For example, thermal decomposition of metal dithiophosphates formed from ligands produced by allowing secondary alcohols to react with P_2S_5 leads to substantial olefin formation.[28] Phosphines also apparently promote a carbon–oxygen bond cleavage since nearly quantitative yields of $L_2PdS_2P(O)OC_2H_5$ are obtained when the palladium diethyldithiophosphate is treated with methyldiphenylphosphine in chloroform.

The nucleophilicity of the sulfur atoms in the 1:1 dithiolate complexes is shown by the reactions, Figure 1, we have observed between L_2PtS_2CO and various alkylating agents. Benzyl bromide reacts readily with the dithiocarbonate complex to produce benzyl disulfide and the *cis*-L_2PtBr_2 complex. Carbon monoxide must be produced in this reaction, but it is not present in the isolated products which are obtained in essentially quantitative yield. An infrared spectrum of the reaction mixture shows that the carbon monoxide remains in the chloroform solution in considerable excess of its normal solubility. It can be removed by bubbling nitrogen or argon through the solution and also by evaporation of the solvent. The frequency of this CO band, $\bar{\nu}$ 2040 cm^{-1}, indicates that the carbon monoxide is associated with the metal. While a *cis*-$L_2PtCOBr^+$ species might be expected as a reaction product, the CO frequency appears to be too low by comparison with the known $\bar{\nu}_{CO}$ values of $\sim$2100 cm^{-1} in *trans*-(phosphine)$_2$Pt(CO)X^+ species.[29] However, *cis*-(phosphine)$_2$Pt(CO)X^+ species have not been reported so no direct comparison can be made. The ease with which CO is removed and the irreversibility of its removal are still puzzling. Also a detailed explanation of why a disulfide is formed with benzyl bromide while sulfides are produced, along with COS, when some other alkylating agents are used, Figure 1, is not available at present.

Acknowledgment.—The donors of the Petroleum Research Fund as administered by the American Chemical Society are gratefully acknowledged for partial support of this work, along with the National Science Foundation (Grant GP-7889).

(29) M. J. Church and M. J. Mays, *J. Chem. Soc., A*, 3074 (1968).

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The Stepwise Aquation of the 1,6-Dibromo-2-aquo-3-ammineethylenediaminechromium(III) Cation to the Tetraaquoethylenediaminechromium(III) Cation[1]

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The kinetics of the successive aquation steps of green Cr(en)$(NH_3)(OH_2)Br_2^+$ to Cr(en)$(OH_2)_4^{3+}$ have been investigated by spectrophotometry and also by Br^- release for the first two aquation steps. The first step produces magenta Cr(en)$(NH_3)(OH_2)_2Br^{2+}$, and was studied in 0.1–2 F $HClO_4$ ($\mu = 0.3$–$2\ M$, $NaClO_4$) from 20 to 35°. At 25° the first-order rate constant is $k_1 = 4.1 \times 10^{-4}\ sec^{-1}$ (0.1–0.3 F $HClO_4$; $\mu = 0.3\ M$, $NaClO_4$), $E_a = 20.7 \pm 0.3$ kcal mol^{-1}, and log $PZ(sec^{-1}) = 11.81 \pm 0.23$. Aquation of the monobromo product appears to give a single pink isomer of Cr(en)$(NH_3)(OH_2)_3^{3+}$. In 0.15–1 F $HClO_4$ ($\mu = 1\ M$, $NaClO_4$) at 34–53° the observed hydrolysis rate constant $k_{2,obsd}$ has the form $k_{2,obsd} = k_2 + (k_2'/[H^+])$, where k_2 is the first-order rate constant for aquation of magenta Cr(en)$(NH_3)(OH_2)_2Br^{2+}$ and k_2' has been interpreted as $k_{2h}K_a$, where k_{2h} is the first-order rate constant for aquation of Cr(en)$(NH_3)(OH_2)(OH)Br^+$ and K_a is the first acid dissociation constant of magenta Cr(en)$(NH_3)(OH_2)_2Br^{2+}$. At 25° $k_2 = 4 \times 10^{-6}\ sec^{-1}$ (by extrapolation), $E_a = 23.2 \pm 0.1$ kcal mol^{-1}, and log $PZ(sec^{-1}) = 11.57 \pm 0.09$. At 34° and $\mu = 1\ M$, $k_{2h} \approx 0.01\ sec^{-1}$. Aquation of pink Cr(en)$(NH_3)(OH_2)_3^{3+}$ to Cr(en)$(OH_2)_4^{3+}$ was studied in 0.15–3 F $HClO_4$ from 45 to 60° and was found to be first order. In 0.15–1 F $HClO_4$ ($\mu = 1.0\ M$), $k_3 = 5.7 \times 10^{-5}\ sec^{-1}$ at 52.50° (*ca.* $1 \times 10^{-6}\ sec^{-1}$ at 25° by extrapolation), $E_a = 27.5 \pm 0.3$ kcal mol^{-1}, and log $PZ(sec^{-1}) = 14.08 \pm 0.17$. There is no evidence for Cr–N bond rupture involving the ethylenediamine ligand in any of these reactions. The kinetic results confirm the *trans*-dibromo and *trans*-bromoaquo configurations spectrophotometrically assigned earlier to green Cr(en)$(NH_3)(OH_2)Br_2^+$ and magenta Cr(en)$(NH_3)(OH_2)_2Br^{2+}$.

