acterization has generally been incomplete, with some workers reporting nonstoichiometric materials. The phosphato and sulfato complexes reported here as formed on dissolution of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in 5 F H_3PO_4 and in 6 F H_2SO_4 are evidently true complexes, although we have not been successful in their full characterization.

The nature of the equations by which the products described in this and previous papers are formed is not well understood. In all cases reaction in acid media takes place with reduction from Cr(IV) to Cr(III) together with the evolution of oxygen; it is not known, however, whether this is formed directly or from decomposition of the H_2O_2 or O_2^{2-}. In dilute acid solution, the product of reaction is $Cr(en)(OH_2)_4^{3+}$, independent of the anion, and it is possible that the products formed in concentrated acids are formed by anation of this, which would be expected to be a slow process, or of a Cr(IV) species such as $Cr(en)(OH_2)_4^{4+}$. The reaction is further complicated by the side reactions that occur with oxidation of ligand anions and production of other Cr(III) complexes.

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Hydrolysis Kinetics of the Blue Isomer of Dichlorodiaquoethylenediaminechromium(III) Cation and of the Magenta Isomer of Chlorotriaquoethylenediaminechromium(III) Cation[1a]

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The aquation of $Cr(en)(OH_2)_2Cl_2^+$ (blue isomer) has been investigated spectrophotometrically and by Cl^- release in 0.01–3 F $HClO_4$ from 15 to 35°. At 25.00° the aquation rate constant is $k_1 = (3.1 \pm 0.3) \times 10^{-5}$ sec^{-1} in 0.1–0.01 F $HClO_4$ ($\mu = 0.1$ M, $NaClO_4$); $E_a = 25.3 \pm 0.6$ kcal mole^{-1} and log $PZ = 14.0 \pm 0.4$ (sec^{-1}). The product is the previously unreported complex $Cr(en)(OH_2)_3Cl^{2+}$ (magenta isomer). The rate constant k_2 for hydrolysis of the latter in 1.5 F $HClO_4$ was evaluated from 50 to 70°. At 50.12° $k_2 = (1.11 \pm 0.03) \times 10^{-5}$ sec^{-1}; $E_a = 2.74 \pm 0.2$ kcal mole^{-1} and log $PZ = 13.55 \pm 0.10$ (sec^{-1}), giving $k_2 = 3 \times 10^{-7}$ sec^{-1} at 25° by extrapolation. The product is $Cr(en)(OH_2)_4^{3+}$.

Introduction

Blue dichlorodiaquoethylenediaminechromium(III) chloride, $[Cr(en)(OH_2)_2Cl_2]Cl$,[2] has been prepared by Weinmann[3] from oxalatobis(ethylenediamine)chromium(III) dioxalatoethylenediaminechromate(III). More recently, the blue compound has been synthesized[4,5] much more simply from diperoxoaquoethylenediaminechromium(IV) monohydrate, and the purple analogs dichloroaquopropylenediaminechromium(III) cation, $Cr(pn)(OH_2)_2Cl_2^+$, and dichloroaquoisobutylenediaminechromium(III) cation, $Cr(ibn)(OH_2)_2Cl_2^+$, obtained in solution.[6]

We report here the kinetics of hydrolysis of this blue complex (geometric configuration unknown), which we have found to hydrolyze in perchloric acid solution to a previously unreported magenta complex which we have characterized as one of the two theoretically possible geometric isomers of chlorotriaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_3Cl^{2+}$. An investigation of the hydrolysis of the magenta complex to tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$, is also reported.

These complexes are kinetically of interest for comparison well with the well-studied[7–13] dichloro- and chloroaquobis(ethylenediamine)chromium(III) cations, and to examine further the possibility of Cr–N bond breakage in competition with Cr–Cl bond breakage. Such competitive Cr–N bond breakage has been observed with some other chromium(III) chloroamine complexes.[9–12,14,15]

Experimental Section

Blue Dichlorodiaquoethylenediaminechromium(III) Chloride.—This compound was prepared in several lots by the methods of

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[2] Abbreviations used: en = ethylenediamine, pn = propylenediamine = 1,2-diaminopropane, ibn = isobutylenediamine = 2-methyl-1,2-diaminopropane.

