$Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $[Co(NH_3)_6](ClO_4)_3$, 13820-83-2; $Co(NH_3)_6^{3+}$, 14695-95-5; $[Cr(NH_3)_5Cl](ClO_4)_2$, 22478-30-4; $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $[Cr(NH_3)_5Br]Br_2$, 13601-60-0; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; $[Cr(NH_3)_5I](ClO_4)_2$, 64146-51-6; $Cr(NH_3)_5I^{2+}$, 17979-08-7; $[Cr(NH_3)_5NCS](ClO_4)_2$, 22478-28-0; $Cr(NH_3)_5NCS^{2+}$, 16884-60-9; $[Cr(NH_3)_5OH_2](ClO_4)_3$, 32700-25-7; $Cr(NH_3)_5OH_2^{3+}$, 15975-47-0; $[Cr(NH_3)_6]I_3$, 31656-04-9; $Cr(NH_3)_6^{3+}$, 14695-96-6; $Me_2SO$, 67-68-5; $KClO_4$, 7778-74-7; $KNO_3$, 7757-79-1; KCl, 7447-40-7; KBr, 7758-02-3; KI, 7681-11-0.

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# Kinetics of Rupture of Chromium–Ethylenediamine Bonds in Trans-Disubstituted Bis(ethylenediamine)chromium(III) Complexes

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The rate of aquation of several Cr(III) complexes of general type *trans*-$Cr(en)_2AX^{n+}$ are reported. Two types of aquation occur: loss of X ($k_{-x}$) or loss of one end of the chelated ethylenediamine ($k_{-n}$). The values of these rate constants and their corresponding activation parameters are (leaving halide italicized; rate constants in s, $\Delta H^‡$ in kcal mol$^{-1}$, and $\Delta S^‡$ in gibbs mol$^{-1}$): *trans*-$Cr(en)_2F\mathit{Br}^+$, $k_{-x} = 5.0 \times 10^{-4}$, 21.0, −3; *trans*-$Cr(en)_2F\mathit{Cl}^+$, $k_{-x} = 4.85 \times 10^{-5}$, 24.6, 4; $k_{-n} = 1.2 \times 10^{-5}$, 24.6, 2; *trans*-$Cr(en)_2FH_2O^{2+}$, $k_{-n} = 2.56 \times 10^{-5}$, 24.2, 2; *trans*-$Cr(en)_2NCS(\mathit{Br})^+$, $k_{-x} = 3.2 \times 10^{-5}$, 25, 5; $k_{-n} = 3.6 \times 10^{-6}$, 25, 1; *trans*-$Cr(en)_2NCS(H_2O)^{2+}$, $k_{-n} = 9.3 \times 10^{-6}$, 24.4, 0.7. Examination of these data and information in the literature indicate that a trans directing labilization is present but that this effect is not efficiently felt by the *cis*-ethylenediamine ligands. The great lability of ethylenediamine in *trans*-$Cr(en)_2AX^{n+}$ complexes but not in the corresponding cis isomers or in mono-en complexes is established.

The effect of nonlabile ligands on the rate of loss of a group from a six-coordinate transition metal–ion complex is, even after a great deal of experimentation, still a poorly understood phenomenon. From some of the earliest experiments on Co(III) complexes, it has been recognized that the effect of the so-called "directing group" in $Co(en)_2ACl^{n+}$ can be striking,[1] but the explanation of this phenomena in terms of a mechanistic change from dissociative to associative has not been verified and has been challenged.[2,3] Although certain ligands such as $SO_3^{2-}$ enhance "trans" lability,[4,5] within the scope of ligands containing $\pi$ saturated orbitals (amines, $H_2O$, halides), attempts to determine special directional labilizing phenomena have had little success.[6]

In the chemistry of Cr(III)–amine complexes, especially ethylenediamine complexes, as opposed to the corresponding Co(III) systems, an added factor is involved: the striking lability of the Cr(III)–amine bond.[7] This means that in a study of the "directing group" effect on rate of aquation of, say, $Cl^-$ from complexes of the type $Cr(en)_2ACl^{n+}$, concern for loss of $Cl^-$ and breakage of the Cr(III)–en bond must be manifest. Some time ago it was demonstrated that monodentate ethylenediamine persisted in the coordination shell of Cr(III) long enough for ion-exchange isolation of $Cr(enH)(H_2O)_5^{4+}$.[8] Since then, numerous other "one-ended" ethylenediamine complexes have been isolated even with anionic groups present: $Cr(en)(enH)(H_2O)F_2^{2+}$,[9] $Cr(en)(enH)H_2O(NCS)_2^{2+}$.[10] Indeed it was suggested in a study[9] of the aquation of *trans*-$Cr(en)_2F_2^+$ that breakage of the Cr(III)–en bond in complexes of trans geometry might be rather independent of the nature of the ligands along the axis, in somewhat of a contrast to the behavior of anionic leaving groups from Co(III) centers. In this paper that concept is tested by presentation of data on the aquation of *trans*-$Cr(en)_2(F)Cl^+$, *trans*-$Cr(en)_2(F)Br^+$, *trans*-$Cr(en)_2(F)H_2O^{2+}$, *trans*-$Cr(en)_2(NCS)Br^+$, and *trans*-$Cr(en)_2(H_2O)NCS^{2+}$. These systems, coupled with some data already in the literature, allow some conclusions to be drawn concerning factors important in Cr(III)–en bond rupture in *trans*-$Cr(en)_2AX^{n+}$ complexes.