Introduction

The aquation kinetics of the green isomer of dibromoaquoammineethylenediaminechromium(III) cation, Cr(en)$(NH_3)(OH_2)Br_2^+$, and its successive aquation products is interesting for a number of reasons. As members of a series of halomonoethylenediaminechromium(III) cationic complexes, this dibromo complex and its monobromo daughter provide data for comparison with their analogs. These comparisons can be used to support the earlier tentative isomeric assignments made for the dibromo and monobromo complexes. Other comparisons demonstrate the effect on the loss of a ligand through aquation due to a change in other ligands of the coordination sphere. A comparison of the aqua-

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(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 170, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P170-1 to the AEC. (b) Abbreviations used: en, ethylenediamine; dien, diethylenetriamine.

tion steps with those of $Cr(en)_2Br_2{}^+$,[2] $Cr(NH_3)_3(OH_2)Br_2{}^+$,[3] $Cr(en)(OH_2)_2Br_2{}^+$,[4] and $Cr(NH_3)_2(OH_2)_2Br_2{}^+$[5] is particularly noteworthy in this respect. The $Cr(en)(NH_3)(OH_2)Br_2{}^+$ cation is intermediate in the number of Cr–N bonds between the bis- and monoethylenediamine complexes mentioned, giving some indication of the relation between these two types of chromium(III) complexes. The following study presents kinetic results for the first three successive aquation steps of this mixed-amine-ligand chromium(III) complex. These results, together with the earlier work on the aquation of $Cr(en)(OH_2)_4{}^{3+}$ and $Cr(enH)(OH_2)_5{}^{4+}$,[6] allow a comparison of the five successive aquation steps to the final hexaaquo product.

Experimental Section

Green Dibromoaquoammineethylenediaminechromium(III) Cation.—This complex was prepared as described earlier.[7] Although the complex was originally described as blue-green, chromatography of larger amounts of the crude complex salt revealed small amounts of a relatively intense green-blue material which was eluted just ahead of the green band. This green-blue band was collected and its visible absorption spectrum was found to be the same as that reported[4] for the green-blue isomer of $Cr(en)(OH_2)_2Br_2{}^+$. By allowing some of the ammine complex to be eluted before collecting samples for kinetic runs, most of this impurity was avoided. The spectrum of the ammine complex obtained corresponded closely to that previously given,[7] and analysis gave a Br:Cr atom ratio of 2.06.

Magenta Bromodiaquoammineethylenediaminechromium(III) Cation.—The preparation of this complex and its chromatographic purification has also been described.[7] For most kinetic runs, especially where low acidity or ionic strength was desired, the chromatographically purified dibromo complex was allowed to age in 0.3 *F* $HClO_4$ for 2.5 hr at 25°. The visible absorption spectrum of the magenta complex obtained from this preparation matched that of the purified $Cr(en)(NH_3)(OH_2)_2Br^{2+}$, which was the same as that previously given[7] for magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$, and analysis gave a Br:Cr atom ratio of 0.98.

Pink Triaquoammineethylenediaminechromium(III) Cation.—Aquation of the monobromo complex at 52° gave a mixture of pink $Cr(en)(NH_3)(OH_2)_3{}^{3+}$ with considerable $Cr(en)(OH_2)_4{}^{3+}$ in the time necessary to age out all of the monobromo species. Although this procedure was used to prepare some solutions for kinetic runs, in other cases the pink triaquo complex was isolated by charging a solution of the monobromo complex aged for *ca.* 1 half-life onto a 6-cm × 1-cm diameter column of H^+ AG50W-X8 cation-exchange resin (100–200 mesh), removing the unreacted dibromo complex with *ca.* 150 ml of 1.5 *F* $HClO_4$, and then eluting the species of charge 3+ with *ca.* 100 ml of 3 *F* $HClO_4$. Although this chromatogaphy does not necessarily separate the small amounts of $Cr(en)(OH_2)_4{}^{3+}$ which could possibly have been present in the aged solution, the visible absorption spectrum of the pink complex obtained by the latter procedure gave visible absorption maximum and minimum values similar to those reported[7] for $Cr(en)(NH_3)(OH_2)_3{}^{3+}$, isomer II. Rechromatography on H^+ Dowex AG50W-X4 cation-exchange resin (100–200 mesh) of the isolated $Cr(en)(NH_3)(OH_2)_3{}^{3+}$ failed to give any indication of the presence of more than the one isomer. Analysis showed that no Br was present in the complex.

Other Chemicals.—All other chemicals used have been previously described.[8]

Analytical Methods.—Near-ultraviolet and visible absorption spectra were obtained with a Cary Model 15 recording spectrophotometer and matched 10-cm silica cells. The methods used for Cr and Br analysis have been given earlier.[2]

Kinetic Runs.—Solutions of the complexes were adjusted to the desired $HClO_4$ and $NaClO_4$ concentrations and rapidly warmed to approximately the desired reaction temperature. These reaction solutions were then quickly transferred to a 10.00-cm silica cell which was placed in the spectrophotometer cell compartment thermostated to ±0.02° (at 20–45°) or ±0.07° (at 50–60°). Scans of the reaction solution were made (700–320 nm) at convenient time intervals, with water in the reference cell. In most cases the reaction was followed to at least 1 half-life, with a few of the slower reactions followed to only 30% reaction.

Aquation rates of the bromo complexes were also followed by measuring the rate of Br^- release, using a procedure described earlier.[4]

Results

For the spectrophotometric determination of the rates wavelengths were chosen at which the absorbance decrease with time was optimum. The reaction half-life, $t_{1/2}$, was found by plotting log $(1 - f)$ *vs.* reaction time t and reading $t_{1/2}$ at $1 - f = 0.5$. The fraction of reaction, f, is defined by the relation

$$f = (A_0 - A)/(A_0 - A_\infty) \qquad (1)$$

where A_0, A, and A_∞ are the optical absorbances (at a given wavelength) at reaction time zero, at time t, and at 100% reaction, respectively. The rate plots gave good linearity to at least 1 half-life, with standard deviations of random errors being much less than that for the major source of error, the uncertainty in A_∞. The A_∞ values were calculated from spectra of the chromatographically isolated products of the various aquation steps and showed deviations of as much as ±10%, probably due to small amounts of impurities and errors in the Cr analyses. Trial calculations showed, however, that the standard deviation in the rate constant is approximately half that found for A_∞. The first-order rate constants, k_n, were found from

$$k_n(\text{sec}^{-1}) = (0.693/60)/t_{1/2}(\text{min}) \qquad (2)$$

where k_n is defined by

$$-\mathrm{d}C_n/\mathrm{d}t = k_nC_n \qquad (3)$$

C_n being the molar concentration of the unaquated parent complex in the nth aquation step.

