deg^{-1}. At 25° $k_0 = 1.2 \times 10^{-8}$ sec^{-1} and $k_{-1} = 9.9 \times 10^{-11}$ M sec^{-1}.

The rates given in Table II for 90° and ionic strength 4.0 M were treated according to expression 2. The calculated values of the function agreed with the experimental values of k_{obsd} with an average deviation of 2.9%. The computed rate constants for the two terms in the rate law have the value $k_0 = (3.40 \pm 0.08) \times 10^{-5}$ sec^{-1} and $k_{-1} = (1.77 \pm 0.04) \times 10^{-6}$ M sec^{-1}. Corresponding values for 1.0 M ionic strength at 90° are $k_0 = (5.18 \pm 0.13) \times 10^{-5}$ sec^{-1} and $k_{-1} = (5.60 \pm 0.07) \times 10^{-6}$ M sec^{-1}.

The moderate ionic strength effect on the rate constant for an acid-independent path gives a support to the assumption that the parameters in expression 2 describe chemically significant reaction paths, though a medium effect caused by varying hydrogen ion concentrations at constant ionic strength cannot be ruled out.

A good conformity of data given in Table II with expressions 2 and 3 is seen from the relatively small average deviation of the calculated from the experimentally observed values of the functions. At a constant ionic strength and temperature, the concentration of hydrogen ions was varied for a factor of $\sim 10^3$ causing a $\sim$60-fold change in the rate of aquation. At the temperatures used in 1 M perchloric acid 90–95% of the reaction proceeds *via* the acid-independent path and in the low acidities used almost completely *via* the acid-inverse path.

The rate law is consistent with k_0 in expression 2 being the rate constant for the aquation of $Cr(H_2O)_5py^{3+}$ and k_{-1}/K_h the rate constant for the aquation of the conjugate base, $Cr(H_2O)_4(OH)py^{2+}$, where K_h is the equilibrium constant for the acid dissociation reaction

$$Cr(H_2O)_5py^{3+} \rightleftharpoons Cr(H_2O)_4(OH)py^{2+} + H^+$$

Similar rate law terms with respect to hydrogen ion concentration were observed for $Cr(H_2O)_5X^{n+}$ complexes where X represents an acidic ligand.[15-18] An additional term, of first power in the hydrogen ion concentration due to a pathway involving protonated ligand in the transition state, was observed when X was a more basic ligand such as fluoride,[16] azide,[19] cyanide,[20] sulfate,[21] and acetate.[22] Pyridinechromium(III) shows a "normal" behavior in this respect. Though basic as the free ligand, pyridine does not possess a residual basicity in the complex since it is coordinated through the nitrogen atom. Analogous rate laws were found for ammine[23] and unidentate diethylenetriamine[6] complexes of monosubstituted chromium(III), while the unidentate ethylenediamine complex showed only an acid-independent path in the acidity range studied.[5] The rates of aquation of these unidentate amine complexes[5,6] and of the pyridine complex *via* the acid-independent path have very similar values in the temperature range studied.

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The Rate of Aquation of *trans*-Difluorobis(ethylenediamine)chromium(III) through an Isolable Monodentate Ethylenediamine Complex

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The stoichiometry and rate of aquation of *trans*-$Cr(en)_2F_2^+$ have been determined. The sole product (>98%) is $Cr(en)(enH)H_2OF_2^{2+}$ which is a monodentate ethylenediamine complex with the two fluorides probably trans to one another. This complex is isolated in solution by ion-exchange chromatography. It aquates in turn to form *cis*-$Cr(en)_2H_2OF^{2+}$ and $Cr(en)(H_2O)_2F_2^+$ (which is assigned the stereochemistry 1,6-difluoro-2,3-diaquoethylenediaminechromium(III)) in a ratio of 1.0:3.25. The rate constant for aquation of *trans*-$Cr(en)_2F_2^+$ is $(1.23 \pm 0.02) \times 10^{-5}$ sec^{-1} at 25.0° and $I = 1.0$ M. The activation parameters are $\Delta H^{\ddagger} = 24.1 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.3 \pm 0.5$ cal mol^{-1} deg^{-1}. The values at $I = 0.12$ M are also reported. These data are compared with those for analogous systems and the implications are discussed.