## Experimental Section

**Materials.** The complexes used in this study were prepared by procedures given in the literature and purity was checked by determining percentage Cr, spectral analysis, and ion-exchange chromatography. The pertinent references are: *trans*-$[Cr(en)_2(F)Br]ClO_4$ and *trans*-$[Cr(en)_2(F)Cl]ClO_4$;[11] *trans*-$[Cr(en)_2(F)H_2O](ClO_4)_2$.[12] *trans*-$[Cr(en)_2(NCS)Br]ClO_4$ was prepared by slight modification of the procedure of Fee, MacHarrowfield, and Jackson.[13]

This complex is difficult to separate from *trans*-$[Cr(en)_2(NCS)_2]ClO_4$, a species of similar solubility that arises in the final step of the synthesis. Only repeated recrystallizations yielded a material pure upon ion-exchange chromatography.

Anal. Calcd for *trans*-$[Cr(en)_2(NCS)Br]ClO_4$: Cr, 12.72; NCS, 14.20. Found: Cr, 12.93; NCS, 14.17. Only a solution of *trans*-$Cr(en)_2(H_2O)NCS^{2+}$ could be obtained.[14]

All other reagents used were of Reagent Grade. Perchloric acid was from G. F. Smith. Mercury(II) perchlorate solutions were prepared and standardized as previously described.[15] The ion-exchange resin was Dowex 50W-X8 of 200–400 mesh in the $H^+$ form, partially screened by flotation after washing with basic peroxide and reacidification.

**Techniques.** All materials were handled in subdued light to prevent photolysis. The rate of reaction was monitored either by continuous spectrophotometric measurement at a fixed wavelength, by repeated spectral scans, or by ion-exchange separation and determination of concentrations. The method used was dependent on the complexity of the kinetic scheme as described below. All spectral measurements were made on a Cary Model 14 recording spectrophotometer. Ion-exchange separations were carried out at 0–5 °C.

Analyses for Cr were achieved by basic peroxide oxidation and spectrophotometric observation as described by Haupt.[16] In the analysis for $NCS^-$ the Fe(III) complex was used to develop the color after the $NCS^-$ was liberated from the Cr(III) complex by treatment with EDTA at pH 5.[10] Chloride ion was analyzed by the technique described by Vogel.[17] Bromide ion was determined as described by Boltz.[18]

## Results

**Aquation of *trans*-$Cr(en)_2(F)Br^+$.** A solution of *trans*-$Cr(en)_2(F)Br^+$ made by dissolving the solid complex in 1.00 M $HClO_4$ shows spectral changes during the first 2500 s of aquation consistent with the lack of secondary phenomena; isosbestic points are observed at 5425 ($\epsilon$ 19.9), 4230 (19.0), and 3780 Å (28.8 $M^{-1}$ $cm^{-1}$). At these wavelengths the extinction coefficients of *trans*-$Cr(en)_2(F)H_2O^{2+}$ are 19.5, 18.7, and 28.9, respectively. Therefore, the reaction by which *trans*-$Cr(en)_2(F)Br^+$ disappears can be written:

$$trans\text{-}Cr(en)_2(F)Br^+ \rightarrow trans\text{-}Cr(en)_2(F)H_2O^{2+} + Br^-$$

(At times greater than 2500 s the system no longer obeys isosbestic behavior because *trans*-$Cr(en)_2(F)H_2O^{2+}$ undergoes aquation; see below.)

The rate at which *trans*-$Cr(en)_2(F)Br^+$ aquates is easily determined spectrophotometrically at fixed wavelength. Because of the secondary aquation of *trans*-$Cr(en)_2(F)H_2O^{2+}$, however, a calculated value for the absorbance at the end of reaction must be used for $A_\infty$ in the expression:

$$A_t - A_\infty = (A_0 - A_\infty)e^{-k_1 t}$$

where $A_t$ and $A_0$ are the absorbancies at times $t$ and zero and $k_1$ is the first-order rate constant. The corrected $A_\infty$ is only slightly different from the value when isosbestic behavior ceases because the reaction is >90% complete when secondary aquation becomes significant. Experiments were carried out at several temperatures and two ionic strengths over a range of $[H^+]$. The data are listed in Table I and indicate the rate law is:

$$-d[trans\text{-}Cr(en)_2(F)Br^+]/dt = k_1[trans\text{-}Cr(en)_2(F)Br^+]$$

The rate law is independent of $[H^+]$ within experimental error and not very sensitive to ionic strength. The activation parameters were determined by a nonlinear least-squares program and are given in Table VII.