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Weinmann[3] and of House and Garner,[4,5] and characterized as described earlier.[5]

Magenta Chlorotriaquoethylenediaminechromium(III) Cation.—This new complex was prepared by dissolving 0.5–0.7 g of blue $[Cr(en)(OH_2)_2Cl_2]Cl$ in 50–100 ml of 0.01 *F* $HClO_4$ and allowing the complex to hydrolyze in the dark for *ca.* 7.5 hr at 35° or 50 min at 50°. The solution was cooled and charged onto an 8-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 0–2°, then 50–100 ml of 0.3 *F* $HClO_4$ was used to elute unreacted blue $Cr(en)(OH_2)_2Cl_2^+$. *Ca.* 100 ml of 1.5 *F* $HClO_4$ was then used to elute the magenta $Cr(en)(OH_2)_3Cl^{2+}$, giving a solution usually *ca.* 10 m*F* in the complex. Center cuts of the 1.5 *F* $HClO_4$ effluent were used in the kinetic and spectral studies.

Tetraaquoethylenediaminechromium(III) Cation.—Solutions of this pink complex were prepared and chromatographed as described earlier[5] to obtain the complete visible absorption spectrum accurately.

Other Chemicals.—All other chemicals were CP or reagent grade, except the $NaClO_4$, which was prepared by dissolution of reagent grade Na_2CO_3 in CP $HClO_4$ and recrystallized twice from water. All water was doubly distilled water which was passed through a mixed-bed cation–anion-exchange resin and monitored for purity by electrical conductivity.

Analytical Methods.—Analyses of solids and certain solutions for Cr, Cl, C, H, and N were made as described earlier.[6,8]

Kinetic Runs.—Weighed samples of blue $[Cr(en)(OH_2)_2Cl_2]Cl$ were dissolved in the appropriate $HClO_4$–$NaClO_4$ solutions in glass-stoppered volumetric flasks, which were wrapped in Al foil to exclude light and immersed in baths thermostated at 14.81 ± 0.02, 25.00 ± 0.10, or 35.00 ± 0.05° for the primary hydrolysis studies. For the secondary hydrolysis runs, magenta $Cr(en)(OH_2)_3Cl^{2+}$ chromatographically isolated with 1.5 *F* $HClO_4$ was allowed to react in glass-stoppered flasks (*ca.* 50% of the runs) or was sealed by torch in Pyrex ampoules, which were wrapped in Al foil and put in baths thermostated at 50.12 ± 0.05, 59.92 ± 0.02, 60.15 ± 0.02, or 70.10 ± 0.05°. Zero reaction time was taken as 10–20 min after the reaction solutions were put in the baths.

In the spectrophotometric method, aliquots of reaction solution were removed at known times and the visible absorption spectrum scanned at 20–25° (for the spectral runs at 15 and 25° the reaction was followed by leaving the cells containing the reaction solution in the thermostated cell compartment of the spectrophotometer). To gain precision in obtaining the locations of isosbestic points, samples were held refrigerated at 0° until all the samples in a given run were taken, at which time the spectral scans were made one after the other after warming to 20–25°.

In the titrimetric method, 2.00- or 5.00-ml aliquots of reaction solution removed at known times were quenched by delivery into 23.0 or 20.0 ml, respectively, of 0° water, then 75.0 ml of acetone–detergent solution (1 gal of CP acetone, 50 ml of Tergitol NPX Nonionic detergent, and 25 ml of concentrated HNO_3) at 0° were added, and the free Cl^- was determined by potentiometric titration with $AgNO_3$ at 0°.[8] Chloride blanks were determined on control solutions containing everything except the complex and subtracted from the reaction sample titration volumes. Tests showed that the presence of the Cr(III) complexes did not interfere with the determination of free Cl^-. In the $Cr(en)(OH_2)_3Cl^{2+}$ hydrolysis runs, the Cl^- titrations were made on solutions the spectra of which were taken first.

Spectrophotometry.—All spectra were recorded in 10.00-cm matched silica cells with Cary Model 11 or Model 15 spectrophotometers, with identical solutions except for the complex in the reference cell.

