(but not the former ions) affects the identity of the products.

According to the rate data, at the lower [HSO_4^-]/[H^+] ratio used for product analysis, 21% of the reaction takes place by the SO_4^{2-}-dependent path, while at the higher [HSO_4^-]/[H^+] ratio, 43% takes place by this path. If it is assumed that the sulfate product is formed when SO_4^{2-} is involved in the attack of chromium(II) on NH_3OH^+, but not in the reaction of chromium(II) with NH_3^+, it would be expected that 10.5 and 22%, respectively, of the chromium(II) would appear as the sulfate complex. The experimental values of 7.4 and 22% of the chromium(III) appearing as the sulfate complex are in reasonable agreement with the supposition advanced.

The rate data for the several oxidants are summarized in Table V. The values of $\Delta S^{\ddagger}$ are remarkably constant for the series of reactions differing quite markedly in the nature of the substituents on the nitrogen. The increase in rates is in line with the increased stability of the radical generated when OH is abstracted by the reducing agent.

TABLE V
SUMMARY OF KINETIC PARAMETERS

Oxidant	k(298°K), M^{-1} sec^{-1}	μ	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
NH_3OH^+	0.0141	1.3	10.5 ± 0.5	-37 ± 2
$(CH_3)_3NOH^+$	0.66	1.0	7.9 ± 0.3	-33 ± 1
$(CH_3)_2C_6H_5NOH^+$	36	1.0	5.7 ± 0.2	-33 ± 1

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Aquation Kinetics of the Green-Blue Isomer of Dibromodiaquoethylenediaminechromium(III) Cation and of the Magenta Isomer of Bromotriaquoethylenediaminechromium(III) Cation[1]

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The aquation of $Cr(en)(OH_2)_2Br_2^+$ (green-blue isomer) has been investigated by spectrophotometry and by Br^- release in 0.01–2 F $HClO_4$ from 17 to 35°. At 25.01° the aquation rate constant is $k_1 = (3.95 \pm 0.05) \times 10^{-4}$ sec^{-1} in 0.3–2 F $HClO_4$ ($\mu = 2$ M, $NaClO_4$); $E_a = 19.8 \pm 0.2$ kcal mol^{-1} and log PZ(sec^{-1}) = 11.20 ± 0.01. The product is magenta $Cr(en)(OH_2)_3Br^{2+}$. Alternatively, but less probably, k_1 could be associated with a rate-controlling isomerization to one of the other two possible geometric isomers of $Cr(en)(OH_2)_2Br_2^+$, followed by relatively fast aquation to the observed product. The apparent first-order rate constant k_2 for hydrolysis of the latter was determined by spectrophotometry and by Br^- release in 0.01–3 F $HClO_4$ from 25 to 60°; $Cr(en)(OH_2)_4^{3+}$ is the product. In 0.03–3 F $HClO_4$ ($\mu = 3$ M, $NaClO_4$) at 40, 50, and 60°, $k_2 = k_{2a} + (k_2'/[H^+])$, where k_{2a} is the first-order rate constant for aquation of magenta $Cr(en)(OH_2)_3Br^{2+}$ and k_2' has been interpreted as $k_{2h}K_a$, k_{2h} being the first-order rate constant for aquation of $Cr(en)(OH_2)_2(OH)Br^+$ and K_a being the first acid dissociation constant of magenta $Cr(en)(OH_2)_3Br^{2+}$. At 25° $k_{2a} = (3 \pm 1) \times 10^{-6}$ sec^{-1} (by extrapolation), $E_a = 22.0 \pm 0.3$ kcal mol^{-1}, and log PZ(sec^{-1}) = 11.62 ± 0.07. At 40° and $\mu = 3$ M, k_{2h} is estimated as $\sim$0.2 sec^{-1}. There is no evidence for Cr–N bond rupture in these aquations. Visible absorption spectra are presented for green-blue $Cr(en)(OH_2)_2Br_2^+$ and magenta $Cr(en)(OH_2)_3Br^{2+}$.

Introduction

Recently we synthesized the green-blue dibromodiaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_2Br_2^+$, in aqueous solution by reaction of diperoxoaquoethylenediaminechromium(IV) monohydrate, $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$, with hydrobromic acid.[2] We observed that this dibromo complex hydrolyzed in perchloric acid solution to the magenta bromotriaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_3Br^{2+}$, which in turn hydrolyzed to the tetraaquoethylenediaminechromium(III) cation, $Cr(en)(OH_2)_4^{3+}$.

We report here a kinetic study of these two reactions, which are of interest for comparison with the corresponding reactions of their chloro analogs[3] and the related dibromo-[4,5] and bromoaquobis(ethylenediamine)chromium(III)[4] cations. This study also provides a further opportunity to examine the possibility of Cr–N bond breakage in competition with Cr–X (X = halogen or pseudohalogen) bond breakage. Such competitive Cr–N breakage has been reported in a variety of chromium(III)–amine complexes.[4,6–11] The

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(1) (a) Work partly supported by Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P12-70 to the AEC. (b) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

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(3) D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *ibid.*, **6**, 1524 (1967).

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previously unreported visible absorption spectra of the dibromodiaquo- and bromotriaquoethylenediaminechromium(III) cations are presented.