As shown later, the rate constants at 52.5° for aquation of magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and its product, pink $Cr(en)(NH_3)(OH_2)_3{}^{3+}$, are in a ratio of *ca.* 2:1 (the ratio is larger at lower temperatures used), and normally a consecutive first-order kinetics treatment would be necessary. However, by analyzing the rate data for aquation of the monobromo complex at 410 nm, where the absorbance change is large and the molar absorptivities of $Cr(en)(NH_3)(OH_2)_3{}^{3+}$ and $Cr(en)(OH_2)_4{}^{3+}$ are nearly the same (19.5 and 17.5 M^{-1} cm^{-1}, respectively; see Figure 1), a simple first-order kinetics analysis can be made with errors smaller than the experimental errors, at least up to one reaction half-time (as far as reaction was followed experimentally).

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[2] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

[3] S. H. Caldwell and D. A. House, *ibid.*, **8**, 151 (1969).

[4] R. G. Hughes and C. S. Garner, *ibid.*, **7**, 1988 (1968).

[5] D. A. House, *Australian J. Chem.*, **22**, 647 (1969).

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

[7] R. G. Hughes and C. S. Garner, *ibid.*, **7**, 74, 2678 (errata) (1968).

[8] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *ibid.*, **6**, 1524, 2273 (errata) (1967); **7**, 2678 (errata) (1968).

Under these conditions, taking A_∞ as that for $Cr(en)(NH_3)(OH_2)_3^{3+}$ alone produces a *maximum* error of only 1.5% in A_∞ and *ca.* 0.8% in $k_{2,\mathrm{obsd}}$. At 590 nm (one determination only) the maximum error increases to 7% in A_∞ and *ca.* 4% in $k_{2,\mathrm{obsd}}$. Inasmuch as uncertainties in A_∞ of chromatographically isolated $Cr(en)(NH_3)(OH_2)_3^{3+}$ exceed the above maximum errors in A_∞ arising from neglect of $Cr(en)(NH_3)(OH_2)_3^{3+}$ aquation, the use of the more complicated consecutive first-order analysis is unwarranted. There is negligible kinetic overlap in the other successive aquations studied.

For the Br^--release method, k_n was found using

$$f = (V - V_0)/(V_\infty - V_0) \qquad (4)$$

where V_0, V, and V_∞ are the volumes of $AgNO_3$ titrant required for a standard aliquot of reaction solution at time zero, at time t, and for the complete release of either one ($n = 1$) or two ($n = 2$) bromo ligands, respectively. The latter was calculated from the concentration of the titrant standardized against KBr and from the analytically determined Cr concentration which was equated to the initial concentration of $Cr(en)(NH_3)(OH_2)Br_2^+$. In this case the principal source of error was the deviation from linearity in the rate plot, with the standard deviation for V_∞ being only *ca.* ±1%.

The observed first-order rate constants determined for the aquation of green $Cr(en)(NH_3)(OH_2)Br_2^+$, magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$, and pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ for various temperatures, hydrogen ion concentrations, and ionic strengths are presented in Tables I–III, respectively. Plots of molar absorptivity ϵ *vs.* wavelength for the presumed pure complexes, which were used to calculate the A_∞ values for the various aquation steps and the "theoretical" isosbestic points, and typical changes in spectra as a function of time are shown in Figures 1 and 2, respectively.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF GREEN $Cr(en)(NH_3)(OH_2)Br_2^+$ IN THE DARK[a]

Method[b]	Temp, °C	$[HClO_4]$, F	C_0, mF	μ, M[c]	10^4k_1, sec^{-1} [d]
Sp	19.98	0.30	1.98	0.30	2.06 ± 0.10
Sp	19.98	0.30	3.26	0.30	2.16 ± 0.11
Sp[e]	19.98	2.0	6.22	2.0	1.77 ± 0.09
Sp	19.98	2.0	6.22	2.0	1.62 ± 0.08
Sp	19.98	2.0	4.05	2.0	1.59 ± 0.08
Sp	19.98	0.30	5.34	2.0	1.54 ± 0.08
Sp	19.98	0.30	1.70	2.0	1.64 ± 0.08
Sp	19.98	0.10	3.94	2.0	1.75 ± 0.09
Sp	19.98	0.10	2.35	2.0	1.70 ± 0.09
Br^-	21.00	0.30	3.25	0.30	2.36 ± 0.08
Sp	25.78	0.30	4.78	0.30	4.23 ± 0.20
Sp	30.16	0.30	2.85	0.30	7.22 ± 0.25
Br^-	31.42	0.30	3.24	0.30	7.60 ± 0.20
Sp	35.16	0.30	2.58	0.30	12.4 ± 0.5

[a] Exposed to spectrophotometric light beam during scans, except for Br^--release method. [b] Sp, spectrophotometric determination at 630 nm except as noted; Br^-, titration of released Br^-. [c] Ionic strength, controlled with $NaClO_4$. [d] Errors are standard deviations arising from the major source of error (*ca.* ±9% uncertainties in A_∞ for the spectral determinations). [e] At 390 nm.

TABLE II

OBSERVED FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF MAGENTA $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ IN THE DARK[a]

Method[b]	Temp, °C	$[HClO_4]$, F	C_0, mF	μ, M[c]	$10^5k_{2,\mathrm{obsd}}$, sec^{-1} [d]
Sp	33.60	1.0	2.94	1.0	1.26 ± 0.05
Sp	33.60	0.50	3.00	1.0	1.39 ± 0.06
Sp	33.60	0.30	3.02	1.0	1.52 ± 0.06
Sp	33.58	0.15	2.94	1.0	1.85 ± 0.07
Sp	33.82	0.30	5.44	0.30	1.89 ± 0.08
Sp	44.00	1.0	2.56	1.0	4.66 ± 0.18
Sp	44.00	0.50	2.46	1.0	4.91 ± 0.20
Sp	44.00	0.30	2.46	1.0	5.31 ± 0.22
Sp	44.00	0.15	2.44	1.0	6.48 ± 0.26
Sp	52.50	1.0	2.48	1.0	12.2 ± 0.5
Sp[e]	52.50	1.0	2.48	1.0	12.5 ± 0.5
Br^-	52.50	1.0	4.36	1.0	12.0 ± 0.3
Sp	52.48	0.50	2.50	1.0	13.5 ± 0.5
Sp	52.48	0.30	2.49	1.0	15.8 ± 0.6
Br^-	52.50	0.30	4.36	1.0	16.7 ± 0.3