**Table I.** Rate of Aquation of *trans*-$Cr(en)_2(F)Br^+$

| Temp, °C | $[Cr^{III}] \times 10^2$, M | $[H^+]$, M | $I$, M | $k \times 10^4$, $s^{-1}$ |
|---|---|---|---|---|
| 17.0 | 0.76 | 0.1 | 0.11 | 1.82 |
| | 1.49 | 0.1 | 0.11 | 1.81 |
| | 2.28 | 0.1 | 0.12 | 1.83 |
| | 1.17 | 0.1 | 0.11 | 1.86 |
| | 1.39 | 1.0 | 1.01 | 1.74 |
| | 1.14 | 0.8[a] | 1.01 | 1.67 |
| | 0.90 | 0.04[a] | 1.01 | 1.55 |
| | 2.32 | 1.0 | 1.02 | 1.71 |
| | 1.70 | 1.0 | 1.02 | 1.69 |
| | 2.16 | 1.0 | 1.02 | 1.68 |
| 23.0 | 1.93 | 0.1 | 0.12 | 3.8 |
| | 1.01 | 0.1 | 0.11 | 3.8 |
| | 1.61 | 1.0 | 1.02 | 3.6 |
| | 1.31 | 1.0 | 1.01 | 3.5 |
| | 1.76 | 0.07[a] | 1.02 | 4.3 |
| 25.5 | 1.12 | 0.1 | 0.11 | 5.7 |
| | 0.72 | 0.1 | 0.11 | 5.2 |
| | 1.11 | 1.0 | 1.01 | 5.2 |
| | 1.51 | 1.0 | 1.02 | 5.6 |
| | 0.94 | 0.07[a] | 1.01 | 5.0 |
| 37.7 | 0.28 | 0.1 | 0.1 | 22.3 |
| | 0.18 | 1.0 | 1.0 | 19.4 |
| | 0.34 | 1.0 | 1.0 | 20.0 |
| | 0.13 | 1.0 | 1.0 | 19.6 |

[a] Ionic strength made up with $LiClO_4$.

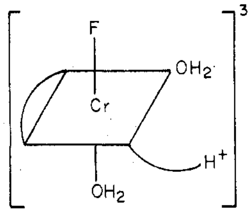
**Table II.** Spectral Data on Complexes

| Complex | λ, Å($\epsilon$, $M^{-1}$ $cm^{-1}$), at maxima | | |
|---|---|---|---|
| A. Fluoro Complexes | | | |
| *trans*-$Cr(en)_2(F)Br^+$ | 5630 (22.7) | ≃4600 (22.2)[a] | 3850 (30.1) |
| *trans*-$Cr(en)_2(F)Cl^+$ | 5505 (19.3) | 4600 (21.1) | 3810 (27.6) |
| *trans*-$Cr(en)_2(F)H_2O^{2+}$ | 5190 (23.1) | 4570 (23.9) | 3690 (29.9) |
| $Cr(en)(enH)H_2O(F)Cl^{2+}$ | 5190 (41.6) | | 3945 (30.7) |
| $Cr(en)(enH)(H_2O)_2F^{3+}$ | 5120 (49.1) | | 3810 (31.7) |
| $Cr(en)(H_2O)_3F^{2+}$ | 5290 (38.3) | | 3825 (22.0) |
| B. Isothiocyanato Complexes | | | |
| *trans*-$Cr(en)_2(NCS)Br^+$ | 5430 (60.7) | 4640 (24.8)[b] | 3820 (57.5) |
| *trans*-$Cr(en)(NCS)H_2O^{2+}$ | 5010 (52.4) | | 3650 (49.6) |
| $Cr(en)(enH)H_2O(NCS)Br^{2+}$ | 5400 (78.5) | | 4000 (60.7) |
| $Cr(en)(enH)(H_2O)_2NCS^{3+}$ | 5080 (82.0) | | 3840 (56.5) |
| $Cr(en)(H_2O)_3NCS^{2+}$ | 5260 (73.0) | | 3890 (43.0) |

[a] See ref 11 for details. [b] Shoulder.