Introduction

We have been interested for some time in the nature of the lowest lying σ-antibonding orbital in metal complexes.[1,2] There is now ample spectroscopic evidence that fluorine in fluorochromium(III) complexes is a strong σ-bonding ligand.[3-5] This feature makes molecules such as *trans*-$Cr(en)_2F_2^+$ of importance in electron-transfer studies and in photochemical investigations of Cr(III) complexes. In order to investigate these systems, we felt it was of importance to understand the thermal aquation of *trans*-$Cr(en)_2F_2^+$. In this paper we report on that aquation.

A recent development in studies of the aquation of Cr(III) complexes involving multidentate amine ligands has been the isolation of products in which multidentate ligands are partially unwrapped.[6-9] In this study we

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have also observed such a species. In addition to the usual reaction path—complete loss of the partially unwrapped ligand—we also present evidence for the reclosure of the monodentate ethylenediamine to form a new chelated complex.

Experimental Section

Materials.—*trans*-$[Cr(en)_2F_2]ClO_4$ was prepared by two synthetic procedures, both with minor modifications. The first method used was that described by Vaughn, Stvan, and Magnuson,[10] except that the amount of ethylenediamine was decreased from a 100-fold to a 3-fold excess. The yield still was low—8%. In the second method, *trans*-$[Cr(en)_2F_2]ClO_4$ was prepared from *trans*-$[Cr(py)_4F_2]ClO_4$ as described,[11] except that 95% ethanol was used in place of the 2-methoxyethanol as a solvent for the conversion. The material recovered from the ethanol was recrystallized from hot water as the perchlorate salt. Further recrystallizations did not change the spectrum. The yield in this method was 45%. *Anal.* Calcd for $Cr(en)_2F_2ClO_4$: Cr, 16.80; N, 18.10. Found: Cr, 16.76; N, 17.79. The spectral data, which are reported in Table I, are in excellent agreement with those reported by Glerup, *et al.*[11] In most of the work reported below, the complex from the second method of synthesis was used.

TABLE I
SPECTRAL DATA FOR COMPLEXES STUDIED

Complex	λ,[a] Å	ϵ, M^{-1} cm^{-1}
trans-$Cr(en)_2F_2^+$	5250 sh	16.3
(0.004–0.1 *M* HCl or $HClO_4$)	4660	21.1
	4000 sh	12.8
	3500	14.5
$Cr(en)(enH)H_2OF_2^{2+}$	5190	40.0
(0.4–0.7 *M* HCl or $HClO_4$)	4100 sh	11.0
	3660	18.6
$Cr(en)(H_2O)_2F_2^+$	5420	37.0
(0.25–0.5 *M* HCl or $HClO_4$)	4100	10.1
	3710	12.5
cis-$Cr(en)_2H_2OF^{2+}$	5120	47.3
(2.0–5.0 *M* HCl)	3780	29.4

[a] These values are peak positions unless marked as shoulder.

Acid solutions were prepared from Baker Analyzed 70% $HClO_4$ by dilution with water doubly distilled in a quartz apparatus. The ion-exchange resin used was Baker Analyzed Dowex 50W-X2, 200–400 mesh; this material was treated with warm basic peroxide, followed by reacidification with 5 *M* HCl and extensive washing with water.

Methods and Analyses.—Analyses for Cr were performed by oxidizing the complex with basic peroxide and observing the absorbance at 3730 Å, ϵ 4815.[12] Nitrogen was determined by a micro Kjeldahl technique. Fluorine was determined by spectrophotometric titration with Th(IV) as described by Horton[13] after decomposition of the complex with basic peroxide. Blank experiments showed that Cr(VI) does not interfere with the F determination.