[a–d] Same as footnotes *a–d*, Table I, except the wavelength is 410 nm and there is *ca.* ±7% uncertainty in A_∞. [e] At 590 nm.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF PINK $Cr(en)(NH_3)(OH_2)_3^{3+}$ IN THE DARK[a,b]

Temp, °C	$[HClO_4]$, F	C_0, mF	μ, M[c]	10^5k_3, sec^{-1} [d]
44.90	3.0	3.82	3.0	1.00 ± 0.07
52.50	0.30	4.06	0.30	8.69 ± 0.62
52.50	1.0	2.68	1.0	6.00 ± 0.42
52.50	0.30	2.66	1.0	5.53 ± 0.39
52.45	0.15	2.68	1.0	5.60 ± 0.39
52.45	3.0	2.70	3.0	4.43 ± 0.31
52.45	3.0	2.70	3.0	4.20 ± 0.29[e]
52.50	0.30	4.06	3.0	4.62 ± 0.32
60.40	3.0	3.72	3.0	13.3 ± 0.9

[a–d] Same as footnotes *a–d*, Table I, except the wavelength is 470 nm and there is *ca.* ±10% uncertainty in A_∞. [e] At 370 nm.

Discussion

Aquation and Configuration of Green $Cr(en)(NH_3)(OH_2)Br_2^+$.—Figure 1 shows the isosbestic points predicted for the aquation of the green isomer of $Cr(en)(NH_3)(OH_2)Br_2^+$ to magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ as the only Cr product. From a number of measurements on the chromatographically purified complexes these points were found to be 578 ± 3 (ϵ 24.0 ± 0.5), 484 ± 3 (ϵ 32.0 ± 0.2), 430 ± 2 (ϵ 30.0 ± 0.4), and 349 ± 2 nm (ϵ 8.5 ± 0.6). Experimentally, four well-defined isosbestic points were observed for as much as 2 half-lives, as shown in Figure 2, the average values found being 577 ± 1 (ϵ 23.5 ± 0.5), 482 ± 2 (ϵ 32.5 ± 0.7), 429 ± 1 (ϵ 30.6 ± 1.0), and 350 ± 1 nm (ϵ 9.8 ± 0.6) in good agreement with the above values predicted for the reaction

$$\text{green } Cr(en)(NH_3)(OH_2)Br_2^+ + H_2O \xrightarrow{k_1} \text{magenta } Cr(en)(NH_3)(OH_2)_2Br^{2+} + Br^- \qquad (5)$$

The agreement between observed and predicted isosbestic points and the fact that the Br^--release rates fall on the Arrhenius plot for the spectral rates within experimental error indicate that reactions involving the breaking of a Cr–N bond do not contribute significantly

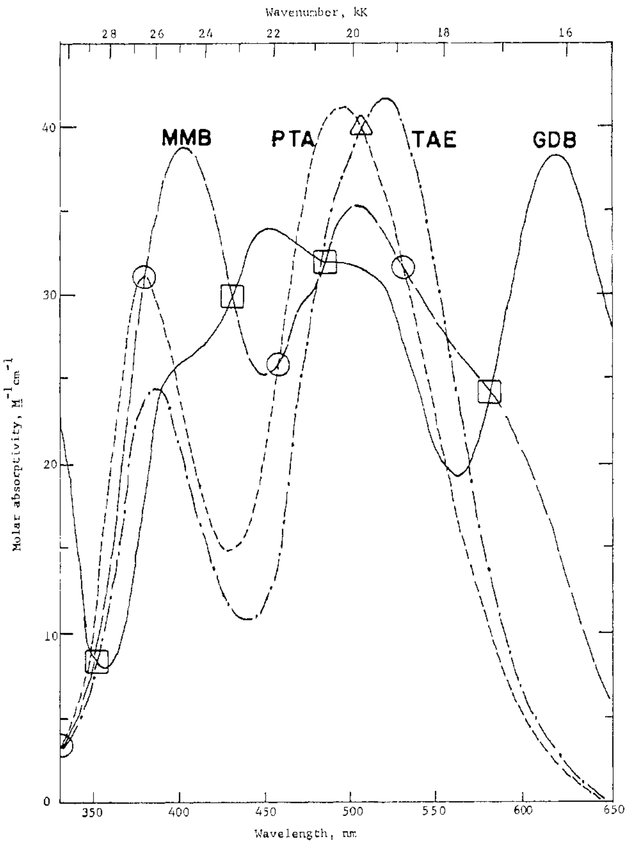

Figure 1.—Visible absorption spectra of some chromatographically isolated chromium(III)–ethylenediamine complexes at 20–25°: GDB, green isomer of $Cr(en)(NH_3)(OH_2)Br_2^+$ in 0.3 *F* $HClO_4$; MMB, magenta isomer of $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ in 1.5 *F* $HClO_4$; PTA, pink isomer II of $Cr(en)(NH_3)(OH_2)_3^{3+}$ in 3 *F* $HClO_4$; TAE, $Cr(en)(OH_2)_4^{3+}$ in 3 *F* $HClO_4$; the molar absorptivity or molar extinction coefficient ϵ is defined by the relation $\log (I_0/I) = A = \epsilon cl$, where *c* is the molarity of the absorbing complex and *l* is the optical path in centimeters.

to the measured aquation rates. The possibility does exist, however, that the rate-controlling step in the aquation is the isomerization of the dibromo complex, followed by the aquation of the newly formed isomer with a rate constant much larger than k_1. This path seems unlikely, however, since the related $Cr(en)(OH_2)_2Cl_2^+$ and $Cr(en)(OH_2)_3Cl^{2+}$ isomers isomerize too slowly to account for the observed aquation rates in that system,[8] and indeed most chromium(III)–amine complexes appear to aquate faster than they isomerize in aqueous solution.