Experimental Section

Green-Blue Dibromodiaquoethylenediaminechromium(III) Cation.—This cation was prepared in solution and chromatographically purified as described earlier.[2] One preparation of the solid bromide salt resulted in purple crystals found to consist of *ca.* 90% $[Cr(en)(OH_2)_2Br_2]Br$, the remainder being bromide salts of $Cr(en)(OH_2)_3Br^+$ and $Cr(en)(OH_2)_4^{3+}$, without any of the green polymer reported earlier.[2] Some kinetic runs in 0.15–0.01 M H^+ were made with those crystals without further purification.

Magenta Bromotriaquoethylenediaminechromium(III) Cation.—This complex was prepared and purified as described earlier.[2] For some of the kinetic runs this complex was generated by aquation of $HClO_4$ solution of the above purple crystals or of chromatographically isolated green-blue $Cr(en)(OH_2)_2Br_2^+$ for 10 half-lives.

Other Chemicals.—Same as described earlier.[3]

Chemical Analyses.—Chromium and bromide were determined as described previously.[2]

Kinetic Runs.—Solutions of green-blue $Cr(en)(OH_2)_2Br_2^+$ or of magenta $Cr(en)(OH_2)_3Br^{2+}$ at *ca.* 2° were adjusted with $HClO_4$ and/or $NaClO_4$ to the desired acid concentrations and ionic strengths and warmed rapidly to the desired run temperature; they were then transferred into 10.00-cm silica cells which were put immediately into the thermostated cell compartment (±0.02°) of a Cary Model 15 recording spectrophotometer. In some runs spectral scans were made from 700 to 380 mμ at known times to search for isosbestic points, as well as to obtain kinetic data. In other spectrophotometric runs the recorder was simply allowed to run at a constant wavelength to obtain kinetic data of greater accuracy.

Several titrimetric runs were made of Br^- release, using the Cl^- titrimetric method described earlier,[3] except that 5.00- or 10.00-ml aliquots of reaction solution were quenched with 50.0 ml of the 0° acetone–detergent mixture. Bromide blanks were negligible, and tests showed that free Br^- could be accurately titrated at 0° in the presence of the bromo complexes.

Spectrophotometry.—All spectra were recorded in 10.00-cm silica cells with a Cary Model 15 spectrophotometer, using water in the matched silica reference cell.

Results

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

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

for the disappearance of green-blue $Cr(en)(OH_2)_2Br_2^+$ in $HClO_4$–$NaClO_4$ solutions of various acidities and ionic strengths and at various temperatures. In the spectrophotometric method k_1 was evaluated for each 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 bromo ligand, respectively. Rate plots based on eq 2 gave good linearity to 75–95% reaction, with a least-squares standard deviation one-tenth that estimated from uncertainties in A_∞ (computed from the spectrum of magenta $Cr(en)(OH_2)_3Br^{2+}$). In the Br^- 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 bromo ligand, respectively. Plots of eq 3 were linear to 50–85% reaction.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF GREEN-BLUE $Cr(en)(OH_2)_2Br_2^+$ IN THE DARK[a]

Method[b]	Temp, °C	$[HClO_4]$, F	C_0, mF	μ, M[c]	10^4k_1, sec^{-1} [d]
Sp	35.10	0.30	4.3	0.30	14.8 ± 0.2
Sp	34.10	0.30	3.7	0.30	12.8 ± 0.2
Sp	29.62	0.30	5.6	0.30	8.04 ± 0.15
Sp	29.61	0.30	9.5	0.30	8.03 ± 0.15
Sp[e]	24.91	0.30	7.1	0.30	5.12 ± 0.10
Sp	24.75	0.30	5.6	0.30	4.55 ± 0.10
Sp	22.50	0.30	3.8	0.30	3.74 ± 0.08
Br^-	20.86	0.30	2.7	0.30	3.05 ± 0.08
Sp	20.01	0.30	4.8	0.30	2.75 ± 0.06
Sp	17.52	0.30	3.2	0.30	2.04 ± 0.04
Sp	17.51	0.30	4.5	0.30	2.06 ± 0.03
Br^-	17.15	0.30	2.2	0.30	1.78 ± 0.03
Sp[f]	16.80	0.30	2.9	0.30	1.87 ± 0.06
Sp	25.01	2.0	3.4	2.0	3.89 ± 0.08
Sp	25.01	0.30	5.1	2.0	3.99 ± 0.08
Sp	25.01	0.30	1.7	2.0	3.88 ± 0.08
Sp	25.01	0.01	3.4	2.0	4.12 ± 0.08

[a] Exposed to spectrophotometric light beam during scans. [b] Sp, spectrophotometric determination at 630 mμ except as noted; Br^-, titration of released Br^-. [c] Ionic strength, controlled with $NaClO_4$. [d] Errors are standard deviations estimated from uncertainties in A_∞ (least-squares standard deviations is one-tenth of this). [e] At 650 mμ. [f] Average of data at 450 and 630 mμ.

Hydrolysis of Magenta $Cr(en)(OH)_2)_3Br^{2+}$.—Table II gives the rate constants k_2 defined by

$$-d[Cr(en)(OH_2)_3Br^{2+}]/dt = k_2[Cr(en)(OH_2)_3Br^{2+}] \qquad (4)$$

and evaluated spectrophotometrically and titrimetrically by equations analogous to eq 2 and 3; A_∞ was computed from the known spectrum of $Cr(en)(OH_2)_4^{3+}$.[12] Rate plots were linear to 50–90% reaction.

