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The Use of Chromium(IV) Diperoxoamines in the Synthesis of Chromium(III)–Amine Complexes. V. The Hydrolysis Products of the Dichloro- and Dibromoaquotriamminechromium(III) Cations[1]

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The reaction between $Cr(NH_3)_3(O_2)_2$ and 12 *F* HCl, originally thought to produce two forms (violet and green) of $[Cr(NH_3)_3(OH_2)Cl_2]Cl$, has been reinvestigated. The green form is shown by X-ray powder diffraction to be a mixture of the violet form and green $Cr(NH_3)_3Cl_3$. The diperoxide also reacts with 63% HBr to give a mixture of green $[Cr(NH_3)_3(OH_2)Br_2]Br$ and violet $[Cr(NH_3)_3(OH_2)_2Br]Br_2$. On the basis of hydrolysis rates, visible absorption spectra, and ion-exchange properties, the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ and green $Cr(NH_3)_3(OH_2)Br_2^+$ cations are assigned a *trans*-dihalo-*trans*-triammine structure. Using ion-exchange chromatography, the magenta *trans*-haloaquo-*trans*-triammine $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ and $Cr(NH_3)_3(OH_2)_2Br^{2+}$ cations have been isolated and characterized in solution. The final hydrolysis product from these halo ions is the *trans*-$Cr(NH_3)_3(OH_2)_3^{3+}$ ion. Visible absorption spectra are presented for these cations.

The reaction between $Cr(NH_3)_3(O_2)_2$ and 12 *F* HCl was first investigated by Werner,[2,3] who obtained three products, *viz.*, violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$, green $[Cr(NH_3)_3(OH_2)Cl_2]Cl$, and green $Cr(NH_3)_3Cl_3$. These compounds were later reinvestigated by Riesenfeld and Seemann,[4] who, in addition to the above violet and green forms, reported a third deep green $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ isomer. This latter form could not be reproduced by Bhatnagar, *et al.*,[5] and repeated attempts to prepare this modification in these laboratories have failed. The synthesis of the violet and green forms of $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ has subsequently been described elsewhere.[6,7]

We have repeated these syntheses and, despite satisfactory analyses reported in the original literature,[2,4,5] find from X-ray powder diffraction that the green form is a mixture of violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ and $Cr(NH_3)_3Cl_3$.

Violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ (or the green $Cr(NH_3)_3Cl_3$–$[Cr(NH_3)_3(OH_2)Cl_2]Cl$ mixture) dissolves in dilute $HClO_4$ solution to give the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation which has been isolated using ion-exchange chromatography and characterized in solution by Cr:Cl:N ratios. It hydrolyzes in acid solution to the magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cation which has also been characterized by absorption spectra and Cr:Cl ratios. Subsequent hydrolysis to the pink $Cr(NH_3)_3(OH_2)_3^{3+}$ ion is slow.

The green $Cr(NH_3)_3(OH_2)Br_2^+$ and magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ cations have been similarly isolated and characterized in solution. The monobromotriammine hydrolyzes to the same triaquotriammine as the monochlorotriammine.

Experimental Section

Materials.—All chemicals used were of reagent grade quality. The ion-exchange material used was Zeo Karb 225 cation-exchange resin in the H^+ form (14–52 mesh) in a 10 × 1 cm column cooled by a jacket of circulating tap water. Perchloric acid solutions were prepared by diluting 60% $HClO_4$ with chloride-free distilled water.

Diperoxotriamminechromium(IV).—This was prepared by the method of Werner[2] by adding moist $Cr(py)O(O_2)_2$ to 15 *F* NH_3 solution. Care must be taken as this pyridine complex is explosive when dry.[8]

Trichlorotriamminechromium(III).—This was prepared by the method of Schlessinger,[7] which involves the dehydration of violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ or the green $Cr(NH_3)_3Cl_3$–$[Cr(NH_3)_3(OH_2)Cl_2]Cl$ mixture at 150°. The product was washed well with cold water to remove small quantities of a green, deamminated decomposition product.

Blue Dichloroaquotriamminechromium(III) Cation.—Violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ and the green $[Cr(NH_3)_3(OH_2)Cl_2]Cl$–$Cr(NH_3)_3Cl_3$ mixture were prepared as impure solids according to Schlessinger,[7] by allowing $Cr(NH_3)_3(O_2)_2$, in cold glacial acetic acid, to react with 12 *F* HCl. The green mixture was also made directly by adding the diperoxide in small portions to cooled 12 *F* HCl.[2,3,6] Yields were in the 70–80% range.

The blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation was obtained by suspending *ca.* 150 mg of violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ (or the green dichloro–trichloro mixture) in 0.05 *F* $HClO_4$ in a filter funnel above a cation-exchange column prewashed with 1 *F* and then 0.05 *F* $HClO_4$. A blue band formed at the top of the resin column as the reactant solution flowed through the filter paper. Unreacted green $Cr(NH_3)_3Cl_3$ remained in the paper when the dichloro–trichloro mixture was used. The column was washed with 150 ml of 0.05 *F* $HClO_4$ to remove free chloride ion and any dissolved $Cr(NH_3)_3Cl_3$ in solution and the blue band was eluted with 0.6 *F* $HClO_4$ into an ice-cooled 50-ml flask. The visible absorption spectrum was measured immediately and analysis of the effluent solution (*ca.* 2 m*F* in complex) gave a Cr:Cl:N ratio of 1:2.03:3.11 which is in acceptable agreement with the formula $Cr(NH_3)_3(OH_2)Cl_2^+$. The blue effluent from the green dichloro–trichloro mixture gave an identical absorption spectrum and a Cr:Cl ratio of 1:2.01.

The preparations and analyses of this and the following complex cations were repeated at least three times to check reproducibility of the absorption spectra and element ratios.

This blue cation was also obtained by suspending *ca.* 150 mg of green $Cr(NH_3)_3Cl_3$ in 30 ml of 0.05 *F* $HClO_4$ and warming the solution to 50° for 1–2 min until a noticeable blue color developed.

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[1] Part IV: R. G. Hughes and C. S. Garner, *Inorg. Chem.*, **7**, 74 (1968).

[2] A. Werner, *Ber.*, **39**, 2656 (1906).

[3] A. Werner, *ibid.*, **43**, 2286 (1910).

[4] E. H. Riesenfeld and F. Seemann, *ibid.*, **42**, 4222 (1909).

[5] S. S. Bhatnagar, B. Prakash, and A. Hamid, *J. Chem. Soc.*, 1428 (1938).

[6] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd. ed, Academic Press, New York, N. Y., 1965, p 1381.

[7] G. G. Schlessinger, "Inorganic Laboratory Preparations," Chemical Publishing Co., New York, N. Y., 1962, pp 249, 250.

[8] D. M. Adams and J. B. Raynor, *J. Chem. Educ.*, **43**, 94 (1966).

The cooled solution was filtered onto a cation-exchange column, prewashed with 1 *F* and then 0.05 *F* $HClO_4$. The blue band that formed was washed and eluted as above. The absorption spectrum was identical with that of the cation prepared above and analysis of the solution gave a Cr:Cl ratio of 1:2.00. Effective elution of this cation can also be obtained with 0.3 *F* $HClO_4$.

Magenta Chlorodiaquotriamminechromium(III) Cation.—About 150 mg of green $Cr(NH_3)_3Cl_3$, green $Cr(NH_3)_3Cl_3$–$[Cr(NH_3)_3(OH_2)Cl_2]Cl$ mixture, and violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ were suspended separately in 30 ml of 0.05 *F* $HClO_4$. The solutions were warmed to about 55° for approximately 5 min, until all of the solids had dissolved and the solutions became magenta in color. The cooled solutions were run through cation-exchange columns (prewashed with 3 and then 0.05 *F* $HClO_4$) and the columns were washed with 1 *F* $HClO_4$ to remove free chloride and any unreacted dichloro ion. The red bands that formed were eluted with 2 *F* $HClO_4$, the first 15–20 ml being discarded. The visible absorption spectra of the next 50-ml samples were measured immediately and were identical. Analyses of these solutions (*ca.* 2 m*F* in complex) gave Cr:Cl ratios of 1:1.00, 1:1.14, and 1:1.06, respectively, in agreement with the formula $Cr(NH_3)_3(OH_2)_2Cl^{2+}$.

Green Dibromoaquotriamminechromium(III) Cation.—A mixture of green $[Cr(NH_3)_3(OH_2)Br_2]Br$ and violet $[Cr(NH_3)_3(OH_2)_2Br]Br_2$ was prepared using Werner's method[2,3] by the slow addition of $Cr(NH_3)_3(O_2)_2$ (1 g) to 5.8 ml of cooled 63% HBr. The precipitated product was filtered and the mother liquor deposited a further crop of the monobromo bromide salt after 2 days. The yield of the combined dibromo and monobromo salts was about 0.5 g. Greater amounts of the green dibromo salt were obtained by suspending a powdered sample of the first precipitated product in 63% HBr for 3 days. The green solid formed in this manner was still impure.