Table I shows that the rate of aquation of green $Cr(en)(NH_3)(OH_2)Br_2^+$ is independent of acid concentration within experimental error for 0.1–2 *F* $HClO_4$ ($\mu = 2$ *M*). A sevenfold increase in ionic strength from 0.3 to 2 *M* decreases the rate constant by *ca.* 25%. This effect is similar to that found for $Cr(en)(OH_2)_2Br_2^+$ [4] and is small enough to be attributed to a specific salt effect. In 0.1–0.3 *F* $HClO_4$ at ionic strength 0.3 *M* ($NaClO_4$), $k_1 = 4.1 \times 10^{-4}$ sec^{-1} at 25°.

Using the k_1 values in Table I a linear Arrhenius plot was obtained. Least-squares activation parameters are $E_a = 20.7 \pm 0.3$ kcal mol^{-1}, $\log PZ(\text{sec}^{-1}) = 11.81 \pm 0.23$, and $\Delta S^*_{298} = -7 \pm 1$ cal deg^{-1} mol^{-1}.

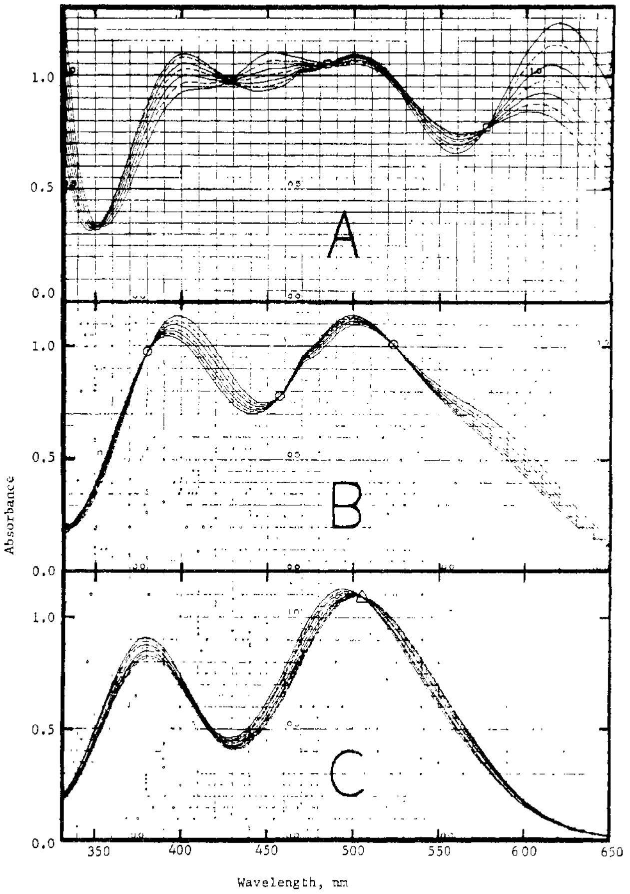

Figure 2.—Change in absorption spectra during hydrolysis: A, green $Cr(en)(NH_3)(OH_2)Br_2^+$ (C_0 = 3.26 m*F*) in 0.3 *F* $HClO_4$ (μ = 0.3 *M*) at 19.98°; reading downward at 630 nm, reaction time is 0, 10, 20, 30, 40, 50, and 60 min; B, magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ (C_0 = 3.02 m*F*) in 0.3 *F* $HClO_4$ (μ = 1 *M*) at 33.60°; reading downward at 400 nm, reaction time is 0, 60, 120, 140, 240, 300, and 360 min; C, pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ (isomer II?, C_0 = 2.70 m*F*) in 3 *F* $HClO_4$ (μ = 3 *M*) at 52.45°; reading downward at 380 nm, reaction time is 40, 80, 120, 160, 200, 240, and 280 min; alternate curves are dashed for convenience in reading.

Table IV compares the aquation rate parameters of green $Cr(en)(NH_3)(OH_2)Br_2^+$ with those found for related dibromo complexes. Earlier tentative assignments of a *trans*-dibromo configuration for green $Cr(en)(NH_3)(OH_2)Br_2^+$ and the three complexes below it in Table IV were based mainly upon splitting of the d–d absorption bands[7] and on indications that the general method of synthesis of these and related dihalo complexes (namely, treatment of the diperoxoaminechromium(IV) complexes with hydrobromic or hydrochloric acid) gives the *trans*-dihalo product,[3] as has been confirmed for blue $Cr(en)(OH_2)_2Cl_2^+$ by X-ray crystallography.[9] In view of the *k* values for *cis*- and *trans*-$Cr(en)_2Br_2^+$, it is apparent that the *k* value for green $Cr(en)(NH_3)(OH_2)Br_2^+$ is too low for a *cis*-dibromo configuration, thus strongly supporting the earlier *trans*-dibromo assignment. It is well known for Co(III) complexes of this general type that aquation rates increase as one nonleaving ligand is changed from ethylenediamine to NH_3 to H_2O providing the diacido ligands

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(9) R. Stomberg and I. Larking, private communication *via* Dr. D. A. House.

TABLE IV

AQUATION RATE PARAMETERS OF SOME DIBROMOCHROMIUM(III)-AMINE COMPLEXES AT 25°

Complex	Medium	10^4k, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
cis-$Cr(en)_2Br_2^+$ [a]	0.1 *F* $HClO_4$	28	...	...
trans-$Cr(en)_2Br_2^+$ [b]	0.1 *F* HNO_3	3.3	22.4	−1
Green $Cr(en)(NH_3)(OH_2)Br_2^+$ [c]	0.3 *F* $HClO_4$	4.1	20.7	−7
Green-blue $Cr(en)(OH_2)_2Br_2^+$ [d] (*trans*-dibromo?)	0.6 *F* $HClO_4$	5.1	19.8	−9
Green $Cr(NH_3)_3(OH_2)Br_2^+$ [e] (*trans*-dibromo?)	0.3 *F* $HClO_4$	8	...	...
Green $Cr(NH_3)_2(OH_2)_2Br_2^+$ [f] (*trans*-dibromo-*trans*-diaquo?)	0.6 *F* $HClO_4$	10.2	...	...