Ion-exchange separations were performed in the dark on columns of 6 × 1 and 9 × 1 cm. These columns as well as collection vessels were maintained at 0°. The separations were accomplished as follows: *trans*-$Cr(en)_2F_2^+$ (usually $\simeq$0.25 mmol in 0.1 *M* $HClO_4$) was allowed to aquate for a length of time (less than 2 half-lives) and was subsequently charged onto the column. Elution with 20 ml of 0.3 *M* HCl yielded a solution of complex whose spectral characteristics were nearly identical with those of starting material (the contaminant in this material is discussed below). At this point two bands remained on the column. The major band had moved about halfway down the column during elution of the first band; a second, and very minor, component remained at the top of the column. The major band was eluted and collected with 50 ml of 0.5 *M* HCl. The third band could be eluted with 50 ml of 1.0 *M* HCl. If the *trans*-$Cr(en)_2F_2^+$ was allowed to aquate for 4–6 half-lives and then charged onto the column, elution with 0.25 *M* HCl separated the material into four bands. The first and second bands were eluted with 0.3 *M* HCl; the second band, which was incompletely separated from the first, had qualitative spectral characteristics of *trans*-$Cr(en)_2F_2^+$. The third and fourth bands which were identical with the last two bands of the short-time aquation were eluted as described above.

The kinetic studies were accomplished spectrophotometrically using a Cary Model 14 recording spectrophotometer. For the 25° runs, sample vessels were maintained in a thermostated bath and were removed at appropriate time intervals and the absorbance determined. The higher temperature experiments were carried out by continuous monitoring of the absorbance. Temperature control was to within ±0.1°. The raw absorbance data were used by a nonlinear least-squares computer program to yield first-order rate constants. In this program each point is given weight according to the variance of the point. The rate constant–temperature data were analyzed by the previously described[2] least-squares program, CELIA, to yield activation parameters.

Results

Composition of Products.—The major product of the aquation of *trans*-$Cr(en)_2F_2^+$ was isolated in solution by ion-exchange chromatography. We assign this material the composition $Cr(en)(enH)(H_2O)F_2^{2+}$ on the basis of its ion-exchange behavior as well as Cr, N, and F analyses. The complex is eluted from Dowex 50W-X2 in the hydrogen form more slowly than a typical unipositive ion, *trans*-$Cr(en)_2F_2^+$, but more rapidly than dipositive ions, such as *trans*-$Cr(en)_2H_2OF^{2+}$ [14] and *cis*-$Cr(en)_2H_2OF^{2+}$ (see below). We infer from this behavior that the material is either a 1+ or 2+ ion. Analyses for Cr and F yielded a F:Cr ratio of 1.94 ± 0.06 (three determinations); N analyses yielded an N:Cr ratio of 4.00 ± 0.26 (12 determinations). The spectral characteristics of this ion are given in Table I.

When aquation of *trans*-$Cr(en)_2F_2^+$ is carried out for 4–6 half-lives, two products other than that characterized as $Cr(en)(enH)H_2OF_2^{2+}$ are produced in substantial quantitity. The first product is eluted more rapidly than is *trans*-$Cr(en)_2F_2^+$ and has been found to have an N:Cr ratio of 1.99 ± 0.01 (two determinations). The composition $Cr(en)(H_2O)_2F_2^{2+}$ is consistent with this analysis and the ion-exchange behavior that is typical of a unipositive ion. The presence of this material in low concentrations in the band identified as *trans*-$Cr(en)_2F_2^+$ in short-time experiments causes the spectral anomalies mentioned in the Experimental Section. The second of these two products is eluted more slowly than is *trans*-$Cr(en)_2H_2OF^{2+}$ but more rapidly than typical 3+ ions; the visible absorption spectra show peaks at wavelengths which agree with those reported for the product of the reaction of Ag^+ with *cis*-$Cr(en)_2FCl^+$. The analysis of this material yields an F:Cr ratio of 0.98 ± 0.04 (two determinations) and an N:Cr ratio of 4.26. This material is *cis*-$Cr(en)_2H_2OF^{2+}$. The spectral properties of these two products are also shown in Table I.