**Aquation of *trans*-$Cr(en)_2(F)Cl^+$.** A solution of *trans*-$Cr(en)_2(F)Cl^+$ in $10^{-2}$ M $HClO_4$ exhibits spectral changes over a period of several hours. Repeated spectral scans show that isosbestic behavior persists for only a short time, indicating reaction of the primary products to form secondary products. To determine the nature of the primary products a solution of *trans*-$Cr(en)_2(F)Cl^+$ that had aquated for about a half-life (see below) was placed on an ion-exchange column. Elution with 0.5 N HCl split the material on the column into four bands, the first of which was eluted with 0.5 N HCl and identified by spectral comparison as starting material, *trans*-$Cr(en)_2(F)Cl^+$. The second band on the column was eluted with 1.0 N HCl. This material contains $Cl^-$ in a ratio to Cr of 0.95 ± 0.07. Since no $F^-$ is released to the solution in the aquation of *trans*-$Cr(en)_2(F)Cl^+$, the complex in the second band contains fluorine as well. Both the ion-exchange behavior (characteristic of a 2+ ion) and the aquation behavior (see below) are consistent with the formulation $Cr(en)(enH)H_2O(F)Cl^{2+}$. The spectral data (an average of over 20 preparations of this material) are in Table II. The third band, eluted off the column with 1.5 N HCl, has spectral characteristics[11] of *trans*-$Cr(en)_2(F)H_2O^{2+}$. The final band to be eluted from the column (with 2.0 N HCl) is $Cr(en)(enH)(H_2O)_2F^{3+}$, a compound previously found to have the stoichiometry Cr:N:F of 1:4:1[9] and assigned structure I.[19]

In order to ascertain the scheme by which these three products arise, several supplementary experiments have been



I

performed. Since $Cr(en)(enH)(H_2O)_2F^{3+}$ has broken two bonds relative to the starting material, *trans*-$Cr(en)_2(F)Cl^+$, it would seem likely that this material is a product of secondary aquation. To verify this presumption, solutions of both $Cr(en)(enH)(H_2O)(F)Cl^{2+}$ and *trans*-$Cr(en)_2(F)H_2O^{2+}$ were allowed to aquate for a brief period and then were separated by ion-exchange chromatography. Both yielded as the sole product $Cr(en)(enH)(H_2O)_2F^{3+}$. In addition, $Hg^{2+}$-induced aquation of $Cr(en)(enH)(H_2O)(F)Cl^{2+}$ also leads to $Cr(en)(enH)(H_2O)_2F^{3+}$. This latter material is therefore a secondary product.

If both $Cr(en)(enH)(H_2O)(F)Cl^{2+}$ and *trans*-$Cr(en)_2H_2O(F)^{2+}$ are primary products, in what ratio are they produced? To answer this question, attention can be directed to the isosbestic point present early in the reaction. The wavelength of this isosbestic point is 5550 Å with an apparent extinction coefficient of 19.3 $M^{-1}$ $cm^{-1}$. As long as it persists, there must be only a slight buildup of secondary aquation product, $Cr(en)(enH)(H_2O)_2F^{3+}$, because the latter has $\epsilon$ 30.6 $M^{-1}$ $cm^{-1}$ at this wavelength.[20] Since the two primary products must have a weighted extinction coefficient at 5550 Å of 19.3 $M^{-1}$ $cm^{-1}$ to account for the isosbestic behavior, knowledge of the extinction coefficients of each allows solution of the fraction of each formed. It was found that the average value of the fraction of *trans*-$Cr(en)_2(H_2O)F^{2+}$ formed was 0.81 ± 0.02, the remainder being $Cr(en)(enH)(H_2O)(F)Cl^{2+}$. This value was also found to be, within the experiment error, independent of temperature over the range 18–36 °C.

The rate of aquation of *trans*-$Cr(en)_2(F)Cl^+$, was determined by spectrophotometric methods, utilizing data points only while isosbestic behavior at 5550 Å persisted. Under these conditions, the absorbance change is directly proportional to the concentration change. Observations were made at 5050 Å, the wavelength of maximum change, and the value of the absorbance at completion of reaction was calculated assuming the stoichiometry:

$$\textit{trans}\text{-}Cr(en)_2(F)Cl^+ \rightarrow$$
$$0.81(\textit{trans}\text{-}Cr(en)F(H_2O)^{2+}) + 0.19(Cr(en)(enH)(H_2O)(F)Cl^{2+})$$

as determined above. The rate of secondary aquation is great enough that the data points covered only the first half-life for aquation. The rate constant was determined at three temperatures and the values are listed in Table III. Activation parameters are listed in Table VII.

Table III. Aquation of *trans*-$Cr(en)_2(F)Cl^{2+}$ in $ClO_4^-$ Medium

| [Cr(III)], mM | [H⁺], M | *T*, °C | *k* × 10⁵, s⁻¹ |
|---|---|---|---|
| 11.4 | 0.01 | 18.4 | 2.3 |
| 11.2 | 0.01 | 25.0 | 6.2 |
| 11.3 | 0.01 | 25.0 | 5.8 |
| 5.6 | 1.0[a] | 25.0 | 4.6 |
| 13.9 | 1.0[a] | 25.0 | 4.1 |
| 13.1 | 0.01 | 36.0 | 26 |

[a] $HNO_3$.

