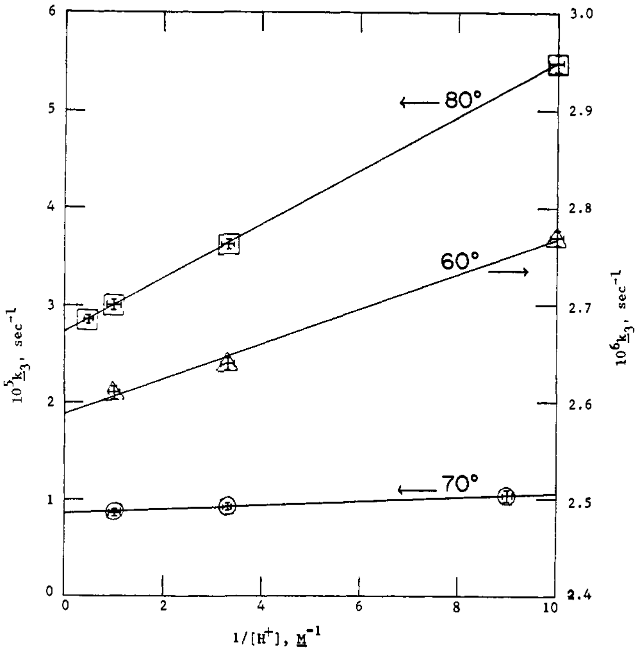

Figure 4. Hydrogen ion dependence of hydrolysis rate of $Cr(dienH_2)(OH_2)_5^{5+}$ (μ = 1.03 M, $NaClO_4$).

The presence of an acid-dependent term in the hydrolysis of $Cr(dienH_2)(OH_2)_5^{5+}$, but not in the other aquations reported here, may arise from the fact that K_a

Table VI. Rate Constants for Hydrolysis of $Cr(dienH_2)(OH_2)_5^{5+}$ (μ = 1.0 M)

Temp, °C	10^6k_3, sec^{-1}	10^7k_3 , M sec^{-1}	$10^{-5}k_{3b}$,^{a} M^{-1} sec^{-1}	10^2k_{3h},^{b} sec^{-1}
80.80	27.3 ± 0.5	27.8 ± 0.8	~200	~28
70.20	8.62 ± 0.17	1.63 ± 0.07	~20	~2
59.80	2.59 ± 0.13	0.17 ± 0.01	~2	~0.2

^{a} Assuming [H$^+$]-dependent term arises wholly from path 2 and that K_w has the same values as in pure water (J. N. Butler, "Ionic Equilibrium,"Addison-Wesley Publishing Co., Reading, Mass., 1964, p 53). ^{b} Assuming [H$^+$]-dependent term arises wholly from path 3 and that K_a is *ca.* 10^{-4} at 60–80°. (From values for other Cr(III)–aquoamine complexes at 25°, we estimate roughly that K_a is *ca.* 10^{-4} at 60–80°; see, *e.g.*, F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 32.)

Table VII. Rate Parameters for Aquation of Some Cr(III) Aquoamine Complexes at 60°

Complex	Medium	k, sec^{-1}	E_a, kcal mol^{-1}	$\Delta S^{\circ *}$, cal deg^{-1} mol^{-1}
1,2,3-$Cr(dien)(OH_2)_3^{3+}$ ^{a}	1 F $HClO_4$	5.89×10^{-5}	24.3	−7
1,2,6-$Cr(dien)(OH_2)_3^{3+}$ ^{a}	1 F $HClO_4$	1.8×10^{-2} ^{b}	19.2	−11
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ ^{c}	3 F $HClO_4$	1.33×10^{-4}	27.5	+3
$Cr(dienH)(OH_2)_4^{4+}$ ^{a} (1,2,3,6-tetraaquo)	1 F $HClO_4$	2.16×10^{-5}	24.0	−10
$Cr(en)(OH_2)_4^{3+}$ ^{d}	3 F $HClO_4$	3.0×10^{-6}	27.7	−3
trans ?-$Cr(NH_3)_2(OH_2)_4^{3+}$ ^{e}	0.2 F HNO_3^{2-} 0.2 F KNO_3	$\sim 1 \times 10^{-4}$?^{f}		
cis ?-$Cr(NH_3)_2(OH_2)_4^{3+}$ ^{e}	0.2 F HNO_3^{2-} 0.2 F KNO_3	$\lesssim 1 \times 10^{-5}$?^{f}		
$Cr(dienH_2)(OH_2)_5^{5+}$ ^{a}	1 F $HClO_4$	2.59×10^{-6} ^{g}	26.5^{g}	−7^{g}
$Cr(enH)(OH_2)_5^{4+}$ ^{d}	3 F $HClO_4$	1.9×10^{-6}	25.4	−11
$Cr(NH_3)(OH_2)_5^{3+}$ ^{h}	0.1 F $HClO_4^{2-}$ 0.07 F $LiClO_4$	$\sim 2 \times 10^{-7}$?^{f}		
$Cr(NH_3)(OH_2)_5^{3+}$ ^{e}	0.2 F HNO_3^{3-} 0.2 F KNO_3	$\sim 1 \times 10^{-5}$?^{f}		