The pure green $Cr(NH_3)_3(OH_2)Br_2^+$ cation was isolated in solution from the impure green bromide salt using conditions similar to those for the preparation of the blue $Cr(NH_3)_3(OH)_2Cl_2^+$ cation from violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$. Analysis of the green effluent solution, *ca.* 2 m*F* in complex, gave a Cr:Br ratio of 1:2.08 in agreement with the formula $Cr(NH_3)_3(OH_2)Br_2^+$.

Magenta Bromodiaquotriamminechromium(III) Cation.—This was prepared in a similar manner to the chloro analog using the impure dibromo–monobromo mixture. Analysis of the magenta effluent solution gave a Cr:Br:N ratio of 1:1.08:2.82. The formula $Cr(NH_3)_3(OH_2)_2Br^{2+}$ requires a ratio of 1:1:3.

Triaquotriamminechromium(III) Cation.—Three methods have been used to generate this cation.

(a) Solid mercury(II) acetate (200 mg) was added to 25 ml of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation (*ca.* 3 m*F* in 0.6 *F* $HClO_4$), prepared using ion-exchange chromatography, and the solution was made up to 50 ml with 0.05 *F* $HClO_4$. The visible absorption spectrum showed no change after 20 hr and repeated experiments gave identical spectra. Similar results were obtained when the magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cation was used.

(b) The blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation, prepared in solution by ion-exchange chromatography (25 ml, *ca.* 6 m*F* in 0.6 *F* $HClO_4$), was added to 12 ml of 1.5 *F* NaOH solution. The color changed to violet-pink and the solution was made up to 50 ml with 1 *F* $HClO_4$ within 2 min. The absorption spectrum of this pink solution was identical with that from the Hg^{2+} method. Similar results were obtained when the magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cation was used.

(c) The cation mixtures $Cr(NH_3)_3(OH_2)_nCl_{3-n}{}^{n+}$ and $Cr(NH_3)_3(OH_2)_nBr_{3-n}{}^{n+}$, prepared by warming the impure solids in 0.05 *F* HCO_4, were charged on separate ion-exchange columns, prewashed with 0.05 *F* $HClO_4$. The resulting purple bands were washed with distilled water until the effluents had a pH above 6. The columns were then eluted with 0.2 *F* NaOH into 50-ml flasks containing 15 ml of 1 *F* $HClO_4$. The spectra of these solutions were identical with those previously obtained and analysis of the solution generated from the bromo complex gave a Cr:N ratio of 1:3.21 for the $Cr(NH_3)_3(OH_2)_3{}^{3+}$ cation.

Kinetics.—The rates of hydrolysis, in 0.6 *F* $HClO_4$ at 25°, of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$, blue 1,2,3-$Cr(dien)(OH_2)Cl_2^+$,[9] and green $Cr(NH_3)_3(OH_2)Br_2^+$ cations to the magenta monohalo products were investigated by spectrophotometry and by halide-release methods (triamminedichloro complex only) using standard techniques,[10,11] with chromotographically purified solutions.

Chemical Analyses.—Cr and Cl were estimated as previously described.[9] N was determined using a micro Kjeldahl apparatus. The complex was decomposed with hot NaOH solution, and the released ammonia was steam distilled into 2% boric acid and titrated with standard HCl.

Spectral Measurements.—Absorbance *vs.* wavelength scans of the visible absorption spectra of these complexes were made on a Beckman DBG recording spectrophotometer using matched 4-cm silica cells with water as the reference. This instrument was also used for the spectrophotometric analysis of Cr and for the spectrophotometric kinetic data. A Philips PW 1050/25 wide-range goniometer coupled to a Philips PR 2500 one-line recorder was used to obtain the powder diffraction patterns of the solids in the 4–60° (2θ) range.

Results

Absorption Spectra.—The wavelengths of the maxima and minima in the visible absorption spectra (320–700 mμ; aqueous $HClO_4$ at 20–25°) and the corresponding molar absorbancy indices, for the complex cations described here, are listed in Table I. Molar absorbancy indices *vs.* wavelength plots are presented in Figures 1 and 2.