Discussion

Aquation and Configuration of Green-Blue $Cr(en)(OH_2)_2Br_2^+$.—Figure 1 shows the previously unreported near-ultraviolet and visible absorption spectra of green-blue $Cr(en)(OH_2)_2Br_2^+$ and magenta $Cr(en)(OH_2)_3Br^{2+}$,[13] together with the spectrum of $Cr(en)(OH_2)_4^{3+}$.[12] We see that spectral scans made between 380 and 700 mμ during aquation of green-blue $Cr(en)(OH_2)_2Br_2^+$ should give three isosbestic points, at 434 ± 2 mμ (a_M = 24.3 ± 0.5 M^{-1} cm^{-1}), 493 ± 3 mμ (a_M = 24.5 ± 0.5 M^{-1} cm^{-1}), and 580 ± 4 mμ (a_M = 32.0 ± 0.6 M^{-1} cm^{-1}), if the aquation product is magenta $Cr(en)(OH_2)_3Br^{2+}$ and no other species are formed in spectrophotometrically detectable amounts. Experimentally, we find three isosbestic points over a period of *ca.* 2 half-lives at 433 ± 3 mμ (a_M = 24.7 ± 0.5 M^{-1}

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

(13) Absorption maxima and minima for these two complexes were inadvertently given incorrectly in ref 2. The correct values are [mμ (a_M in M^{-1} cm^{-1})]: green-blue $Cr(en)(OH_2)_2Br_2^+$, 363 (min, 10.5), 412 (max, 25.4), 440 (min, 24.2), 470 (max, 24.7), 490 (min. 24.3), 543 (max, 31.4), 565 (min, 30.8), 630 (max, 48.0); magenta $Cr(en)(OH_2)_3Br^{2+}$, 410 (max, 30.3), 460 (min, 17.8), 475 (plateau, 19.6), 537 (max, 36.4), and ~600 (sh, ~28).

Table II

First-Order Rate Constants for Hydrolysis of Magenta $Cr(en)(OH_2)_3Br^{2+}$ in the Dark[a]

Method[b]	Temp, °C	$[HClO_4]$, F	C_0, mF	μ, M[c]	10^4k_2, sec^{-1} [d]
Sp	59.95	3.0	4.6	3.0	14.8 ± 0.3
Sp	59.95	0.150	7.5	3.0	27.5 ± 0.6
Sp	59.95	0.051	3.9	3.0	43.7 ± 0.8
Sp	59.95	0.030	5.0	3.0	69.2 ± 1.1
Sp	59.95	0.020	4.0	3.0	86.9 ± 1.3
Sp	50.01	3.0	5.2	3.0	5.32 ± 0.08
Sp	50.01	0.150	5.8	3.0	9.38 ± 0.17
Sp	50.01	0.051	4.9	3.0	15.7 ± 0.3
Sp	50.01	0.030	5.1	3.0	22.9 ± 0.5
Sp	50.01	0.011	6.2	3.0	50.4 ± 1.0
Sp[e]	40.02	3.0	5.2	3.0	1.94 ± 0.04
Br^-	40.02	3.0	4.8	3.0	1.97 ± 0.05
Sp[e]	40.02	0.154	9.7	3.0	2.99 ± 0.06
Br^-	40.02	0.094	1.2	3.0	3.96 ± 0.07
Sp	40.02	0.054	7.0	3.0	5.68 ± 0.13
Sp	40.02	0.026	7.2	3.0	8.80 ± 0.16
Sp[e]	40.02	1.0	3.5	1.0	2.86 ± 0.06
Sp[f]	24.91	0.30	7.1	0.30	0.055 ± 0.002
Sp[g]	24.75	0.30	5.6	0.30	0.056 ± 0.002
Sp	50.01	0.100	4.0	5.5	6.95 ± 0.10
Sp	50.01	0.100	5.1	2.5	14.7 ± 0.5
Sp	50.01	0.100	5.6	1.3	20.4 ± 0.6
Sp	50.01	0.100	4.1	0.70	24.8 ± 0.6
Sp	50.01	0.100	3.9	0.22	31.6 ± 0.8
Sp	50.01	0.100	5.4	0.10	32.2 ± 0.7

[a–d] These footnotes are the same as in Table I, except Sp here is 600 mμ except as noted. [e] Average of data at 420 and 600 mμ. [f] At 650 mμ. [g] At 630 mμ.

cm^{-1}), 491 ± 3 mμ (a_M = 24.9 ± 0.5 M^{-1} cm^{-1}), and 583 ± 3 mμ (a_M = 31.6 ± 0.3 M^{-1} cm^{-1}) (see Figure 2 for a typical run), in agreement with the theoretical values for the reaction

$$Cr(en)(OH_2)_2Br_2^{+}(\text{green-blue}) + H_2O \xrightarrow{k_1} Cr(en)(OH_2)_3Br^{2+}(\text{magenta}) + Br^- \quad (5)$$

This evidence and the agreement of k_1 values obtained by spectrophotometry (with A_∞ based on the spectrum of magenta $Cr(en)(OH_2)_3Br^{2+}$) and by Br^- release (see Table I; the Br^- points fall on the Arrhenius plot within experimental error) indicate that reactions in which a Cr–N bond is broken contribute negligibly to the aquation. However, the possibility exists that k_1 is associated with isomerization of green-blue $Cr(en)(OH_2)_2Br_2^+$ to one or a mixture of the other two possible geometric isomers of the dibromo complex in a rate-controlling step, followed by aquation of that isomer to magenta $Cr(en)(OH_2)_3Br^{2+}$ with a rate constant much greater than k_1.[14] We regard this alternative path as improbable because the various isomers in the related $Cr(en)(OH_2)_2Cl_2^+$–$Cr(en)(OH_2)_3Cl^{2+}$ system isomerize much too slowly to account for the observed aquation rates.[3]