Results

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF BLUE $Cr(en)(OH_2)_2Cl_2^+$ IN AQUEOUS $HClO_4$ IN THE DARK

Method[a]	Temp, °C	$HClO_4$, *F*	C_0, m*F*	μ, *M*[b]	10^5k_1, sec^{-1}[c]
Cl^-	35.00	1.5	0.99	1.5	13.8 ± 0.4
Cl^-	35.00	1.5	0.85	1.5	13.9 ± 0.4
Cl^-	35.00	0.10	0.53	0.10	12.7 ± 0.4
Cl^-	25.00	3.0	1.4	3.0	4.35 ± 0.12
Spectro	25.00	3.0	2.9	3.0	3.0 ± 1.0
Spectro	25.00	3.0	2.5	3.0	4.3 ± 0.9
Spectro	25.00	1.0	2.6	3.0	4.0 ± 0.9[d]
Cl^-	25.00	1.0	1.2	3.0	3.78 ± 0.19
Cl^-	25.00	0.10	1.8	3.0	3.53 ± 0.10
Cl^-	25.00	0.10	1.5	3.0	3.21 ± 0.32
Spectro	25.00	0.10	2.2	3.0	3.3 ± 0.7[e]
Spectro	25.00	0.10	3.0	3.0	3.5 ± 0.7
Spectro	25.00	0.10	2.6	0.10	2.8 ± 0.6[f]
Spectro	25.00	0.10	2.3	0.10	3.1 ± 0.8
Spectro	25.00	0.10	2.5	0.10	3.1 ± 0.6
Spectro	25.00	0.10	3.0	0.10	3.0 ± 0.6
Spectro	25.00	0.10	3.1	0.10	2.9 ± 0.6
Spectro	25.00	0.10	2.6	0.10	3.1 ± 0.6
Spectro	25.00	0.10	3.3	0.10	3.2 ± 0.6
Cl^-	25.00	0.10	1.3	0.10	3.13 ± 0.10
Cl^-	25.00	0.10	1.7	0.10	3.00 ± 0.10
Cl^-	25.00	0.010	1.3	0.10	3.40 ± 0.34
Spectro	25.00	0.010	2.7	0.10	2.7 ± 0.6
Spectro	25.00	0.010	3.0	0.10	3.0 ± 0.6
Cl^-	14.81	0.10	0.52	0.10	0.729 ± 0.025
Cl^-	14.81	0.10	0.46	0.10	0.741 ± 0.074
Spectro	14.81	0.10	3.2	0.10	0.73 ± 0.15[d]

[a] Cl^- = titration of released Cl^-; spectro = spectrophotometric analysis at 580 mμ, except as noted otherwise. [b] Ionic strength, controlled with $NaClO_4$. [c] Errors are standard deviations estimated from uncertainties in A_∞. [d] Same value also obtained from 400-mμ data. [e] Value from 400-mμ data 15% larger. [f] 585-mμ data.

Aquation of Blue $Cr(en)(OH_2)_2Cl_2^+$.—Table I presents the rate constants k_1 defined by the equation

$$-d(Cr(en)(OH_2)_2Cl_2^+)/dt = k_1(Cr(en)(OH_2)_2Cl_2^+) \qquad (1)$$

for the disappearance of blue $Cr(en)(OH_2)_2Cl_2^+$ in $HClO_4$–$NaClO_4$ solutions of various acidities and ionic strengths at 35, 25, and 15°. In the spectrophotometric method k_1 was evaluated for each kinetic run by the relation

$$2.303 \log [(A_0 - A_\infty)/(A - A_\infty)] = k_1t \qquad (2)$$

where A_0, A, and A_∞ are the optical absorbancies (at a given wavelength) at reaction time zero, at time *t*, and at 100% aquation of one chloro ligand, respectively; A_∞ was obtained by letting the reaction solution age for 4.3–8 half-lives, since the secondary hydrolysis is negligible under those conditions.[16] Rate plots based on eq 2 gave good linearity to 50–75% reaction (except for three runs linear to only 35–40% reaction). In the Cl^- release method k_1 was determined with the relation

$$2.303 \log [(V_\infty - V_0)/(V_\infty - V)] = k_1t \qquad (3)$$

where V_0, V, and V_∞ are the volumes of $AgNO_3$ titrant for a standard aliquot at reaction time zero, at time *t*, and for complete release of one chloro ligand, respectively. Plots of eq 3 were linear to 50–85% reaction.

Characterization of Magenta $Cr(en)(OH_2)_3Cl^{2+}$.