Kinetic Data.—Preliminary data on the rates of hydrolysis in acid solution at 25° have been obtained for the halide-release reactions: $Cr(NH_3)_3(OH_2)Cl_2^+ \rightarrow Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_3(OH_2)Br_2^+ \rightarrow Cr(NH_3)_3(OH_2)_2Br^{2+}$, and 1,2,3-$Cr(dien)(OH_2)Cl_2^+ \rightarrow$ 1,2,3-$Cr(dien)(OH_2)_2Cl^{2+}$.[9] The results are reported in Table II, along with more accurate data from related Cr(III) complexes. Complete kinetic investigations were not undertaken, as the data are used here only to support structural assignments. However, the spectral scans in the 320–700-mμ region during the hydrolysis of these cations held good isosbestic points for 3–4 half-lives and the positions and intensities of these points were in good agreement with those predicted theoretically (Figures 1 and 2). This suggests that the hydrolysis products are those indicated above and that no other species are formed, *e.g.*, by isomerization, in spectrophotometrically detectable amounts. The half-lives for the hydrolysis of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation were within experimental error for both the spectrophotometric and halide-release titration runs.

X-Ray Powder Diffraction.—The X-ray powder diffraction patterns of green $Cr(NH_3)_3Cl_3$ (A), violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ (C), and the green product from the $Cr(NH_3)_3(O_2)_2$–HCl reaction (B) are shown schematically in Figure 3. The diffraction pattern of the green product contains only lines found from $Cr(NH_3)_3Cl_3$ and violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ and is thus a mixture of these two compounds. This conclusion is supported by the fact that the only cations isolated by ion-exchange chromatography of the hydrolyzed green product are the blue $Cr(NH_3)_3(OH_2)$-

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[9] S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, in press.

[10] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

[11] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.*, **6**, 1524 (1967).

TABLE I

ABSORPTION MAXIMA AND MINIMA IN THE 320–700 mμ RANGE OF AQUO-, CHLOROAQUO-, AND BROMOAQUOTRIAMMINECHROMIUM(III) COMPLEXES IN AQUEOUS $HClO_4$ AT 20–25°

λ, mμ	a_M, M^{-1} cm^{-1} [a]
Blue $Cr(NH_3)_3(OH_2)Cl_2^+$ in 0.6 *F* $HClO_4$	
410 (max)	25.2
469 (min)	9.4
525 (sh)	14.5
595 (max)	23.5
Magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ in 2 *F* $HClO_4$	
396 (max)	29.5
456 (min)	9.8
539 (max)	20.3
Pink $Cr(NH_3)_3(OH_2)_3^{3+}$ in 0.6–2 *F* $HClO_4$	
376 (max)	26.0
432 (min)	9.1
504 (max)	26.3
$Cr(NH_3)_3(OH_2)_3^{3+}$ [b] in 3 *F* $HClO_4$	
373 (max)	25.6
428 (min)	8.0
502 (max)	25.6
Green $Cr(NH_3)_3(OH_2)Br_2^+$ in 0.6 *F* $HClO_4$	
358 (min)	9.9
405 (max)	28.2
486 (min)	14.8
512 (max)	15.6
548 (min)	13.9
627 (max)	42.0
Magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ in 2 *F* $HClO_4$	
337 (min)	7.7
397 (max)	34.1
457 (min)	13.5
472 (max)	16.0
477 (min)	15.7
516 (sh)	21.4
562 (max)	22.9

[a] Molar absorbancy index (molar extinction coefficient ε), defined by $A = \log (I_0/I) = a_M cd$, where *c* is the molarity of absorbing complex and *d* is the optical path length in centimeters. [b] R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, *Inorg. Chem.*, **7**, 882 (1968), Table I.

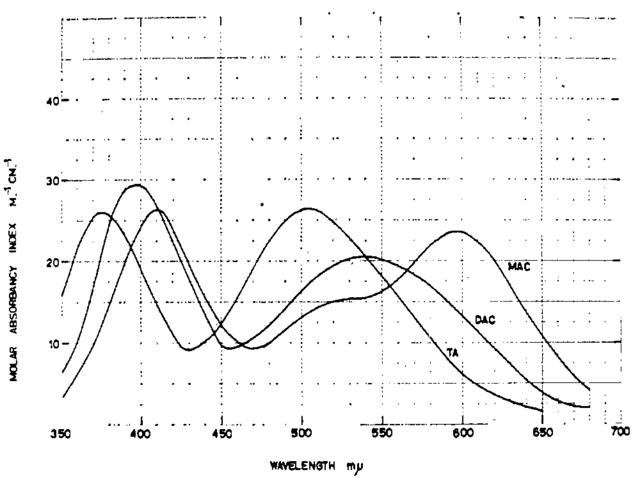

Figure 1.—Visible absorption spectra of some $Cr(NH_3)_3(OH_2)_nCl_{3-n}^{n+}$ complexes at 20–25°: MAC, blue $Cr(NH_3)_3(OH_2)Cl_2^+$ in 0.6 *F* $HClO_4$; DAC, magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ in 2 *F* $HClO_4$; TA, pink $Cr(NH_3)_3(OH_2)_3^{3+}$ in 0.6 *F* $HClO_4$ + Hg^{2+}.