Reaction Stoichiometry.—Of the three products observed, that of composition $Cr(en)(H_2O)_2F_2^+$, which differs from the starting material by the rupture of two Cr–ligand bonds, must surely arise from a two-step process; therefore, to establish the reaction stoichiometry of the aquation of *trans*-$Cr(en)_2F_2^+$ we need only ask whether *cis*-$Cr(en)_2H_2OF^{2+}$ arises directly from *trans*-

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$\text{Cr(en)}_2\text{F}_2^+$ or is a product of secondary aquation (or both). In an attempt to answer this question aquations of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ were carried out for 465 and 560 min (22°). The fractions of total Cr in the form of $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$ and *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ were, respectively, 0.38, ≤ 0.02; and 0.44, ≤ 0.02. In another aquation carried out for 2450 min at 22°, 1.7% of the total Cr was *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$. Knowing the amount of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ that has aquated and having upper limits on the amount of *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ produced, we can calculate an upper limit on the number of moles of the latter produced per mole of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ aquated. This value is less than or equal to 0.02. Because *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ is produced in the aquation of $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$, we believe the overwhelming path for aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ is given by the equation

$$\textit{trans}\text{-Cr(en)}_2\text{F}_2^+ + \text{H}^+ \xrightarrow{k_1} \text{Cr(en)(enH)H}_2\text{OF}_2^{2+} \quad (1)$$

and little, if any, *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ is produced in the aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$. If this analysis is correct, the aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ followed spectrophotometrically should exhibit, at short reaction times, isosbestic behavior characteristic of the two species in solution, *trans*-$\text{Cr(en)}_2\text{F}_2^+$ and $\text{Cr(en)(enH)(H}_2\text{O)F}_2^{2+}$. From the known spectra of these materials we predict isosbestic points at 4750 Å (ϵ 20.0), 3895 Å (ϵ 12.1), and 3480 Å (ϵ 13.7). An experiment with initial *trans*-$\text{Cr(en)}_2\text{F}_2^+$ 2.80×10^{-3} *M* in 0.10 *M* HClO_4 exhibited isosbestic points for the first 200 min of reaction at 4740 Å (ϵ 20.4), 3920 Å (ϵ 12.3), and 3480 Å (ϵ 14.0). These experimental values agree satisfactorily with the calculated values. At reaction times longer than 200 min, the absorbances during an aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ at 4740 and 3480 Å decreased, whereas that at 3920 Å remained approximately constant with a small increase noticed only after 2100 min. These observations are consistent with the secondary aquation of $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$ to *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ and $\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+$. This feature has been independently verified; we chromatographically isolated pure $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$ and allowed it to aquate for 4200 and 4300 min in 0.5 *M* HCl. The products of this aquation were separated by ion-exchange chromatography: the amount of *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ found was 9.6 and 12.2% of the total Cr, respectively and the amount of $\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+$ was 32.4 and 38.1%, respectively. Based on the average ratio (3.25:1) of $\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+$ to *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ the stoichiometry of the secondary aquation is approximated by the equation

$$\text{Cr(en)(enH)H}_2\text{OF}_2^{2+} \xrightarrow{\text{H}^+} 0.76\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+ + 0.24\textit{cis}\text{-Cr(en)}_2\text{H}_2\text{OF}^{2+} + 0.24\text{HF} + 0.76\text{enH}_2^{2+} \quad (2)$$

Using this ratio we calculate effective extinction coefficients for the mixture of $\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+$ and *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ and qualitatively account for the deviations from isosbestic behavior at longer reaction times. Thus eq 1 and 2 adequately account for the spectral changes observed during the aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$.