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[16] The use of A_∞ values calculated from the spectrum of magenta $Cr(en)(OH_2)_3Cl^{2+}$ gave k_1 values *ca.* 5–15% different from the Table I values and with less linear first-order rate plots, probably due to spectrophotometer errors and slight errors in molar absorbancy indices.

—The new complex $Cr(en)(OH_2)_3Cl^{2+}$ (magenta isomer) was characterized by its mode of formation (aquation of blue $Cr(en)(OH_2)_2Cl_2^+$), its hydrolysis product ($Cr(en)(OH_2)_4^{3+}$), its Cl:Cr atom ratio (1.00–1.05), and its elution behavior (typical of a 2+ cation of this size) in cation-exchange chromatography. As expected for this species, its visible absorption spectrum (Figure 1) exhibits d–d absorption bands at wavelengths intermediate to those of blue $Cr(en)(OH_2)_2Cl_2^+$ and $Cr(en)(OH_2)_4^{3+}$. The spectrum is substantially different from that of the purple isomer[17] of $Cr(en)(OH_2)_3Cl^{2+}$, but almost identical, except for small intensity differences, with the spectra of the magenta isomers of $Cr(pn)(OH_2)_3Cl^{2+}$ and $Cr(ibn)(OH_2)_3Cl^{2+}$,[6] as expected. At present the geometrical configurations of these species are unknown.

Hydrolysis of Magenta $Cr(en)(OH_2)_3Cl^{2+}$.—Table II gives the rate constants k_2 defined by the equation

$$-d(Cr(en)(OH_2)_3Cl^{2+})/dt = k_2(Cr(en)(OH_2)_3Cl^{2+}) \qquad (4)$$

for the disappearance of magenta $Cr(en)(OH_2)_3Cl^{2+}$ in 1.5 *F* $HClO_4$. Equations analogous to eq 2 and 3 were used to evaluate k_2, with A_∞ calculated from the spectrum of $Cr(en)(OH_2)_4^{3+}$. The rate plots were linear to 50–75% reaction.

Table II

First-Order Rate Constants for Hydrolysis of Magenta $Cr(en)(OH_2)_3Cl^{2+}$ in 1.5 *F* $HClO_4$ ($\mu = 1.5\ M^a$) in the Dark

Method[b]	Temp, °C	C_0, m*F*	10^5k_2, sec$^{-1\,c}$
Cl^-	70.10	2.5	13.4 ± 0.4
Cl^-	70.10	3.3	13.4 ± 0.4
Spectro	70.10	2.5	12.3 ± 0.9
Spectro	70.10	3.3	12.6 ± 1.3
Cl^-	60.15	1.8	4.02 ± 0.12
Spectro	60.15	1.8	3.30 ± 0.33
Cl^-	59.92	1.5	3.90 ± 0.12
Cl^-	59.92	1.4	4.03 ± 0.16
Cl^-	50.12	0.67	1.16 ± 0.04
Cl^-	50.12	0.71	1.06 ± 0.04

[a] Ionic strength. [b] Cl^- = titration of released Cl^-; spectro = weighted average of spectrophotometric values from 405- and 580-mμ data. [c] Errors are estimated standard deviations.