Table IV. Rate of Aquation of *trans*-$Cr(en)_2F(H_2O)^{2+}$

| [Cr(III)], mM | [H⁺], M | *I*, M | *T*, °C | *k* × 10⁵, s⁻¹ |
|---|---|---|---|---|
| 4.56 | 0.1 | 0.12 | 25.1 | 2.56 |
| 23.2 | 0.1 | 0.17 | 25.1 | 2.57 |
| 49.6 | 0.1 | 0.25 | 25.1 | 2.57 |
| 4.48 | 0.1 | 0.12 | 25.1 | 2.54 |
| 33.2 | 0.1 | 0.20 | 35.3 | 10.7 |
| 17.7 | 0.1 | 0.15 | 35.3 | 11.0 |
| 21.9 | 0.1 | 0.17 | 35.3 | 10.7 |
| 3.2 | 1.0 | 1.00 | 34.0 | 6.0 |
| 13.6 | 0.11[a] | 1.04 | 35.3 | 7.0 |
| 14.2 | 1.0 | 1.04 | 35.3 | 8.0 |

[a] $Na^+$ is used to replace $H^+$ for ionic strength.

**Aquation of *trans*-$Cr(en)_2H_2O(F)^{2+}$.** As mentioned above, if a solution of *trans*-$Cr(en)_2H_2O(F)^{2+}$ is allowed to aquate for a short time, the sole product identified by ion-exchange chromatography is $Cr(en)(enH)(H_2O)_2F^{3+}$. This result is verified by isosbestic behavior seen during spectrophotometric observation of the aquation. Isosbestic points are observed at $\lambda$ ($\epsilon$) of: 4670 (25.0), 4120 (20.6), and 3750 (31.0). The corresponding values for a solution of chromatographically pure $Cr(en)(enH)(H_2O)_2F^{3+}$ are 4670 (24.7), 4120 (20.1), and 3750 (31.0). To determine the rate at which this process takes place it is convenient to use spectrophotometric observation at 5100 Å, the wavelength of largest absorbance change. Because, however, as is the pattern in these aquations, $Cr(en)(enH)(H_2O)_2F^{3+}$ further aquates in competition with the aquation of *trans*-$Cr(en)_2(F)(H_2O)^{2+}$, the value of the absorbance at the end of reaction must be calculated. Under this condition plots of ln $(A_t - A_\infty)$ versus time were linear for a half-life (before secondary aquation becomes important as evidenced by deviation from isosbestic behavior). Alternatively, observation can be made at 5420 Å, an isosbestic point for $Cr(en)(enH)(H_2O)_2F^{3+}$ and its aquation product, $Cr(en)(H_2O)_3F^{2+}$. The absorbance change is not as large at this wavelength, but the reaction can be followed for more than 3 half-lives. The rate data obtained by these two types of measurements are presented in Table IV. Activation parameters are given in Table VII. (During experiments on *trans*-$Cr(en)_2(H_2O)F^{2+}$, a quantity of its aquation product $Cr(en)(enH)(H_2O)_3F^{2+}$ was isolated by column chromatography. This material aquates to form $Cr(en)(H_2O)_3F^{2+}$, a fact determined by ion-exchange separation of a partially aquated solution of $Cr(en)(enH)(H_2O)_2F^{3+}$. The rate constant for this process at 25.1 °C is about 3 × $10^{-6}$ $s^{-1}$ in 1.5 M $HClO_4$.)

**Aquation of *trans*-$Cr(en)_2NCS(Br^+)$.** A study of the aquation of this complex is complicated by exactly the same features as that of *trans*-$Cr(en)_2(F)Cl^+$: two primary products are formed, each of which undergoes secondary aquation at a rate comparable to the primary step; and, indeed, before *trans*-$Cr(en)_2NCS(Br^+)$ has aquated for 5 half-lives, tertiary aquation products begin to appear in small amounts. The method of dissection into the individual paths that are occurring during aquation is similar to that described above for *trans*-$Cr(en)_2(F)Cl^+$.