At ionic strength 2.0 M, a weighted average aquation rate constant for green-blue $Cr(en)(OH_2)_2Br_2^+$ may be taken as (3.95 ± 0.05) × 10^{-4} sec^{-1} ($t_{1/2}$ = 29.3 min) at 25.01°, independent of $HClO_4$ concentration in the range 0.3–2 F (see Table I; the value of k_1 in 0.01 F

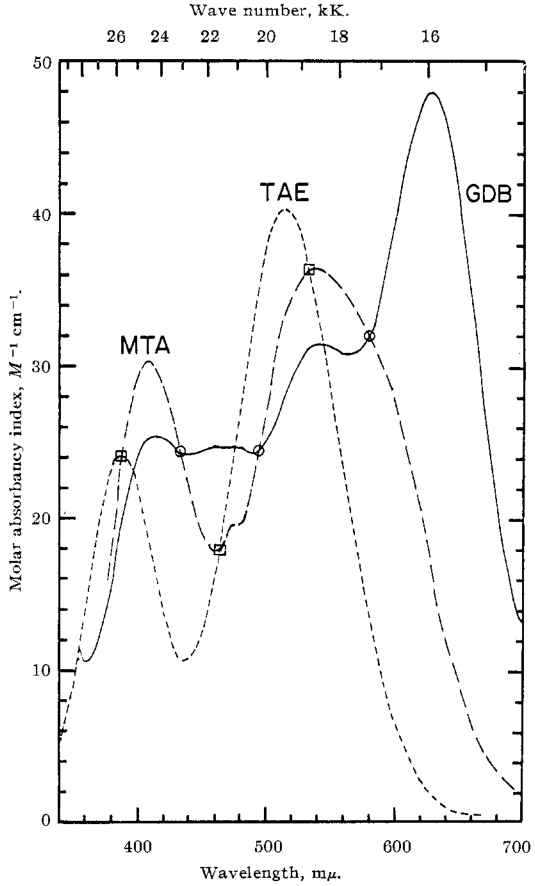

Figure 1.—Visible absorption spectra of some chromium(III)–ethylenediamine complexes at 20–25°: GDB, green-blue isomer of $Cr(en)(OH_2)_2Br_2^+$ in 0.3 F $HClO_4$; MTA, magenta isomer of $Cr(en)(OH_2)_3Br^{2+}$ in 3 F $HClO_4$; TAE, $Cr(en)(OH_2)_4^{3+}$ in 2 F $HClO_4$; the molar absorbancy index a_M (molar extinction coefficient ϵ) is defined by the relation $\log (I_0/I) = A = a_M c d$, where c is the molarity of the absorbing complex and d is the optical path in centimeters.

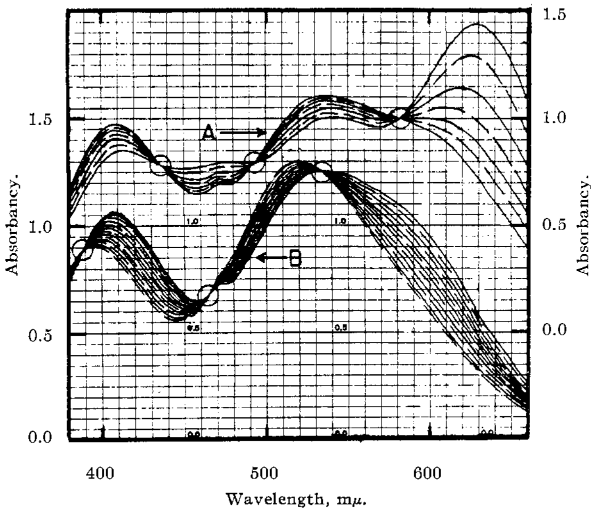

Figure 2.—Change in absorption spectra during hydrolysis: A, green-blue $Cr(en)(OH_2)_2Br_2^+$ (C_0 = 3.14 mF) in 0.3 F $HClO_4$ (μ = 0.3 M) at 24.9°; reading downward at 630 mμ, reaction time is 4, 10, 18, 26, 34, 42, and 54 min, respectively; B, magenta $Cr(en)(OH_2)_3Br^{2+}$ (C_0 = 3.52 mF) in 1 F $HClO_4$ (μ = 1 M) at 40.02°; reading downward at 600 mμ, reaction time is 0, 30, 65, 100, 140, 180, 220, 270, 320, 380, 450, and 500 min, respectively; alternate curves are dashed for convenience in reading.

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(14) Many papers on "aquation" kinetics fail to take into consideration the possibility of an alternative path *via* a preisomerization.

$HClO_4$ suggests the possibility of onset of base hydrolysis or of aquation *via* a presumably more labile dibromohydroxoaquo reactant present in small proportion). Thus, base hydrolysis contributes negligibly in the range 0.3–2 *F* $HClO_4$. At 25° and 0.3 *F* $HClO_4$, decrease of ionic strength from 2 to 0.3 *M* increases k_1 *ca.* 30%, an effect so small as probably to represent an ion-pairing or specific salt effect (a_M values for Cr(en)$(OH_2)_3Br^{2+}$ at the wavelength of kinetic analysis do not appear to change appreciably over this range of ionic strength).