Kinetics.—The chromatographic separations described above demonstrate that the secondary reaction, eq 2, is fast enough to cause interference in a study of the aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$. Fortunately, a peculiar feature of the absorption spectra of the four complexes allows spectrophotometric monitoring of the reaction. At 5450 Å, $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$, $\text{Cr(en)(H}_2\text{O)}_2\text{F}_2^+$, and *cis*-$\text{Cr(en)}_2\text{H}_2\text{OF}^{2+}$ absorb equally, ϵ 35.9–36.7. At this same wavelength, *trans*-$\text{Cr(en)}_2\text{F}_2^+$ has a significantly smaller absorbance, ϵ 15.0. Therefore the change in absorbance at this wavelength accurately reflects the rate of disappearance of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ up to >90% reaction without interference from the secondary reaction. All kinetic experiments were analyzed at 5450 Å. The kinetic experiments were performed at 1.0 and 0.12 *M* ionic strength at 25.0, 37.5, and 43.7°. The results of the individual experiments are given in Table II. No H^+-dependent path is observed over the 13-fold change in $[\text{H}^+]$. Nonlinear least-squares analysis of the individual rate–temperature data at 1.0 *M* ionic strength yielded $\Delta H^{\ddagger} = 24.1 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.3 \pm 0.5$ cal mol^{-1} deg^{-1}. The last column in Table II gives values of the calculated rate constants to illustrate the fit of the data to these activation parameters. The three values at $I = 0.12$ *M* were also analyzed for temperature dependence and gave $\Delta H^{\ddagger} = 21 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11 \pm 8$ cal mol^{-1} deg^{-1}.

Table II

Rate Data for Aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ (I = 1.0 *M* (NaClO_4))

Temp, °C	10^2[Cr(III)], *M*²	[H⁺], *M*	10^5k, sec^{-1}	10^5k_{calcd},[a] sec^{-1}
25.0	2.188	0.211	1.21 ± 0.1	
25.0	2.387	0.135	1.24 ± 0.1	1.23
25.0	2.493	0.114	1.20 ± 0.02	
25.0	2.626	0.044	1.26 ± 0.2	
25.0	2.590	0.1	1.65 ± 0.02[b]	1.75
37.5	1.245	0.273	6.68 ± 0.06	
37.5	1.765	0.197	6.60 ± 0.07	6.58
37.5	2.155	0.121	6.73 ± 0.07	
37.5	2.300	0.044	6.61 ± 0.06	
37.5	2.305	0.100	9.03 ± 0.06[b]	7.40
43.7	1.542	0.573	14.74 ± 0.06	
43.7	1.748	0.388	14.00 ± 0.05	14.40
43.7	1.871	0.238	14.10 ± 0.05	
43.7	2.010	0.044	14.37 ± 0.08	
43.7	2.233	0.100	19.61 ± 0.05[b]	21.19

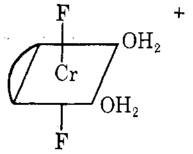
[a] Calculated from activation parameters given in text. [b] I = 0.12 *M*.

Two experiments in which chromatographically pure $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$ was allowed to aquate for about 1 half-life were performed. The reaction mixtures were separated chromatographically and the amount of $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$ remaining unreacted was determined. From these numbers, we calculate a rate constant of about 2.3×10^{-6} sec^{-1} at 22° and $I = [\text{HCl}] = 0.5$ *M* for the disappearance of $\text{Cr(en)(enH)H}_2\text{OF}_2^{2+}$.