The two primary products of aquation are *trans*-$Cr(en)_2(NCS)H_2O^{2+}$, identified by its spectral and ion-exchange characteristics,[14] and a material which is eluted from the column more rapidly than *trans*-$Cr(en)_2(NCS)H_2O^{2+}$ is but much more slowly than is *trans*-$Cr(en)_2(NCS)Br^+$. This is very similar to the ion-exchange behavior of the "one-ended" materials, $Cr(en)(enH)H_2O(F)_2^{2+}$ and $Cr(en)(enH)H_2O(F)Cl^{2+}$. Further, the NCS/Cr ratio of this material is 1.05 and the Br/Cr ratio is 0.82 ± 0.11. In addition, this material further aquates to $Cr(en)(enH)(H_2O)_2NCS^{3+}$. These facts support the assignment of the second primary product to the stoichiometry $Cr(en)(enH)(H_2O)(NCS)Br^{2+}$. The ratio of these two products formed has been established by observing the fractional yield of total products in the form of each by ion-exchange chromatography and extrapolating those fractional yields to zero time. The distribution is such to

**Table V.** Aquation of *trans*-$Cr(en)_2(NCS)Br^+$ ($[HClO_4] = 10^{-2}$ M)

| [Cr(III)], mM | $T$, °C | $k \times 10^5$, $s^{-1}$ |
|---|---|---|
| 4.39 | 25.0 | 3.5 |
| 4.39 | 25.0 | 3.7 |
| 4.39 | 25.0 | 3.6 |
| 5.40 | 25.0 | 3.7 |
| 5.85 | 25.0 | 3.5 |
| 8.26 | 25.0 | 3.6 |
| 3.94 | 35.2 | 17.5 |
| 3.94 | 35.2 | 16.2 |
| 3.94 | 35.2 | 15.0 |
| 3.94 | 35.2 | 17.7 |

**Table VI.** Aquation of *trans*-$Cr(en)_2H_2O(NCS)^{2+}$ ($I = 1.0$ M $HClO_4$)

| [Cr(III)] × $10^3$M | $T$, °C | $k \times 10^5$, $s^{-1}$ |
|---|---|---|
| 1.15 | 25.1 | 0.93 |
| 1.15 | 25.1 | 0.90 |
| 9.58 | 41.5 | 8.8 |
| 9.58 | 41.5 | 8.7 |
| 9.58 | 41.5 | 8.9 |
| 9.58 | 50.0 | 24.5 |
| 9.58 | 50.0 | 19.2 |
| 9.58 | 50.0 | 21.5 |

indicate the stoichiometry for the aquation of *trans*-$Cr(en)_2(NCS)Br^+$ is:

$$trans\text{-}Cr(en)_2(NCS)Br^+ \rightarrow$$
$$0.9(trans\text{-}Cr(en)_2(NCS)H_2O^{2+}) + 0.1(Cr(en)(enH)(H_2O)(NCS)Br^{2+})$$

The rate of aquation of *trans*-$Cr(en)_2(NCS)Br^+$ has been studied by ion-exchange isolation of the starting material remaining after a given time. The data are given in Table V. Activation parameters are presented in Table VII.

**Aquation of *trans*-$Cr(en)_2(H_2O)NCS^{2+}$.** The ion *trans*-$Cr(en)_2(H_2O)NCS^{2+}$ aquates by loss of ethylenediamine nitrogen to form $Cr(en)(enH)(H_2O)_2NCS^{3+}$. This was confirmed by ion-exchange isolation of this material. Secondary aquation of this "one-ended" ion leads to $Cr(en)(H_2O)_3NCS^{2+}$,[21] identified by its spectroscopic parameters (see Table II). The rate of this reaction was followed by isolating by ion-exchange techniques the *trans*-$Cr(en)_2H_2O(NCS)^{2+}$ remaining after a given time at the desired temperature; the data are recorded in Table VI and activation parameters are given in Table VII.

## Discussion

**Substituent Effects or Cr(III)–en Bond Breakage.** The data reported above provide support for the contention made earlier[9] that the loss of the Cr(III)–en bond is not very sensitive to the trans ligands. The most complete data pertain to the series *trans*-$Cr(en)_2(NCS)X^{n+}$ and *trans*-$Cr(en)_2(F)X^{n+}$. The rate constants for rupture of the Cr(III)–en bond ($\times 10^5$, $s^{-1}$) for X = $NCS^-$, $F^-$, $Cl^-$, $Br^-$, and $H_2O$ are for the former series 0.27,[10] 1.0,[22] ≤0.5,[23] 0.35, and 0.93, respectively, and for the latter series 1.0,[22] 1.23,[9] 1.2, ≤2.5,[24] and 2.5, respectively. This similarity holds for the activation parameters as well; the values of $\Delta H^\ddagger$ are about 24–25 kcal $mol^{-1}$ and $\Delta S^\ddagger$ values are always near zero. These values are to be contrasted with the effect of the same set of X upon loss of $Br^-$ from *trans*-$Cr(en)_2(Br)X^{n+}$. The rate constants ($\times 10^{-5}$, $s^{-1}$) for X = $NCS^-$, $F^-$, and $Br^-$ are 3.2, 50, and 16.3.[25] The changes in X that produce a threefold change in the rate constant for ethylenediamine loss produce a greater than 16-fold change in rate of loss of $Br^-$. These factors give rise to the exclusive loss of $Br^-$ from *trans*-$Cr(en)_2(X)Br^+$ when X is an activating ligand ($F^-$, $Br^-$) but competition between $Br^-$ loss and ethylenediamine loss when X is a poor trans activating ligand ($NCS^-$). Stated another way, the competition between the two paths of reaction in *trans*-$Cr(en)_2(F)X^+$ where $X^-$ is $F^-$, $Cl^-$, and $Br^-$ switches from exclusive ethylenediamine loss at $F^-$ to dominant loss of $Cl^-$ at $X^- = Cl^-$ and exclusive loss of $Br^-$ in *trans*-$Cr(en)_2(F)Br^+$, whereas for the same series of $X^-$ in *trans*-$Cr(en)_2(NCS)X^+$, where the "directing" group is now a poor trans activator, the competition persists with $X^- = Br^-$.