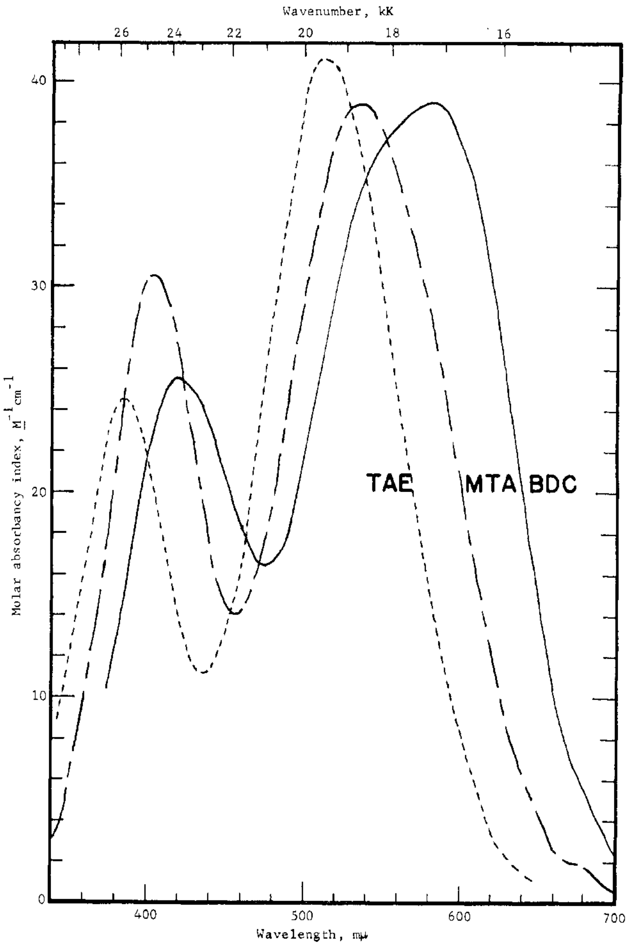

Figure 1.—Visible absorption spectra of some Cr(III) ethylenediamine complexes at 20–25°: BDC, blue isomer of $Cr(en)(OH_2)_2Cl_2^+$ in 0.1 *F* $HClO_4$; MTA, magenta isomer of $Cr(en)(OH_2)_3Cl^{2+}$ in 1.5 *F* $HClO_4$; TAE, $Cr(en)(OH_2)_4^{3+}$ in 2.0 *F* $HClO_4$; the molar absorbancy index a_M (molar extinction coefficient ϵ) is defined by the relation $\log (I_0/I) = A = a_Mcd$, where *c* is the molarity of the absorbing complex and *d* is the optical path in cm.

Discussion

Figure 1 shows the near-ultraviolet and visible absorption spectra of $Cr(en)(OH_2)_2Cl_2^+$ (blue isomer), the new complex $Cr(en)(OH_2)_3Cl^{2+}$ (magenta isomer), and $Cr(en)(OH_2)_4^{3+}$. We see that spectral scans made between 340 and 700 mμ during aquation of blue $Cr(en)(OH_2)_2Cl_2^+$ should give three isosbestic points, at 423 ± 2 mμ ($a_M = 25.4 \pm 0.8\ M^{-1}\ cm^{-1}$), 472 ± 2 mμ ($a_M = 16.5 \pm 0.6\ M^{-1}\ cm^{-1}$), and 551 ± 2 mμ ($a_M = 37.2 \pm 0.8\ M^{-1}\ cm^{-1}$), if the aquation product is magenta $Cr(en)(OH_2)_3Cl^{2+}$ and no other species are formed, *e.g.*, by isomerization, in spectrophotometrically detectible amount. Experimentally, we find three well-defined isosbestic points over a period of *ca.* two half-lives, at 420 ± 2 mμ ($a_M = 25.0 \pm 1.0\ M^{-1}\ cm^{-1}$), 471 ± 2 mμ ($a_M = 16.0 \pm 1.0\ M^{-1}\ cm^{-1}$), and 547 ± 3 mμ ($a_M = 36.9 \pm 0.5\ M^{-1}\ cm^{-1}$) (Figure 2), in reasonable agreement with the theoretical values for the reaction

$$Cr(en)(OH_2)_2Cl_2^+(blue) + H_2O \xrightarrow{k_1} Cr(en)(OH_2)_3Cl^{2+}(magenta) + Cl^- \qquad (5)$$

This evidence and the agreement of k_1 values obtained spectrophotometrically and by Cl^- release (see Table I) suggest that reactions in which a Cr–N bond is broken play a negligible role in the aquation. At first thought an alternative explanation of all of the above results might appear possible. *E.g.*, the blue dichloro reactant might be considered to isomerize with rate k_1 to one of the other two theoretically possible geometric isomers of $Cr(en)(OH_2)_2Cl_2^+$ in a rate-controlling step, followed by aquation of that isomer to magenta $Cr(en)(OH_2)_3Cl^{2+}$ with a rate much greater than k_1; one of these two other dichloro isomers is presumably the pink $Cr(en)(OH_2)_2Cl_2^+$ formed along with *cis-* and *trans-*$Cr(en)_2(OH_2)Cl^{2+}$ in the aquation of *trans*-$Cr(en)_2Cl_2^+$,[9,10] but preliminary experiments in this laboratory

[17] D. A. House and C. S. Garner, unpublished research.