Using the values of k_1 in Table I we obtain an excellent Arrhenius plot, from which we calculate E_a = 19.8 ± 0.2 kcal mol^{-1}, log $PZ(sec^{-1})$ = 11.20 ± 0.01, and $\Delta S^{\circ *}_{298} = -9.2 \pm 0.5$ cal deg^{-1} mol^{-1}.

In Table III we compare the aquation rate parameters of green-blue $Cr(en)(OH_2)_2Br_2^+$ with its dichloro analog and with the dibromo- and dichlorobis(ethylenediamine) complexes. Comparison of the activation entropies and rates is not strictly meaningful inasmuch as the relevant activity coefficients must vary in the different media.

TABLE III

RATES OF AQUATION AT 25° OF SOME DIBROMO AND DICHLORO Cr(III) COMPLEXES

Complex	Medium	10^4k_1, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg mol^{-1}
$Cr(en)(OH_2)_2Br_2^{+a}$	0.3 *F* $HClO_4$	5.1	19.8 ± 0.2	−9.2 ± 0.5
$Cr(en)(OH_2)_2Cl_2^{+b}$	0.1 *F* $HClO_4$	0.31	25.3 ± 0.6	3.8 ± 2.0
trans-$Cr(en)_2Br_2^{+c}$	0.1 *F* $HClO_4$	3.3	...	...
trans-$Cr(en)_2Br_2^{+d}$	0.1 *F* HNO_3	3.26	22.4	−1.4
trans-$Cr(en)Cl_2^{+e}$	0.1 *F* HNO_3	0.225	23.2 ± 0.2	−4.0 ± 0.7
cis-$Cr(en)_2Br^{2+c}$	0.1 *F* $HClO_4$	28	...	...
cis-$Cr(en)_2Cl_2^{+f}$	0.1 *F* $HClO_4$	3.30	21.1	−5.7

[a] Green-blue isomer; this research. [b] The blue *trans*-dichloro isomer.[3] [c] Reference 4. [d] Reference 5. [e] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961); *k* here is for Cl^- release only, and *ca.* 10% additional aquation occurs *via* release of one en ligand.[6,7] [f] J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

Bearing on this comparison is the recent X-ray structure determination made by Stomberg[15] on crystals of blue $[Cr(en)(OH_2)_2Cl_2]Cl$, which has shown that the chloro ligands are *trans* to each other. It now becomes meaningful to compare the aquation rates of the two *trans*-dichloro complexes $Cr(en)(OH_2)_2Cl_2^+$ and $Cr(en)_2Cl_2^+$. We see that these rates are comparable, in agreement with our expectation that probably only a small rate increase would occur on replacement of one of the two ethylenediamine ligands by two water ligands, whereas *cis*-$Cr(en)_2Cl_2^+$ aquates *ca.* 10 times faster. Green-blue $Cr(en)(OH_2)_2Br_2^+$ aquates at essentially the same rate as *trans*-$Cr(en)_2Br_2^+$ and has a rate 16 times that of $Cr(en)(OH_2)_2Cl_2^+$ (*trans*-dichloro), essentially the same rate ratio as for *trans*-$Cr(en)_2Br_2^+$ relative to *trans*-$Cr(en)_2Cl_2^+$, whereas the rate ratio for the *cis* isomers of the latter two complexes is 9. Thus these rate comparisons appear to favor a *trans*-dibromo assignment for green-blue $Cr(en)(OH_2)_2Br_2^+$. Moreover, this complex was made by the same method (action of the hydrohalic acid on $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$) as the blue *trans*-dichloro analog and the visible absorption spectrum of the dibromo complex (Figure 1) is more similar to that of the *trans*-dichloro analog than to that of green $Cr(en)(OH_2)_2Cl_2^+$, suggesting the same configuration for green-blue $Cr(en)(OH_2)_2Br_2^+$ as for the *trans*-dichloro analog. The splitting of both bands I and II in the dibromo complex is larger than observed in *trans*- and *cis*-$Cr(en)_2X_2^+$ (X = Br, Cl) or blue $Cr(en)(OH_2)_2Cl_2^+$ but is comparable to that in blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$;[16] we have discussed the splitting in the latter complex earlier, where we interpreted it as in accord with a *trans*-dibromo configuration of that complex.[16] As in aquation of blue Cr(en)$(OH_2)_2Cl_2^+$ (*trans*-dichloro)[3] and blue-green Cr(en)$(NH_3)(OH_2)Br_2^+$,[16] aquation of green-blue Cr(en)$(OH_2)_2Br_2^+$ gives only a single aquation product (the magenta bromotriaquo complex, which gave no chromatographic evidence of consisting of more than one isomer), as would be expected for a *trans*-dibromo reactant if aquation proceeds *via* a square-pyramidal intermediate or transition state (if aquation goes *via* a trigonal bipyramid, 67% 1,2,3- and 33% 1,2,6-triaquo product would be expected statistically, but the presence of other factors makes a purely statistical calculation qualitative at best). If green-blue $Cr(en)(OH_2)_2Br_2^+$ were the *trans*-diaquo isomer, a single aquation product would again be expected, whereas the third of the three possible geometric isomers of the dibromo complex (the 1,2-dibromo-3,4-diaquo isomer) should aquate to give both isomers of the triaquo product, assuming a dissociative mechanism. Unfortunately, only one isomer of the dibromo complex has been synthesized so far. All of this evidence in support of a *trans*-dibromo configuration for green-blue Cr(en)$(OH_2)_2Br_2^+$ is circumstantial, however, and the activation energy and entropy for aquation of the dibromo complex seems to be out of line with those for the *trans*-dichloro analog. Thus the question of the configuration remains unresolved.