[a] Reference 2. [b] A. M. Weiner and J. A. McLean, Jr., *Inorg. Chem.*, **3,** 1469 (1964). [c] This research. [d] Reference 4. [e] Reference 3. Reference 5.

are either *trans* to each other in all complexes compared or *cis* to each other. If one assumes that the last five complexes of Table IV all have a *trans*-dibromo configuration, then the observed systematic increase in k (and decrease in E_a and ΔS^*) is expected from the similarity in aquation behavior of Cr(III) and Co(III) substrates.

Aquation and Configuration of Magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$.—The spectra of the presumed pure magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and its aquation product, pink $Cr(en)(NH_3)(OH_2)_3^{3+}$, shown in Figure 1, predict four isosbestic points at 525 ± 3 (ϵ 32.4 ± 0.9), 457 ± 3 (ϵ 25.4 ± 1.0), 378 ± 2 (ϵ 31.0 ± 0.7), and 325 ± 8 nm (ϵ 4 ± 1) if the aquation of the bromo complex has no other products in spectrophotometrically detectable amounts. Experimentally, four isosbestic points were observed at 527 ± 4 (ϵ 32.0 ± 1.2), 458 ± 2 (ϵ 26.0 ± 0.5), 380 ± 3 (ϵ 31.7 ± 0.6), and 330 ± 1 nm (ϵ 5.2 ± 0.8) in agreement with those predicted for the reaction

$$\text{magenta } Cr(en)(NH_3)(OH_2)_2Br^{2+} + H_2O \xrightarrow{k_2} \text{pink } Cr(en)(NH_3)(OH_2)_3^{3+} + Br^- \quad (6)$$

The isosbestic points were well defined, as shown in Figure 2, but began to shift after *ca.* 1 half-life due to kinetic overlap from aquation of the product, $Cr(en)(NH_3)(OH_2)_3^{3+}$, to $Cr(en)(OH_2)_4^{3+}$. The appearance of isosbestic points in this second aquation step gives some evidence that the aquation of $Cr(en)(NH_3)(OH_2)Br_2^+$ produces only one isomer, although it is possible to rationalize the points by assuming constant ratios for successive rates of aquation for two different isomers forming an isomeric mixture of the aquated product, $Cr(en)(NH_3)(OH_2)_3^{3+}$ (chromatography failed to reveal an isomeric mixture, however). Agreement of $k_{2,\text{obsd}}$ values obtained by spectrophotometry and by Br^- release, together with the isosbestic point behavior, shows that Cr–N bond rupture does not significantly contribute to the observed aquation reaction. As is true for $Cr(en)(NH_3)(OH_2)Br_2^+$ aquation, the possibility of a preisomerization path cannot be excluded.

Table II shows that $k_{2,\text{obsd}}$ is dependent on both the H^+ concentration and ionic strength. A threefold increase in ionic strength from 0.3 to 1 *M* decreases the observed rate by only *ca.* 20%. The plots in Figure 3 show that in 0.15–1.0 *F* $HClO_4$ (μ = 1 *M*) and at 33.6–52.5° the observed rate constant obeys the relation (7).

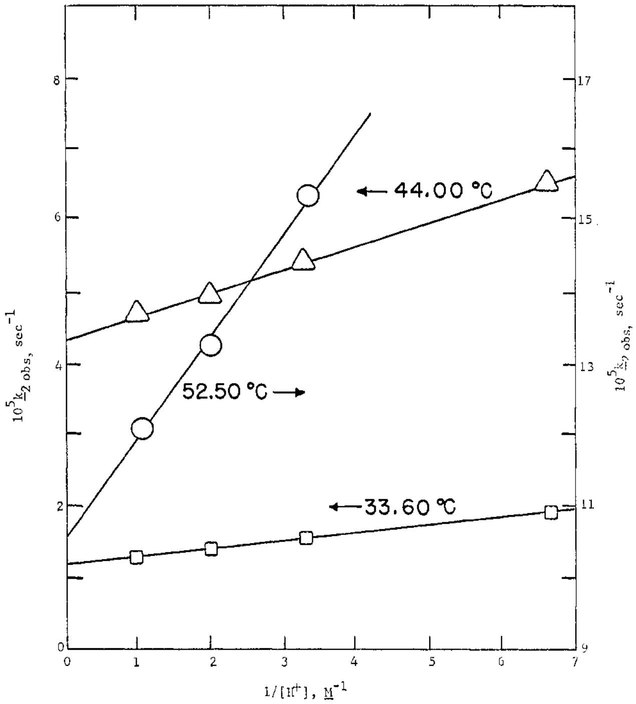

Figure 3.—Hydrogen ion dependence of hydrolysis rate of magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ at μ = 1.0 *M*.

$$k_{2,\text{obsd}} = k_2 + (k_2'/[H^+]) \quad (7)$$

This behavior is similar to that observed for the aquation of magenta $Cr(en)(OH_2)_3Br^{2+}$ [4] and may be rationalized in terms of eq 6 (acid independent) and an acid-dependent path, both of which contribute to the overall rate. The acid-dependent path may correspond to the reactions

$$\text{magenta } Cr(en)(NH_3)(OH_2)_2Br^{2+} + OH^- \xrightarrow{k_{2b}} Cr(en)(NH_3)(OH_2)_2OH^{2+} + Br^- \quad (8a)$$

$$Cr(en)(NH_3)(OH_2)_2OH^{2+} + H^+ \longrightarrow \text{pink } Cr(en)(NH_3)(OH_2)_3^{3+} \quad \text{(fast)} \quad (8b)$$

where $k_2'/[H^+] = (k_2'/K_w)[OH^-] = k_{2b}[OH^-]$ (K_w = ion-product constant for water) and/or

$$\text{magenta } Cr(en)(NH_3)(OH_2)_2Br^{2+} \underset{}{\overset{K_a}{\rightleftharpoons}} Cr(en)(NH_3)(OH_2)(OH)Br^+ + H^+ \quad \text{(fast equilibrium, far to left)} \quad (9a)$$

$$Cr(en)(NH_3)(OH_2)(OH)Br^+ + H_2O \xrightarrow{k_{2h}} Cr(en)(NH_3)(OH_2)_2OH^{2+} + Br^- \quad (9b)$$

reaction 8b

TABLE V

RATE CONSTANTS FOR HYDROLYSIS OF MAGENTA $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ (μ = 1.0 M)