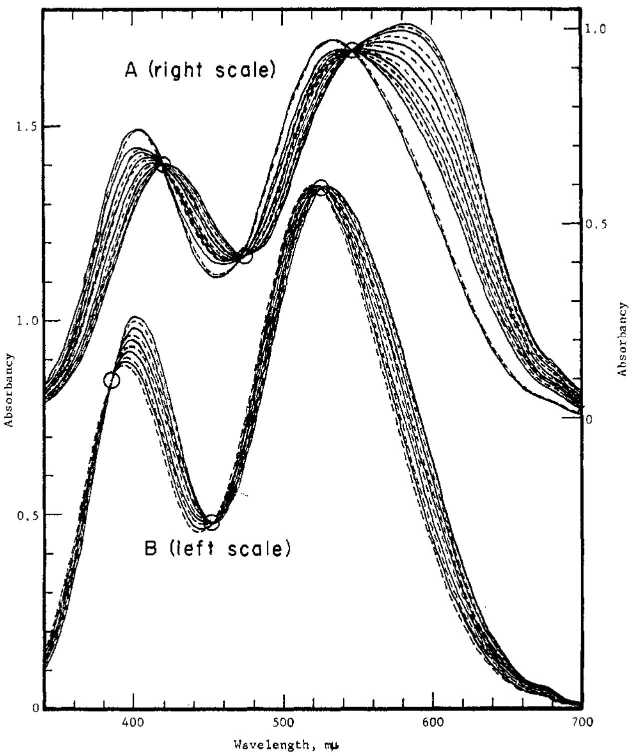

Figure 2.—Change in absorption spectra during hydrolysis: A, blue $Cr(en)(OH_2)_2Cl_2^+$ (C_0 = 2.6 mF) in 0.1 F $HClO_4$ (μ = 0.1 M) at 25.00°, reading downward at 580 mμ, reaction time is 7, 20, 40, 80, 120, 160, 210, 270, 330, 390, 450, 510, 570, 1390, and 1530 min, respectively; B, magenta $Cr(en)(OH_2)_3Cl^{2+}$ (C_0 = 3.3 mF) in 1.5 F $HClO_4$ (μ = 1.5 M) at 70.10°, reading downward at 400 mμ, reaction time is 0, 8, 15, 25, 35, 45, 60, 75, 90, and 105 min, respectively; alternate curves are dashed for convenience in reading.

suggest the pink isomer aquates too slowly to account for the results, and the third dichloro isomer, green $Cr(en)(OH_2)_2Cl_2^+$, although aquating fast enough, gives only a purple isomer of $Cr(en)(OH_2)_3Cl^{2+}$ having an absorption spectrum substantially different from that of the observed product, magenta $Cr(en)(OH_2)_3Cl^{2+}$.[17] Moreover, isomerization between the purple and magenta chlorotriaquo species is slow relative to the time scale involved. Thus, an isomerization pathway may be excluded.

At ionic strength 0.1 M, the aquation rate of blue $Cr(en)(OH_2)_2Cl_2^+$ may be taken as (3.1 ± 0.3) × 10^{-5} sec^{-1} ($t_{1/2}$ = 370 min) at 25.00°, independent of $HClO_4$ concentration in the rate 0.01-0.1 F (see Table I), showing that the contribution of base hydrolysis is negligible under these conditions. At 3 M ionic strength and 25° there appears to be a small decrease in k_1 in going from 3 to 0.1 F $HClO_4$, and in 0.1 F $HClO_4$ at 25° there is a similar decrease in k_1 in decreasing ionic strength from 3 to 0.1 M; the errors are fairly large, however, and at such high ionic strengths the effects may represent ion pairing or specific salt effects. The value of k_1 in 0.1 F $HClO_4$ is approximately the same as found[8,12] for Cl^- release from *trans*-$Cr(en)_2Cl_2^+$ in 0.1 F HNO_3 or $HClO_4$ and *ca.* one-tenth that found[7] for Cl^- release from *cis*-$Cr(en)_2Cl_2^+$ in these media at 25°. The significance of this will not be known until the geometric configuration of the blue $Cr(en)(OH_2)_2Cl_2^+$ becomes known and further comparisons are made of aquation rates of related ethylenediamine and bis(ethylenediamine) complexes.