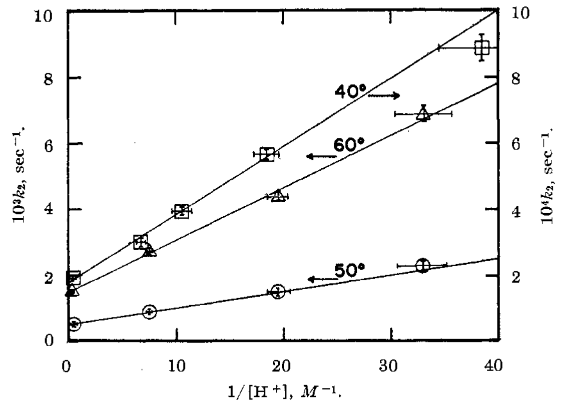

Figure 3.—Hydrogen ion dependence of hydrolysis rate of magenta $Cr(en)(OH_2)_3Br^{2+}$ at μ = 3.0 *M*.

Hydrolysis and Configuration of Magenta Cr(en)$(OH_2)_3Br^{2+}$.—Figure 1 predicts that spectral scans

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(15) R. Stomberg, personal communication through Dr. D. A. House.

(16) R. G. Hughes and C. S. Garner, *Inorg. Chem.*, **7**, 74 (1968).

made between 380 and 700 mμ during aquation of magenta $Cr(en)(OH_2)_3Br^+$ should give three isosbestic points, at 387 ± 3 mμ ($a_M = 24.2 \pm 0.7\ M^{-1}\ cm^{-1}$), 464 ± 3 m$\mu$ ($a_M = 18.2 \pm 0.8\ M^{-1}\ cm^{-1}$), and 534 ± 2 m$\mu$ ($a_M = 36.3 \pm 0.4\ M^{-1}\ cm^{-1}$) if aquation produces $Cr(en)(OH_2)_4^{3+}$ and no other species are formed in spectrophotometrically detectable amounts. Over a period of *ca.* 2 half-lives we find experimentally three isosbestic points at 386 ± 2 mμ ($a_M = 24.9 \pm 1.0\ M^{-1}\ cm^{-1}$), 465 ± 2 m$\mu$ ($a_M = 19.7 \pm 0.8\ M^{-1}\ cm^{-1}$), and 532 ± 2 m$\mu$ ($a_M = 36.1 \pm 0.4\ M^{-1}\ cm^{-1}$) (see Figure 2 for a typical run), in agreement with the expected values for the reactions

$$\mathrm{Cr(en)(OH_2)_3Br^{2+}(magenta) + H_2O \xrightarrow{k_{2a}} Cr(en)(OH_2)_4^{3+} + Br^-} \quad \text{(path 1)} \qquad (6)$$

$$\left.\begin{array}{l} \mathrm{Cr(en)(OH_2)_3Br^{2+}(magenta) + OH^- \xrightarrow{k_{2b}} Cr(en)(OH_2)_3OH^{2+} + Br^-} \\ \mathrm{Cr(en)(OH_2)_3OH^{2+} + H^+ \longrightarrow Cr(en)(OH_2)_4^{3+}} \quad \text{(fast)} \end{array}\right\} \text{(path 2)} \qquad \begin{array}{r} (7a) \\ (7b) \end{array}$$

$$\left.\begin{array}{l} \mathrm{Cr(en)(OH_2)_3Br^{2+}(magenta) \overset{K_a}{\rightleftarrows} Cr(en)(OH_2)_2(OH)Br^+ + H^+} \\ \qquad \text{(fast equilibrium, far to left)} \\ \mathrm{Cr(en)(OH_2)_2(OH)Br^+ + H_2O \xrightarrow{k_{2h}} Cr(en)(OH_2)_3OH^{2+} + Br^-} \\ \text{Reaction 7b} \end{array}\right\} \text{(path 3)} \qquad \begin{array}{r} (8a) \\ (8b) \end{array}$$

Agreement of k_2 values obtained spectrophotometrically (with A_∞ calculated from the spectrum of $Cr(en)(OH_2)_4^{3+}$) and by Br^- release (Table II), together with the above isosbestic point agreement, shows that Cr–N bond rupture is not contributing appreciably to the aquation of magenta $Cr(en)(OH_2)_3Br^{2+}$. As for aquation of $Cr(en)(OH_2)_2Br_2^+$, the possibility of a preisomerization path for the hydrolysis cannot be excluded, although it seems unlikely. Table II shows that k_2 is dependent upon H^+ concentration and upon ionic strength. Figure 3 presents plots of k_2 *vs.* $1/[H^+]$ at 3.0 M ionic strength and at 40, 50, and 60°, where $[H^+]$ is taken as the formality of $HClO_4$ in the reaction solution. Over the range 0.03–3 F $HClO_4$, k_2 obeys a relation of the form

$$k_2 = k_{2a} + (k_2'/[H^+]) \qquad (9)$$

where the second term might indicate either base hydrolysis (path 2), for which $k_2'/[H^+] = (k_2'/K_w)\cdot[OH^-] = k_{2b}[OH^-]$, where K_w is the ion-product constant for water in the reaction solutions at the given temperature, and/or a rapid acid dissociation preequilibrium followed by a rate-controlling aquation of the bromohydroxo complex (path 3), for which $k_2'/[H^+] = k_{2h}K_a/[H^+]$, where K_a is the first acid dissociation constant of magenta $Cr(en)(OH_2)_3Br^{2+}$. Table IV gives the values of k_{2a} associated with aquation reaction 6 and of k_2' obtained by least-squares analysis of the rate data in 3.0 M ionic strength at 40, 50, and 60° (Table II).