Temp, °C	10^5k_2, sec^{-1}	$10^6k_2'$, M sec^{-1}	$10^{-8}k_{2b}$, M^{-1} sec^{-1} [a]	k_{2h}, sec^{-1} [b]
33.60	1.16 ± 0.07	1.05 ± 0.15	~0.7	~0.01
44.00	4.30 ± 0.3	3.2 ± 0.4	~0.8	~0.03
52.50	10.5 ± 0.7	15.5 ± 0.9	~3	~0.2

[a] Assuming that the $[H^+]$-dependent term arises wholly from eq 8 and that K_w has the same values as in pure water. [b] Assuming the $[H^+]$-dependent term arises wholly from eq 9 and estimating K_a as $\sim 10^{-4}$ at 34–53° (see text).

TABLE VI

AQUATION RATE PARAMETERS OF SOME MONOBROMOCHROMIUM(III)-AMINE COMPLEXES AT 25°[a]

Complex	Medium	10^6k, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
cis-$Cr(en)_2(OH_2)Br^{2+}$ [b]	0.06–0.14 F $HClO_4$	180	. . .	. . .
trans-$Cr(en)_2(OH_2)Br^{2+}$ [b]	1.4 F HNO_3	3.0	. . .	. . .
Magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ [c]	0.05–1 F $HClO_4$	4	23.2	−7
Magenta $Cr(en)(OH_2)_3Br^{2+}$ [d] (2,3,6-triaquo?)	0.02–3 F $HClO_4$	3	22.0	−7
Magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ [e] (1-bromo-2,6-diaquo?)	0.6 F $HClO_4$	~10[f]	. . .	. . .
Blue $Cr(NH_3)_2(OH_2)_3Br^{2+}$ [g] (1-bromo-2,4,6-triaquo?)	2 F $HClO_4$?	~10[f]	. . .	. . .

[a] Acid-independent Br^- release only. [b] Reference 2. [c] This research. [d] Reference 4. [e] Reference 3. [f] Single rough measurement at room temperature. [g] Reference 5.

for which $k_2'/[H^+] = k_{2h}K_a/[H^+]$ (K_a = first acid dissociation constant of magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$; from values for some other Cr(III) aquoamine complexes at 25°,[10] we estimate roughly that K_a is *ca.* 10^{-4} at 34–53°). Table V presents the rate constants k_2 and k_2', resolved by finding the slopes and the zero intercepts of the plots in Figure 3, along with calculated values for k_{2b} and k_{2h}. The values calculated for k_{2b} are abnormally high for a Cr(III) complex and it appears that the acid-dependent process is more likely related to aquation of $Cr(en)(NH_3)(OH_2)(OH)Br^+$. This hydroxo species would not have been detected spectrophotometrically here, since for $pK_a \geqslant 4$ less than 1% of this complex would be present.

An Arrhenius plot for the values of k_2 is linear and a least-squares calculation gives $E_a = 23.2 \pm 0.1$ kcal mol^{-1}, $\log PZ(\text{sec}^{-1}) = 11.57 \pm 0.09$, and $\Delta S^*_{298} = -7 \pm 1$ cal deg^{-1} mol^{-1}. An Arrhenius plot for the k_2' values is curved, suggesting the possible presence of two or more competing paths each inverse first order in hydrogen ion. Since the curvature is not large, the major acid-dependent path still appears to be that of reactions 9a and 9b. Since K_a has only been estimated, no attempt was made to calculate activation parameters for k_{2h}.

A comparison of the rate parameters for the aquation of magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ with those of analogous monobromo complexes is made in Table VI. Lack of complete and accurate data prevents a quantitative examination of the relative rate parameters, but qualitatively the values are compatible with the same kind of trends shown in Table IV for the dibromo complexes, which aquate at 25° with *ca.* 100 times the rates for the corresponding monobromo complexes. The much larger k for *cis*-$Cr(en)_2(OH_2)Br^{2+}$ strongly suggests that magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ has a *trans*-bromoaquo configuration, as would be expected if our assignment of a *trans*-dibromo configuration for green $Cr(en)(NH_3)(OH_2)Br^{2+}$ is correct and if the dibromo complex aquates with retention of configuration. A comparison of the visible absorption spectra for magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and magenta (1-bromo-2,6-diaquo?) $Cr(NH_3)_3(OH_2)_2Br^{2+}$ [3] shows bands at approximately the same wavelengths, which further supports this assignment.

Aquation and Configuration of Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$.—The spectra of Figure 1 predict only one isosbestic point, at 507 ± 3 nm (ϵ 40 ± 1), for the reaction

$$\text{pink } Cr(en)(NH_3)(OH_2)_3^{3+} + H_2O \xrightarrow{k_3} Cr(en)(OH_2)_4^{3+} + NH_3 \quad (10)$$

with the NH_3 rapidly converting to NH_4^+ in the acid medium. Experimentally, a single isosbestic point is found (Figure 2), at 507 ± 2 nm (ϵ 40.4 ± 0.4), in good agreement.

The results shown in Table III indicate a first-order rate law for loss of NH_3 *via* reaction 10, with $k_3 = (5.7 \pm 0.4) \times 10^{-5}$ sec^{-1} at 52.5° in 0.15–1 F $HClO_4$ (μ = 1.0 M, $NaClO_4$). The absence of an acid-dependent term in the rate law might be considered surprising in view of an acid-dependent term in aquation of magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$, since K_a would be expected on the basis of charge alone to be greater for the 3+ substrate than for the 2+ substrate. The explanation may be that the presence of a hydroxo ligand, known to labilize loss of bromo and other acido ligands, may not labilize loss of ligand NH_3. Such behavior is suggested by the rate constants at 40° for loss of NH_3 in aquation of $Cr(NH_3)_5OH_2^{3+}$ in 0.1 F HNO_3 (μ = 0.4 M, KNO_3) and $Cr(NH_3)_5OH^{2+}$ in 0.1 F NaOH (μ = 0.4 M, KNO_3), namely, 3×10^{-5} and 1×10^{-5} sec^{-1}, respectively.[11,12]

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[10] See, *e.g.*, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 32.