An even more striking illustration can be made using values for upper limits on reactivity. This concerns the change of directing ligand from charged to neutral. The rate constants for rupture of the Cr(III)–en bond in *trans*-$Cr(en)_2(F)H_2O^{2+}$ and *trans*-$Cr(en)_2(NCS)H_2O^{2+}$ are $2.5 \times 10^{-5}$ and $0.93 \times 10^{-5}$ $s^{-1}$. These values are substantially the same as those for complexes of unipositive charge, *trans*-$Cr(en)_2(NCS)X^+$ and *trans*-$Cr(en)_2(F)X^+$. Yet comparison of these rate constants with those for $Br^-$ loss from the unipositive complexes, *trans*-$Cr(en)_2(Y)Br^+$, where Y = $NCS^-$ or $F^-$, shows that these latter values are much greater than the upper limit for $Br^-$ loss from *trans*-$Cr(en)_2(H_2O)Br^{2+}$, $\leq 0.3 \times 10^{-5}$ $s^{-1}$;[25] the rate constant for Cr(III)–en bond rupture is much less sensitive to charge than that for the Cr(III)–$Br^-$ bond in these trans complexes. Exactly the same result holds for the aquation of *trans*-$Cr(en)_2(H_2O)Cl^{2+}$ in which Cr(III)–en bond rupture is considerably faster than that of Cr(III)–$Cl^-$ breakage ($4.2 \times 10^{-5}$ and $\leq 0.3 \times 10^{-5}$ $s^{-1}$, respectively, at 35 °C in 0.1 N $HNO_3$[26]). Thus although the shift of ligand X in *trans*-$Cr(en)_2(X)Cl^{n+}$ from $F^-$ to $H_2O$ causes a decrease in rate of $Cl^-$ aquation of greater than 60, the rate of Cr(III)–en aquation remains essentially constant.

This analysis is consistent with MacDonald and Garner's[27] early result in which they report as an aquation product of *trans*-$Cr(en)_2Cl_2^+$ the ion they believed to be 1,6-dichlorodiaquoethylenediaminechromium(III). Since $Cl^-$ is a relatively poor leaving group and a trans chloride does not appear even as effective as $F^-$ in labilizing (compare the rate of loss of $Cl^-$ from *trans*-$Cr(en)_2(F)Cl^+$, $4.8 \times 10^{-5}$ $s^{-1}$, and from *trans*-$Cr(en)_2Cl_2^+$,[27] $1.1 \times 10^{-5}$ $s^{-1}$, corrected for statistical difference), it is not surprising that chromium–ethylenediamine cleavage becomes competitive with Cr(III)–$Cl^-$ cleavage. (Whether MacDonald and Garner's product is $Cr(en)(enH)(H_2O)Cl_2^{2+}$ or $Cr(en)(H_2O)_2Cl_2^+$ is still undecided; $NO_3^-$, the counterion in these experiments, could serve to accelerate[28] loss of the pendent ethylenediamine group in the former to generate the latter.)

**Steric Factors.** The argument made above establishes the constancy of Cr(III)–en breakage, independent of substituents in trans-disubstituted bis(ethylenediamine) complexes of Cr(III). It is remarkable, however, that this lability of Cr(III)–en is restricted to the trans-disubstituted molecules. Neither *cis*-$Cr(en)_2F_2^+$ [29] nor *cis*-$Cr(en)_2(NCS)_2^+$ [30] shows any