Table IV

Rate Constants for Hydrolysis of Magenta $Cr(en)(OH_2)_3Br^{2+}$ ($\mu = 3.0\ M$)

Temp, °C	10^4k_{2a}, sec^{-1}	$10^5k_2'$, $M\ sec^{-1}$	$10^{-8}k_{2b}$, $M^{-1}\ sec^{-1}$ [a]	k_{2h}, sec^{-1} [b]
59.95	14.8 ± 0.8	15.9 ± 0.8	~17	~2
50.01	5.41 ± 0.12	5.29 ± 0.13	~10	~0.5
40.02	1.78 ± 0.06	2.06 ± 0.09	~7	~0.2

[a] Assuming the $[H^+]$-dependent term arises wholly from path 2 and that K_w has the same values as in pure water. [b] Assuming the $[H^+]$-dependent term arises wholly from path 3 and estimating K_a as $\sim 10^{-4}$ at 40–60° (see text).

The values of k_{2a} give a good Arrhenius plot, from which we calculate $E_a = 22.0 \pm 0.3$ kcal mol^{-1} and log $PZ(sec^{-1}) = 11.62 \pm 0.07$, and by extrapolation to 25° we obtain $k_{2a} = (3 \pm 1) \times 10^{-6}\ sec^{-1}$ and $\Delta S^{\circ *}_{298} = -7.4 \pm 0.9$ cal deg^{-1} mol^{-1}. The aquation rate parameters are compared with those of some related bromoaquo and chloroaquo Cr(III) complexes in Table V. Magenta $Cr(en)(OH_2)_3Br^{2+}$ aquates at about the same rate as *trans*-$Cr(en)_2(OH_2)Br^{2+}$ and about 10 times faster than magenta $Cr(en)(OH_2)_3Cl^{2+}$, whereas *cis*-$Cr(en)_2(OH_2)Br^{2+}$ and *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ aquate much faster; this is the same as the behavior noted for the dibromo and dichloro complexes of Table III. Again E_a and ΔS^*_{298} are much less for the bromotriaquo complex than for the chlorotriaquo analog, like the behavior noted for the first two related complexes of Table III. Assuming that magenta $Cr(en)(OH_2)_3Cl^{2+}$ is the 1,2,3-triaquo (facial) isomer, as would be expected from its formation from the *trans*-dichloro complex, blue $Cr(en)(OH_2)_2Cl_2^+$ (isomerization rates of the dichloro and triaquo complexes are negligible relative to the respective aquation rates[3]), the above rate evidence suggests that magenta $Cr(en)(OH_2)_3Br^{2+}$ is probably also the 1,2,3-triaquo complex, as tentatively concluded earlier from visible absorption spectra comparisons.[2] However, this assignment must be regarded as tentative until the other isomers of $Cr(en)(OH_2)_3Br^{2+}$ are synthesized and investigated. The aquation rate constant given in Table V for *trans*-$Cr(en)_2(OH_2)Cl^{2+}$, when compared with *trans*-$Cr(en)_2(OH_2)Br^{2+}$ and the relative aquation rates of the dibromo and dichloro bis-ethylenediamine complexes, appears to be too large by a factor of *ca.* 10; Cl^- release for *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ followed a complicated rate law interpreted in terms of a parallel path involving loss of one ethylenediamine ligand and Cl^- release on hydrolysis of that product, and the interpretation and value of the Cl^--release aquation rate constant may be in error.[17]

Returning now to the $[H^+]$-dependent term in eq 9, we see from Table IV that if k_2' were attributed wholly to base hydrolysis of $Cr(en)(OH_2)_3Br^{2+}$ (path 2), the values of the second-order base hydrolysis rate constant k_{2b} would be abnormally high for a Cr(III) complex, and we may exclude any large contribution from this path. On the other hand, if we attribute k_2' to path 3

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(17) Two errors were made on p 1527 of ref 3 in comparing the $Cr(en)(OH_2)_3Cl^{2+}$ aquation rate with *cis*- and *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ aquation rates; as seen from Table V, the triaquo complex aquates 100 times more slowly than the *cis*-chloroaquo complex and 10 times more slowly than the *trans*-chloroaquo complex. If the latter actually aquates at one-tenth the rate reported, as suggested, this would bring its rate into accord with that of $Cr(en)(OH_2)_3Cl^{2+}$.