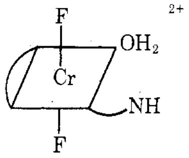
Discussion

The aquation of *trans*-$\text{Cr(en)}_2\text{F}_2^+$ over the range of $[\text{H}^+]$ studied leads to a complex containing four nitrogens and two fluorides per chromium. Since this material is spectrally different from either *cis*-$\text{Cr(en)}_2\text{F}_2^+$ or *trans*-$\text{Cr(en)}_2\text{F}_2^+$, it must involve a monodentate ethylenediamine ligand. Although the assignment of the stereochemistry of this complex cannot be made with complete certainty, the following arguments suggest a configuration in which the two fluorides are trans to one another. An aquation product of the monodentate ethylenediamine complex has the composition Cr(en)-

$(H_2O)_2F_2^+$. This material is eluted from an ion-exchange column much more easily than is *cis*-$Cr(en)_2F_2^+$;[15] indeed its ion-exchange behavior makes separation from *trans*-$Cr(en)_2F_2^+$ difficult. This result implies that $Cr(en)(H_2O)_2F_2^+$ has a smaller dipole moment than does the cis difluoro complex, since both are unipositive ions. Of the three stereochemistries possible for $Cr(en)(H_2O)_2F_2^+$ only 1,6-difluoro-2,3-diaquo-4,5-ethylenediaminechromium(III)

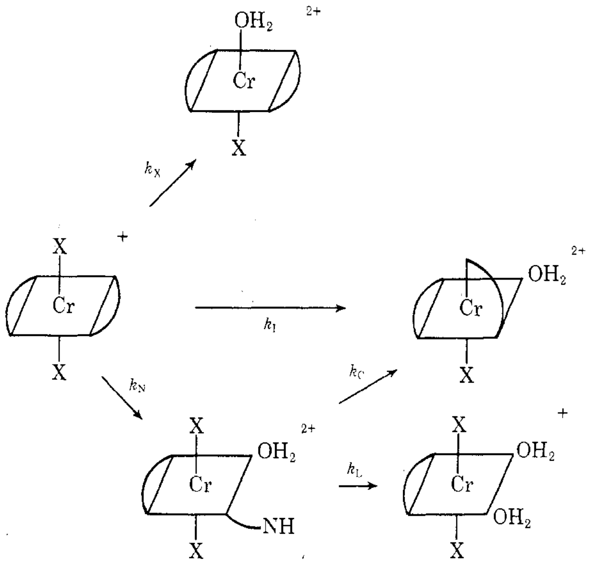


satisfies this criterion. If this geometry is accepted for the diaquo species, then consideration of the usual stereoretentive nature of Cr(III) aquations[16] leads us to the conclusion that the geometry of $Cr(en)(enH)H_2OF_2^{2+}$, a species that originates from *trans*-$Cr(en)_2F_2^+$ and aquates to a complex in which the fluorides are trans, is most compatible with the structure



The path of aquation of *trans*-$Cr(en)_2F_2^+$ is unusual in that rupture of a Cr–N bond is greatly preferred over loss of the acido ligand, the usual process in chromium(III)–amine complexes.[16] The implication of this difference can be ascertained by examination of some data in the literature; Scheme I is relevant to a discussion

SCHEME I



about *trans*-$Cr(en)_2X_2^+$ complexes where $X^- = F^-$, Cl^-, Br^-, NCS^-. In this scheme we assume for simplicity that trans to cis isomerizations are slow compared to other processes.