Using the Cl^--release k_1 values, which are considerably more accurate than the spectrophotometric values, we obtain a good Arrhenius plot, from which we calculate E_a = 25.3 ± 0.6 kcal $mole^{-1}$, log PZ = 1.40 ± 0.4 (sec^{-1}), and $\Delta S^\circ_{298}{}^*$ = 3.8 ± 2.0 cal deg^{-1} $mole^{-1}$.

Because magenta $Cr(en)(OH_2)_3Cl^{2+}$ was available to us only in 1.5 F $HClO_4$ and further significant dilution was not possible because of the low concentration of the complex, we investigated the hydrolysis only in that medium. Hence the contribution of base hydrolysis, if any, is not known. The spectral scans (see Figure 2 for a typical run) gave three good isosbestic points, at 386 ± 2 mμ (a_M = 24.8 ± 1.0 M^{-1} cm^{-1}), 452 ± 2 mμ (a_M = 14.4 ± 0.6 M^{-1} cm^{-1}), and 526 ± 2 mμ (a_M = 39.3 ± 0.6 M^{-1} cm^{-1}), in good agreement with the values 385 ± 2 mμ (a_M = 24.5 ± 1.0 M^{-1} cm^{-1}), 454 ± 2 mμ (a_M = 14.3 ± 0.8 M^{-1} cm^{-1}), and 528 ± 2 mμ (a_M = 38.8 ± 0.8 M^{-1} cm^{-1}) predicted from Figure 1 for the reactions

$$Cr(en)(OH_2)_3Cl^{2+}(\text{magenta}) + H_2O \xrightarrow{k_{2a}} Cr(en)(OH_2)_4^{3+} + Cl^- \quad (6$$

$$Cr(en)(OH_2)_3Cl^{2+}(\text{magenta}) + OH^- \xrightarrow{k_{2b}} Cr(en)(OH_2)_3OH^{2+} + Cl^- \quad (7$$

$$Cr(en)(OH_2)_3OH^{2+} + H^+ \longrightarrow Cr(en)(OH_2)_4^{3+} \text{ (rapid)} \quad (8)$$

Together with the agreement between Cl^--release and spectrophotometric values of the hydrolysis rate constant k_2 (see eq 4 and Table II), the isosbestic-point evidence indicates there is no appreciable contribution to hydrolysis from Cr–N bond breakage, the sole product being $Cr(en)(OH_2)_4^{3+}$.

At 50.12° k_2 = (1.11 ± 0.03) × 10^{-5} sec^{-1} in 1.5 F $HClO_4$ ($t_{1/2}$ = 17.4 hr). The Cl^--release values of k_2, which are more accurate than the spectral values, give an excellent Arrhenius plot, from which E_a = 27.4 ± 0.2 kcal $mole^{-1}$, log PZ = 13.55 ± 0.10 (sec^{-1}), and $\Delta S^\circ_{323}{}^*$ = 1.7 ± 0.4 cal deg^{-1} $mole^{-1}$. Extrapolation to 25° gives k_2 = 3 × 10^{-7} sec^{-1}. This value is the same as the Cl^--release hydrolysis rate constant of *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ in 0.1 F HNO_3,[7] and about ten times the constant for *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ Cl^- release (estimated from 35° Cl^--release k[11]) at 25°.

Thus, there appear to be no large rate differences in the region of 25–50° between the singly-charged blue $Cr(en)(OH_2)_2Cl_2^+$ and $Cr(en)_2Cl_2^+$ isomers on the one hand and between the doubly-charged magenta $Cr(en)(OH_2)_3Cl^{2+}$ and $Cr(en)_2(OH_2)Cl^{2+}$ isomers on the other. We plan kinetic studies of the bromoaquo analogs for comparison purposes.