TABLE V

RATES OF AQUATION AT 25° OF SOME BROMOAQUO AND CHLOROAQUO Cr(III) COMPLEXES

Complex	Medium	10^6k_{2a}, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
$Cr(en)(OH_2)_3Br^{2+}$ [a]	0.02–3 *F* $HClO_4$ (μ = 3 *M*, $NaClO_4$)	3 ± 1[b]	22.0 ± 0.3	−7.4 ± 0.9[b]
$Cr(en)(OH_2)_3Cl^{2+}$ [c]	1.5 *F* $HClO_4$	0.3 ± 0.1[d]	27.4 ± 0.2[e]	1.7 ± 1.6[d]
trans-$Cr(en)_2(OH_2)Br^{2+}$ [f]	1.4 *F* HNO_3	3.0 ± 0.2[g,h]	...	...
trans-$Cr(en)_2(OH_2)Cl^{2+}$ [i]	0.1 *F* HNO_3	~3[h,j]	...	...
cis-$Cr(en)_2(OH_2)Br^{2+}$ [f]	0.1 *F* $HClO_4$	180	...	...
cis-$Cr(en)_2(OH_2)Cl^{2+}$ [k]	0.1 *F* $HClO_4$	28	...	...

[a] Magenta isomer; this research. [b] Extrapolated to 25° from 40–60° data. [c] Reference 3. [d] Extrapolated to 25° from 50–70° data. [e] It now appears (see Discussion below) that this E_a includes a small contribution from a path involving aquation of $Cr(en)(OH_2)_2(OH)Cl^+$ formed in the system by proton loss by $Cr(en)(OH_2)_3Cl^{2+}$. [f] Reference 4. [g] *k* for Br^- release, which could arise from aquation or possible reactant isomerization. [h] Aquation *via* Cr–N bond breakage also occurs. [i] Reference 8. [j] *k* for Cl^- release, extrapolated to 25° from 35° data; it now appears possible this *k* is too great by a factor of 10 (see Discussion below). [k] Footnote *f*, Table III.

(aquation of $Cr(en)(OH_2)_2(OH)Br^+$) and arbitrarily estimate $K_a \sim 10^{-4}$ at 40–60° from similar acid dissociation constants for some aquo Cr(III) complexes at 25°, we get the values of k_{2h} given in Table V. These appear to be of the right order of magnitude relative to k_{2a}, based on aquation rate comparisons of some Co(III) aquo and hydroxo complexes. This explanation of k_2' appears to us to be reasonable and is compatible with the isosbestic points observed, since at the lowest $[H^+]$, namely, 0.01 *M*, only *ca.* 1% of the complex would be in the hydroxodiaquo form if $K_a \sim 10^{-4}$. Because of the uncertainty in K_a and, hence, k_{2h} values, we have not calculated activation parameters for the $Cr(en)(OH_2)_2(OH)Br^+$ aquation.

The hydrolysis rate of magenta $Cr(en)(OH_2)_3Cl^{2+}$ was studied originally only in 1.5 *F* $HClO_4$ at 50–70°.[3] Later the rate was determined[18] in 0.35 and 0.07 *F* $HClO_4$ (μ = 1.5 *M*, $NaClO_4$) at 60°; the observed hydrolysis rate constants at these two acid concentrations, together with the value in 1.5 *F* $HClO_4$ at 60°, give a linear plot of k_2 *vs.* $1/[H^+]$, from which the *y* intercept gives a first-order rate constant for aquation of magenta $Cr(en)(OH_2)_3Cl^{2+}$ of $k_{2a} = 3.2 \times 10^{-5}$ sec^{-1} at 60°, which is within 10% of the unresolved hydrolysis rate constant reported earlier[3] in 1.5 *F* $HClO_4$ at 60°. If we interpret the $[H^+]$ dependence in the same way as for magenta $Cr(en)(OH_2)_3Br^{2+}$, this would give (assuming the first acid dissociation constant of magenta $Cr(en)(OH_2)_3Cl^{2+}$ is also $\sim 10^{-4}$ at 60°) a rate constant of $k_{2h} \sim 0.03$ sec^{-1} for aquation of $Cr(en)(OH_2)_2(OH)Cl^{2+}$ at 60° and μ = 1.5 *M*. This value is smaller than our estimate of $k_{2h} \sim 2$ sec^{-1} for aquation of $Cr(en(OH_2)_2(OH)Br^{2+}$ at 60° and μ = 3.0 *M*, which is in the right direction (chloro complex aquating more slowly than bromo analog).

Table II shows that k_2 is dependent upon ionic strength. A plot of log k_2 *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$ in 0.1 *F* $HClO_4$ at 50° is markedly curved over the entire range μ = 5.5–0.1 *M*, exhibiting an increase in k_2 with decreasing μ. Since k_{2a} should be approximately independent of μ, the dependence presumably arises from the secondary kinetic salt effect on reaction 8a in path 3.

No evidence has been found for Cr–N bond breakage competing with Cr–X (X = Br, Cl, NCS) bond breakage in the aquation of green-blue $Cr(en)(OH_2)_2Br_2^+$ or magenta $Cr(en)(OH_2)_3Br^{2+}$, as was true for the analogous blue $Cr(en)(OH_2)_2Cl_2^+$ and magenta $Cr(en)(OH_2)_3Cl^{2+}$.[3] Thus, so far, such competitive Cr–N bond breakage is limited to certain bis(ethylenediamine)chromium(III) complexes[4,6–10] and *cis*-β- (or *cis*-β′-) chloroaquotriethylenetetraminechromium(III) cation.[11]

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[18] R. K. Kurimoto and C. S. Garner, unpublished research.