^{a} This research. ^{b} Extrapolated from 30° by Arrhenius equation. ^{c} T. J. Williams and C. S. Garner, *Inorg. Chem.*, **8**, 1639 (1969). ^{d} Reference 2. ^{e} J. Bjerrum and E. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 313 (1958); E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958). ^{f} Extrapolated from 40°, estimating E_a = 25 kcal mol^{-1}; values uncertain. ^{g} For k_3 path only (see text). ^{h} J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

for the 5+ substrate would be expected to be appreciably greater on the basis of charge alone than for the other substrates, which have smaller charges.

Table I–IV show that the aquation rate constants decrease only slightly on increase of ionic strength in the ranges involved (k_{1t}, 20% for μ = 0.15–1.1 M at 0.1 M H$^+$ and 20°; for μ = 1–2 M at 1 M H$^+$, k_{1c} decreases 15% at 60°, k_2 8% at 70–80°, and $k_{3\,obsd} < 1\%$ at 80°). These effects may arise from ion pairing or specific salt effects.

Table VII presents aquation rate parameters for the above complexes and some closely related complexes. The aquation rate for 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ in 1 F $HClO_4$ at 60° is 300 times that for the 1,2,3 isomer, chiefly because of a lower activation energy for the former.[16] This behavior is paralleled by that of 1,2,6-$Cr(dien)Cl_3$, which aquates to 1,2,3-$Cr(dien)(OH_2)Cl_2^+$ in aqueous $HClO_4$ at 18–25° as rapidly as it dissolves, whereas under the same conditions 1,2,3-$Cr(dien)Cl_3$ dissolves to give solutions from which 1,2,3-$Cr(dien)Cl_3$ can be isolated.[8] The much greater aquation rate for the 1,2,6 isomer in each case is apparently associated with the greater ring strain for this isomer, which is a consequence of the near planarity of the N atoms (see TTAD, Figure 1); this ring strain is very evident in the 1,2,6 isomer when one uses Fisher-Hirschfelder molecular models to construct models of the two isomers. There appear to be no reports in the literature bearing directly on M–N bond rupture rates as a function of strain in N-containing chelate ligands; it will be interesting to examine other Cr(III) complexes having multidentate amine ligands to see if this effect is general. Although 1,2,6- and 1,2,3-$Co(dien)(OH_2)_3^{3+}$ are known,[8] their aquation cannot be studied because the former isomerizes in acidic solution to the latter ($k \sim 4 \times 10^{-4}$ sec^{-1} at room temperature),[8] and the latter is reduced to Co(II) under all conditions of acidity and temperature which give measurable rates.[17] There are reports that acido ligands in Co(III) complexes with multidentate amine ligands aquate faster for the isomers with the greater ring strain; *e.g.*, in acidic solution at 25°, *cis*-β-$Co(trien)Cl_2^+$ (one planar secondary amino N atom) aquates at 10 times the rate of the *cis*-α isomer (no planar amino N atoms), and in the former, evidence suggests that the chloro ligand *trans* to the "strained" secondary amino N atom is *ca.* 20 times more labile than the chloro ligand *trans* to an "unstrained" primary amino N atom;[18,19] a similar but smaller effect is observed with the two geometric forms of *cis*-β-$Co(trien)(OH_2)Cl^{2+}$ (Cl *trans* to secondary N *ca.* 3 times more labile than Cl *trans* to primary N).[18,19] Sargeson and Searle,[20] however, have presented evidence suggesting that the relative stability of the α and β isomers of Co(III)–trien complexes is a function of the substituents rather than of strain in the chelate ring. These observations, however, all relate to possible ring strain effects on aquation rates of acido ligands, and not to rupture of a Cr–N or Co–N bond, where the ring

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(16) The high rate of aquation of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ initially led us to think that the substrate was possibly not the triaquo complex but rather a chloroaquo complex, which would be expected to be formed as a more labile intermediate in the synthesis of the triaquo complex from 1,2,6-$Cr(dien)Cl_3$. However, the chromatographic behavior of the triaquo preparation is inconsistent with a smaller charge which would arise from the presence of one or more chloro ligands, and analysis showed the absence of Cl and the complete conversion of the trichloro complex to the triaquo complex.

(17) P. Wilairat and C. S. Garner, unpublished research; a kinetic study of the reduction is in progress.

(18) A. M. Sargeson and G. H. Searle, *Nature*, 200, 356 (1963).

(19) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).

(20) A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).

strain could lead to the much larger rate differences found for the Cr(III) complexes under discussion.

Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ (unknown configuration), which also has three Cr–N bonds, aquates at 60° at approximately twice the rate of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ and $^1/_{140}$th the rate of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ (Table VII). The first of these two rate comparisons is about what would be expected if pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ had a 1,2,3-triaquo configuration and if aquation of a Cr–N bond followed the same rate trends as aquation of a Co–Cl (and, by inference, Cr–Cl) bond, as observed in the series *cis*-$Co(NH_3)_4Cl_2^+$, *cis*-$Co(en)(NH_3)_2Cl_2^+$, *cis*-$Co(en)_2Cl_2^+$,[21] and *cis*-α-$Co(trien)Cl_2$,[18,19] and the series $Co(NH_3)_5Cl^{2+}$,[22] *cis*-$Co(en)_2(NH_3)Cl^{2+}$, *cis*-α-$Co(trien)(NH_3)Cl^{2+}$, and ω-$Co(dien)(en)Cl^{2+}$.[21] In each series the aquation rates of a chloro ligand decrease with increasing chelation, which has been ascribed[21] to the tendency of the organic ligands to break up the solvation shell, rendering the transition state less stable since it makes greater demands on solvation due to the separating charges. However, Sargeson and Searle[19] question the validity of the solvation explanation since *cis*-β-$Co(trien)Cl_2^+$ does not fit the pattern. In the Cr–N (or Co–N) type aquations insufficient data exist to allow examination of the effect of chelation; a solvation effect would perhaps be less important since there would be little separation of charge on forming the transition state, so the above comparison cannot be accepted as strong evidence for a 1,2,3 configuration for pink $Cr(en)(NH_3)(OH_2)_3^{3+}$.

For the complexes with two Cr–N bonds, $Cr(dienH)(OH_2)_4^{4+}$ aquates at 60° at 7 times the rate of $Cr(en)(OH_2)_4^{3+}$ (Table VII). The greater rate of the former is expected due to steric crowding from the $(CH_2)_2NH_3$ group attached to the secondary amino N atom, inasmuch as steric crowding would favor a dissociative mechanism (this type of effect has been demonstrated[23] with N-substituted alkyl groups in chloroaminecobalt(III) substrates, *e.g.*). Comparison with *trans*- and *cis*-$Co(NH_3)_2(OH_2)_4^{3+}$ is ambiguous because of the uncertain configuration assignments and rates of the diammines.

For the complexes with one Cr–N bond, $Cr(dienH_2)(OH_2)_5^{5+}$ aquates at 60° faster than $Cr(enH)(OH_2)_5^{4+}$, presumably because of steric crowding in the former. The ammine complex, $Cr(NH_3)(OH_2)_5^{3+}$, appears to aquate somewhat slower than either (taking the values in $HClO_4$ medium).

Successive aquations of either 1,2,3- or 1,2,6-$Cr(dien)(OH_2)_3^{3+}$ to the final product $Cr(OH_2)_6^{3+}$ are progressively slower, as also observed in aquation of $Cr(en)(OH_2)_4^{3+}$ and various haloaquoamine complexes of Cr(III). In contrast, successive aquations of $Cr(NH_3)_6^{3+}$ to $Cr(OH_2)_6^{3+}$ do not appear to follow any systematic trend of rates. The reasons for this are unknown, and further studies of successive Cr–N bond ruptures in Cr(III) complexes with multidentate amine ligands are needed.

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[21] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[22] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

[23] See Basolo and Pearson, Table VI, footnote *b*, p 162.

Aluminum–Aluminum Covalent Bonds. II.[1a]
Bis(dimethylamino)trimethyltrialuminum(5)

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Abstract: The reduction of $[Al(CH_3)_3]_2$ by $B_2[N(CH_3)_2]_4$ has been investigated by varying the reactant stoichiometries, Al : B_2, according to the mole ratios 1.8, 2.8, 3.9, and large excesses of $[Al(CH_3)_3]_2$. The reaction products were found to be dependent on the reaction stoichiometry, order of reagent mixing, and reaction temperature. A new catenated aluminum species was prepared and characterized, bis(dimethylamino)trimethyltrialuminum(5), $Al_3(CH_3)_3[N(CH_3)_2]_2$, as well as a new amino adduct of covalent aluminum, $(CH_3)_3Al \cdot N(CH_3)_2Al(CH_3)_2$. Hydride formation takes place during *in situ* decomposition of methyldimethylaminodiborane(4) derivatives as well as hydride transfer from boron to aluminum.

The reduction of $[Al(CH_3)_3]_2$ by $B_2[N(CH_3)_2]_4$ has been reported to afford the catenated aluminum derivative, $Al_4B[N(CH_3)_2]_3(CH_3)_6$.[1a] The reaction stoichiometry associated with this reduction appears anomalous in that catenated aluminum species are only isolated when the mole ratio of $Al(CH_3)_3 : B_2[N(CH_3)_2]_2$ is greater than *ca.* 3, *i.e.*, employing some minimum quantity of reducing agent. This investigation was undertaken to (a) elucidate the apparent anomaly associated with the reaction stoichiometry, (b) isolate and characterize reaction intermediates, and (c) prepare boron-free catenated organoaluminum species. Item c is of particular importance because interpretation of the experimental data associated with $Al_4B[N(CH_3)_2]_3(CH_3)_6$ in-

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