[11] J. Bjerrum and E. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 313 (1958).

[12] E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

The ionic strength dependence for aquation of the triaquo complex is considerably larger than for the first two aquation steps. Here a threefold increase in ionic strength from 0.3 to 1 *M* decreases the rate by *ca.* 40% while similar increases in ionic strength give rate decreases of less than 20% for the previous aquation steps, an effect possibly associated with greater ion pairing of the 3+ substrate. From the temperature dependence of k_3 a linear Arrhenius plot was obtained, with least-square activation parameters $E_a = 27.5 \pm 0.3$ kcal mol^{-1}, log $PZ(\text{sec}^{-1}) = 14.08 \pm 0.17$, and $\Delta S^*_{298} = 4 \pm 1$ cal deg^{-1} mol^{-1}.

The aquation rate parameters of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ are compared in Table VII with those for the remaining two aquation steps to $Cr(OH_2)_6^{3+}$; in all three aquations Cr–N bonds are ruptured. The activation energies are very similar and substantially different from those for the two preceding steps in which Cr–Br bonds are ruptured. For these aquations involving Cr–N bond rupture, rate differences are chiefly due to differences in ΔS^*.

TABLE VII

RATE PARAMETERS FOR THE AQUATION STEPS FROM PINK $Cr(en)(NH_3)(OH_2)_3^{3+}$ TO $Cr(OH_2)_6^{3+}$ IN 3 *F* $HClO_4$ AT 60°

Substrate	10^6k, sec^{-1}	E_a, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ [a]	133	27.5 ± 0.3	$+3 \pm 1$
$Cr(en)(OH_2)_4^{3+}$ [b]	3.0	27.7 ± 1.5	-3 ± 5
$Cr(enH)(OH_2)_5^{4+}$ [b]	1.9	25.4 ± 2.3	-11 ± 7

[a] This research. [b] Reference 6.

The evidence for the geometric configuration of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ is ambiguous. Assuming the correctness of our configuration assignments for the dibromo and monobromo complexes, we would expect the 1,2,6-triaquo complex to be the aquation product of the monobromo complex if there is configuration retention without isomerization. Comparison of the visible absorption bands of pink $Cr(en)(NH_3)(OH_2)_3^{3+}$, namely, 378 ($\epsilon$ 31) and 496 nm (ϵ 41.0), with those[13] of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$, namely, 375 (ϵ 33) and 510 nm (ϵ 66), and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$, namely, 391 (ϵ 45) and 495 nm (ϵ 90), favors a 1,2,6 assignment if based on the wavelength of the lower energy band but a 1,2,3 assignment if based on the intensity of that band and the wavelength and intensity of the higher energy band. Attempts to make a further comparison with the spectra of 1,2,3- and 1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$ [3,7] are rendered difficult by the uncertain configuration assignments of the triammine complexes and the fact that their spectra resemble that of 1,2,3-$Cr(dien)(OH_2)_3^{3+}$ more than that of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$. In the absence of positive isolation of the second possible geometric isomer of $Cr(en)(NH_3)(OH_2)_3^{3+}$, we regard the above spectral comparison as ambiguous and prefer to make no configurational assignment for pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ at this time.

The successive steps in the aquation of green $Cr(en)(NH_3)(OH_2)Br_2^+$ to $Cr(OH_2)_6^{3+}$ have been shown to be progressively slower, in line with successive aquations of similar bromo- and chlorochromium(III)–amine complexes. The green dibromo complex, which has been confirmed to have a *trans*-dibromo configuration, aquates to magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ without stereochemical change, in agreement with the related *trans*-dibromo isomers of $Cr(en)(OH_2)_2Br_2^+$ [4] and $Cr(NH_3)_3(OH_2)Br_2^+$ [3] and the *trans*-dichloro isomers of $Cr(en)(OH_2)_2Cl_2^+$ [3] and $Cr(NH_3)_3(OH_2)Cl_2^+$ [3] and their aquation.

[13] Unpublished research of D. K. Lin and C. S. Garner, cited by R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, *Inorg. Chem.*, **7**, 882 (1968).

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Complexes of Molybdenum(V) and Tungsten(V). Far-Infrared Spectra and Some Other Properties

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The far-infrared spectra of tetraalkylammonium complexes of $M(OR)Cl_5^-$ and $M(OR)_2X_4^-$ and of the dimeric species $[W(OR)_2Cl_3]_2$ and $[W(OR)_3Cl_2]_2$ (M = W or Mo; X = Cl or Br; R = CH_3, C_2H_5, or C_3H_7) were recorded in the range 80–650 cm^{-1}. The M–OR stretch has been assigned and several trends which depend on the nature of the alkoxide, halide, and metal are reported. In addition, the preparation and properties of $[(C_2H_5)_4N]M(OR)_2X_4$ (M = W or Mo; X = Cl or Br; R = CH_3 or C_2H_5), $[(C_3H_7)_4N]MoOCl_4$, and $[(C_4H_9)_4N]MoOCl_4$ are given.

The far-infrared spectra of a large number of metal hexahalo complexes have been reported,[1-3] and the work has been extended to mixed hexahalo complexes of the type $MX_4Y_2^{2-}$ (M = Ti or Sn; X = Cl, Br, or I).[4] Other workers have studied the vibrations of oxohalo complexes Nb(V), Mo(V), and W(V).[5] Detailed in-

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[1] R. J. H. Clark, *Spectrochim. Acta*, **21**, 955 (1965), and references therein.

[2] S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. H. Horner, F. N. Collier, and S. Y. Tyree, Jr., *Inorg. Chem.*, **7**, 1859 (1968).

[3] J. E. D. Davies and D. A. Long, *J. Chem. Soc.*, *A*, 2560 (1968).

[4] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968).

[5] A. Sabatini and I. Bertini, *ibid.*, **5**, 204 (1966).