In the systems reported in this paper there is no evidence for Cr–N bond rupture competing with Cr–Cl bond rupture despite such evidence in the case of many bis(ethylenediamine)chromium(III) complexes.[9-12,14,15]

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CONTRIBUTION FROM THE INSTITUT FÜR PHYSIKALISCHE CHEMIE
DER UNIVERSITÄT FRANKFURT AM MAIN, FRANKFURT AM MAIN, GERMANY

Luminescence Behavior and Light Absorption of Some Fluoro Complexes of Tervalent Chromium

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Together with spectroscopic data ligand field parameters, *Dq*, B_{55}, and B_{35} obtained from reflectance spectra of the compounds $(NH_4)_3[CrF_6]$, $K_2[CrF_5(H_2O)]$, $[CrF_3(H_2O)_3]$, $[CrF(H_2O)_5][SiF_6]$, $[Cr(H_2O)_6]F_3$, $[Cr(H_2O)_6]Cl_3$, and $NH_4[CrF_4en]$ are reported. The crystalline compounds show at liquid air temperature a broad-band fluorescence, which can be assigned assuming approximately octahedral microsymmetry to a transition ${}^4T_{2g}(d\epsilon^2 d\gamma) \rightarrow {}^4A_{2g}(d\epsilon^3)$. $NH_4[CrF_4en]$ exhibits besides fluorescence a narrow-band phosphorescence ${}^2E_g(d\epsilon^3) \rightarrow {}^4A_{2g}(d\epsilon^3)$ at shorter wavelengths compared to the fluorescence. $[Cr(H_2O)_6]Cl_3$ yields phosphorescence only; $[Cr(H_2O)_6]F_3$ both types of luminescence. These findings are in agreement with a rule for the correlation between ligand field strength and the type of luminescence observed. The lifetime of the doublet state from which phosphorescence originates is, for $NH_4[CrF_4en]$, 2×10^{-7} sec at liquid air temperature.

Chromium(III) complexes in crystalline form or in rigid solutions at low temperatures show when excited by irradiation in the d→d ligand field, the charge-transfer, or the inner ligand bands a characteristic luminescence.[1-3] Sometimes the emission takes place from the first excited quartet state as a broad-band fluorescence. In a great number of compounds the emission occurs from the lowest doublet state as a narrow-band phosphorescence, often with typical vibrational structure.[1,4,5] A majority of complexes yield phosphorescence only, a few give both types of luminescence simultaneously, and others are known where fluorescence only can be detected. In the case of $[CrA_6]$ or $[Cr(AA)_3]$ complexes (A stands for a mono- and AA for a bidentate ligand) with octahedral microsymmetry, we have found a rule[6] which allows one to predict the type of luminescence for a certain compound. Complexes with ligands like Br^-, Cl^-, and F^-, which have small values of the ligand field strength parameter *Dq*, exhibit fluorescence only. Compounds where the coordinating atom is oxygen show both fluorescence and phosphorescence or phosphorescence only. For complexes where nitrogen or carbon is coordinated around chromium, where greater values of *Dq* are obtained, only phosphorescence can be observed.

$$\xrightarrow{\text{increasing } Dq}$$

Br, Cl, F,	O,	N, C
fluorescence only	fluorescence and phosphorescence or phosphorescence only	phosphorescence only

We discussed elsewhere[6] this empirical rule in terms of the shape and intersection of the potential-energy surfaces of the respective electronic states. Particularly of importance is the energy difference between the first excited quartet ${}^4T_{2g}$ and the lowest doublet state ${}^2E_g$. This quantity is closely related to the measurable difference ΔE between the wavenumber $\bar{\nu}_{\max}(I)$ of the absorption maximum of the long-wavelength spin-allowed band ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and $\bar{\nu}_{\max}(J)$ the wavenumber of the maximum of the intercombination band ${}^4A_{2g} \rightarrow {}^2E_g$; $\Delta E = \bar{\nu}_{\max}(I) - \bar{\nu}_{\max}(J)$ (cm^{-1}).

It is of interest to consider the luminescence behavior of mixed chromium(III) complexes $[CrA_{6-n}B_n]$, $n = 1$–5. To be sure that for such compounds the concept of approximate octahedral microsymmetry will still hold, the ligands A and B should be sufficiently close together in the spectrochemical series. Then it is to be expected that the deviation from regular octahedral symmetry, which is present in $[CrA_6]$ or $[CrB_6]$, is not detectable in the absorption spectra by a splitting of the spin-allowed d→d bands. Thus it is possible to obtain an average *Dq* value from the maximum of the long-wavelength spin-allowed band. Such *Dq* values can be calculated approximately from the *Dq* values for A and B using the rule of average environment.[7]

If one is interested in compounds which fluoresce, one has to select the ligand A from the left part of the spectrochemical series (small *Dq* values). That is the

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(7) See C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 109.