We consider first the values of k_X. It has been well established in both Co(III)[17] and pentaaquochromium(III) systems[18] that the rates of aquation decrease along the series $Br^- > Cl^- > F^-$, with $NCS^- \cong F^-$. A similar pattern emerges in the bis-ethylenediamine systems when consideration is given to values of the observed constants listed in Table III.[19–22] It should be noted that the geometry of the product of NCS^- aquation of $Cr(en)_2(NCS)_2^+$ is not known and the value reported is $k_X + k_I$. What is pertinent to the question of the nature of the observed aquation products is the magnitude of k_X compared to the rate constants for all other paths of destruction of *trans*-$Cr(en)_2X_2^+$. The path for the destruction of *trans*-$Cr(en)_2F_2^+$ has been established in this study as k_N. In *trans*-$Cr(en)_2Cl_2^+$, surely $Cr(en)(H_2O)_2Cl_2^+$ must be formed through a "one-ended" species. However, formation of *cis*-$Cr(en)_2H_2OCl^{2+}$ could occur either from closure of a one-ended species, k_C, or directly from *trans*-$Cr(en)_2Cl_2^+$, k_I. We therefore take the value of k_N for *trans*-$Cr(en)_2Cl_2^+$ as being between the rate constant for formation of $Cr(en)(H_2O)_2Cl_2^+$ and the total rate constant for production of this species and *cis*-$Cr(en)_2H_2OCl^{2+}$. In the case of *trans*-$Cr(en)_2Br_2^+$ only a small quantity of products other than *trans*-$Cr(en)_2H_2OBr^{2+}$ is formed,[19] and accordingly we assign only an upper limit to k_N. Holba has reported the rate of formation of $Cr(en)(H_2O)_2(NCS)_2^+$, and we take this value as an approximation to k_N for this system. The values of k_N are also listed in Table III. The key feature of these rate parameters is that they do not vary greatly as the nature of X is changed within this series of X. The nature of the aquation products is thus determined by the ratio of k_X/k_N, where k_X is a sensitive function of the nature of X whereas k_N is nearly independent of X. It is therefore apparent that the nature of the products in the aquation of *trans*-$Cr(en)_2F_2^+$ is not caused by a greatly enhanced Cr–N bond lability but rather by the inherent inertness of the Cr–F bond. On the other hand, the presence of two anionic ligands as opposed to two neutral ligands may increase the lability of the coordinated ethylenediamines. Although a direct comparison with a trans bis-ethylenediame complex is not apparently available, the data accumulated by Garner and coworkers[8,9,23] illustrate that aquoaminechromium-

TABLE III
RATE PARAMETERS FOR AQUATION OF COMPLEXES OF THE TYPE *trans*-$Cr(en)_2X_2^+$ (25°, $I = 0.1$ *M*)

X	10^5k_X	10^5k_N	Ref
Br	32	≤ 1	19
Cl[a]	6.9	0.7–1.9	20
F	≤ 0.01	1.8	This work
NCS	0.9[b]	0.4[c]	21, 22

[a] At 35.0°. [b] At 55°. [c] $I = 0.01$ *M*.

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(16) C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 200 (1970).

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(III) complexes break the Cr–N bond somewhat more slowly than do the complexes listed in Table III.[24–26]

Scheme I then adequately, but not unambiguously, accounts for the aquation behavior of *trans*-$Cr(en)_2X_2^+$ species. In particular, we have found no H^+ catalysis of the aquation of *trans*-$Cr(en)_2F_2^+$. This result is in conflict with other studies of chromium(III) fluoride complexes.[15,27] In these cases, however, the net aquation process apparently involves the loss of a fluoride ligand (although in the case of $Cr(NH_3)_5F^{2+}$ there have been reports that NH_3 is lost[28]). For *trans*-$Cr(en)_2F_2^+$ the rate of fluoride loss is so slow relative to that of Cr–N bond rupture that even at the highest acid concentration studied an insignificant amount of Cr–F bond cleavage occurs. Hence no H^+ catalysis is observed. (In concentrated $HClO_4$, aquation of fluoride does occur.[10]) The disturbing feature of Scheme I is that there is no evidence[20] for an isolable monodentate species with the structure $Cr(en)(enH)H_2OCl_2^{2+}$ but that $Cr(en)(enH)H_2OF_2^{2+}$ is isolated in solution: $k_N/(k_C + k_L)$ is much greater than 1 for X = F but much less than 1 for X = Cl. This latter system is compatible with some of the other monodentate species that have been investigated: rupture of the first Cr–N bond is faster than that of the remaining Cr–N bonds as in the case of $Cr(dien)(H_2O)_3^{3+}$,[9] $Cr(dienH)(H_2O)_4^{4+}$,[9] and $Cr(en)(H_2O)_4^{3+}$.[8] It is not compatible with others.[26] We are puzzled by this feature but can offer no explanations other than *a posteriori* ones.