**Table VII.** Activation Parameters for Aquations

| Complex $Cr(en)_2YX^{n+}$ | $k_{-x}$[a] × $10^5$, $s^{-1}$ | $\Delta H^\ddagger$, kcal $mol^{-1}$ | $\Delta S^\ddagger$, gibbs $mol^{-1}$ | $k_{-n}$[b] × $10^5$, $s^{-1}$ | $\Delta H^\ddagger$, kcal $mol^{-1}$ | $\Delta S^\ddagger$, gibbs $mol^{-1}$ |
|---|---|---|---|---|---|---|
| *trans*-$Cr(en)_2(F)Br^+$ | 50.0 | 21.0 ± 0.3 | −3 ± 1 | | | |
| *trans*-$Cr(en)_2(F)Cl^+$ | 4.85 | 24.6 | 4 | 1.2 | 24.6 | 2 |
| *trans*-$Cr(en)_2(F)H_2O^{2+}$ | | | | 2.56 | 24.2 | 2 |
| *trans*-$Cr(en)_2NCS(Br^+)$ | 3.2 | 25 | 5 | 0.36 | 25 | 1 |
| *trans*-$Cr(en)_2(NCS)H_2O^{2+}$ | | | | 0.93 | 24.4 | 0.7 |

[a] Value at 25 °C for breakage of Cr–X bond. [b] Value at 25 °C for breakage of one Cr–ethylenediamine bond.

lability of Cr(III)–en bonds with rate constant greater than about $7 \times 10^{-7}$ $s^{-1}$.[31] Veigel and Garner[21] report that loss of a Cr(III)–en bond from *cis*-$Cr(en)_2H_2O(NCS)^{2+}$ has a rate constant of about $5 \times 10^{-7}$ $s^{-1}$. They also report the rate constant for loss of any group from $Cr(en)(H_2O)_3NCS^{2+}$[23] to be less than $2 \times 10^{-8}$ $s^{-1}$. The rate of aquation of $Cr(en)(H_2O)_4^{3+}$ is about $2.4 \times 10^{-8}$ $s^{-1}$ at 25 °C.[8] In this laboratory samples of $Cr(en)(H_2O)_3F^{2+}$ have been stored for over 5 years at 0–10 °C with only 30% loss of the Cr(III)–en bond;[33] the rate of aquation (estimated at 25 °C) of the Cr(III)–en bond is less than $2 \times 10^{-8}$ $s^{-1}$. In addition, studies of the aquation of pentaamminechromium(III) complexes show that Cr(III)–$NH_3$ bond rupture is slower in these materials[34–35] than in the trans-disubstituted bis(ethylenediamine) complexes.

All of these examples illustrate that the higher lability of the Cr(III)–en bond in the trans-disubstituted complexes arises because of some peculiar property of these materials. The most likely property to cause this increased rate of Cr–en bond cleavage is strain in the bonding imposed by the chelate ring. Such an explanation has been offered previously in the case of rapid aquation of 1,2,6-$Cr(dien)(H_2O)_3^{3+}$ compared to the corresponding 1,2,3 isomers.[37] This is consistent with a chelate ring N–Cr–N angle of less than 90° as found in several x-ray structural investigations.[38–40] In the case of the trans-disubstituted complexes, however, the effect needs to be inherent in the pair of rings. Exactly what interaction causes this is not revealed by the structural studies; it is possible the hydrogen–hydrogen nonbonded interactions are significant in these *trans*-$Cr(en)_2(X)Y^{n+}$ complexes.

Finally, a remark concerning the ion-exchange properties of the monodentate ethylenediamine complexes is warranted. These molecules seem quite common in aquation of Cr(III) complexes of polyamines, even with anionic groups in the coordination sphere. The effect of a pendent protonated group on ion-exchange properties is a quite characteristic property of this class of molecules. The column mobility is high compared to other ions of the same total charge. For instance, $Cr(en)(enH)H_2O(F)Br^{2+}$ moves much more rapidly down a column than does *trans*-$Cr(en)_2(F)H_2O^{2+}$. Similar behavior holds for other comparisons.

**Registry No.** *trans*-$Cr(en)_2(F)Br^+$, 45838-12-8; *trans*-$Cr(en)_2(F)Cl^+$, 42476-29-9; *trans*-$Cr(en)_2(F)H_2O^{2+}$, 28101-89-5; $Cr(en)(enH)H_2O(F)Cl^{2+}$, 42476-43-7; $Cr(en)(enH)(H_2O)_2F^{3+}$, 42476-34-6; $Cr(en)(H_2O)_3F^{2+}$, 64090-76-2; *trans*-$Cr(en)_2(NCS)Br^+$, 29830-76-0; *trans*-$Cr(en)_2(NCS)H_2O^{2+}$, 25125-60-4; $Cr(en)(enH)H_2O(NCS)Br^{2+}$, 64057-36-9; $Cr(en)(enH)(H_2O)_2NCS^{3+}$, 64057-35-8; $Cr(en)(H_2O)_3NCS^{2+}$, 56726-00-2; *trans*-$[Cr(en)_2(NCS)Br]ClO_4$, 30177-82-3.

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