The system on which we report shows one other unusual feature compared to previously isolated complexes with monodentate ligands: the monodentate ligand closes in acid solution to re-form a chelated system.[29] Although such processes are found with ligands containing carboxylate groups,[30] they may be suspected to be unusual when the pendant group contains such a weak acid as $-NH_3^+$. (Alexander and Spillert reported only a small amount of ring closure in a monodentate ethylenediamine complex of Co(III) even in basic solutions.[31]) It may be that the hydrogen bonding between coordinated F^- and $-NH_3^+$ facilitates this ring closure; partial transfer of the hydrogen would increase the nucleophilicity of the amine and would enhance the leaving ability of F^-.

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[24] Another direct comparison is given in the review of Garner and House.[16] *cis*-$Cr(en)_2(H_2O)_2^{3+}$ aquates to $Cr(en)(H_2O)_4^{3+}$ with $k = 2.9 \times 10^{-4}$ sec^{-1} (30°)[25] whereas *cis*-$Cr(en)_2ox^+$ loses one end of an ethylenediame with $k = 1.1 \times 10^{-5}$ (25°).[26]

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[29] From the limit on the amount of *trans*-$Cr(en)_2F_2^+$ that may be present when chromatographically pure $Cr(en)(enH)H_2OF_2^{2+}$ is allowed to aquate, we estimate that the rate constant for $Cr(en)(enH)H_2OF_2^{2+} \rightarrow$ *trans*-$Cr(en)_2F_2^+ + H^+$ is less than 5×10^{-7} sec^{-1}.

[30] See, for instance, D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

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The Electrochemistry of Molybdenum(VI,V)–8-Quinolinol Complexes in Dimethyl Sulfoxide

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The electrochemistry of dioxobis(8-quinolinolato)molybdenum(VI) ($Mo^{VI}O_2Q_2$) and μ-oxo-dioxotetrakis(8-quinolinolato)-dimolybdenum(V) ($Mo^{V}_2O_3Q_4$) has been studied in dimethyl sulfoxide using cyclic voltammetry, chronopotentiometry, and controlled-potential coulometry at a platinum electrode. The reduction of $Mo^{VI}O_2Q_2$ occurs in two one-electron steps, with solvent attack of the reduction intermediates and displacement of the 8-quinolinolate ligands. A Mo(IV) species produced by the reduction of $Mo^{VI}O_2Q_2$ catalytically reduces any excess 8-quinolinol. $Mo^{V}_2O_3Q_4$ is reduced in two reversible one-electron steps. Unimolecular rate constants for the decomposition of the resulting Mo(V)–Mo(IV) and Mo(IV)–Mo(IV) dimers have been determined. The decomposition products are identical with the reduction intermediates of $Mo^{VI}O_2Q_2$. The oxidation of $Mo^{V}_2O_3Q_4$ is an irreversible one-electron process producing a Mo(VI)–Mo(V) dimer which decomposes and is oxidized further to produce $Mo^{VI}O_2Q_2$.

Molybdenum, which is an important trace element in living organisms, occurs in at least four enzymes: xanthine oxidase,[1] aldehyde oxidase,[2] nitrate reductase,[3] and nitrogenase (molybdoferredoxin).[4] Biochemists[5] generally agree that molybdenum alternates between the 6+ and 5+ oxidation states during enzyme catalytic activity. These oxidation states have been identified in nitrate reductase by complexation with 8-quinolinol.[6,7] Molybdenum(V) epr signals have been recorded for the four molybdenum enzymes in the presence

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[2] H. Beinert and W. H. Orme-Johnson, ref 1, p 221.

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