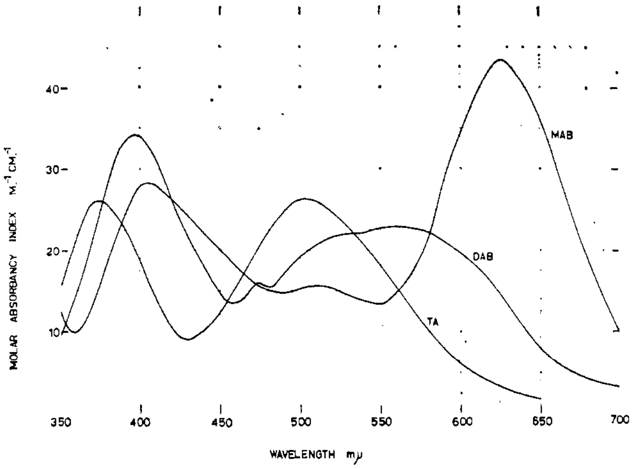

Figure 2.—Visible absorption spectra of some $Cr(NH_3)_3(OH_2)_nBr_{3-n}^{n+}$ complexes at 20–25°: MAB, green $Cr(NH_3)_3(OH_2)Br_2^+$ in 0.6 *F* $HClO_4$; DAB, magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ in 2 *F* $HClO_4$; TA, pink $Cr(NH_3)_3(OH_2)_3^{3+}$ in 0.6 *F* $HClO_4$ + Hg^{2+}.

Cl_2^+ and magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, which are also generated when green $Cr(NH_3)_3Cl_3$ is hydrolyzed and when violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ is dissolved in dilute acid. No cation corresponding to a green $Cr(NH_3)_3(OH_2)Cl_2^+$ isomer was observed.

The Triaquotriamminechromium(III) Cation.—This cation has been generated by the Hg^{2+}-catalyzed hydrolysis of the $Cr(NH_3)_3(OH_2)Cl_2^+$ or $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cation in dilute perchloric acid and the visible absorption spectral characteristics are given in Table I and Figures 2 and 3. The same product is also formed on spontaneous hydrolysis of $Cr(NH_3)_3(OH_2)_2Br^{2+}$ in acid solution or by base hydrolysis of the above cations, followed by rapid acidification. The absorption spectrum of acid solutions of this cation shows little change with time over a period of several days, indicating that isomerization and/or Cr–N bond breaking is slow at room temperature.

The spectral characteristics of the $Cr(NH_3)_3(OH_2)_3^{3+}$ ion reported here are in good agreement with those obtained by Hughes, Ebsworth, and Garner[12] for the $Cr(NH_3)_3(OH_2)_3^{3+}$ ion generated by the decomposition of $Cr(NH_3)_3(O_2)_2$ in 1 *F* $HClO_4$ (Table I).

On the basis of the previously published spectral data for the $Cr(NH_3)_3(OH_2)_3^{3+}$ cation (see references cited in ref 12), these authors tentatively assigned a *cis* configuration to this $Cr(NH_3)_3(OH_2)_3^{3+}$ isomer, while admitting that a *trans* configuration would be the most likely to result from the collapse of the $Cr(NH_3)_3(O_2)_2$ pentagonal bipyramid.[13]

We believe that the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation has the *trans*-dichloro-*trans*-triammine configuration (see Chloroaquo Cations section) and hence the triaquo cation generated from this should also have the *trans*-

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(12) R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, *Inorg. Chem.*, **7**, 882 (1968).

(13) R. Stomberg, *Arkiv Kemi*, **22**, 49 (1963).

Table II

Rates of Hydrolysis in Acid Solution at 25° for Some Dichloro- and Dibromochromium(III)–Amine Complexes

Complex	Medium	$t_{1/2}$, min	Br:Cl rate ratio[a]
trans-$Cr(en)_2Cl_2^+$ [b]	0.1 *F* HNO_3	512	
trans-$Cr(en)_2Br_2^+$ [c]	0.1 *F* HNO_3	35.4	14.5
trans-$Cr(en)(OH_2)_2Cl_2^+$ [d] (*trans*-dichloro-)	0.1 *F* $HClO_4$	370	
trans-$Cr(en)(OH_2)_2Br_2^+$ [e] (*trans*-dibromo?)	0.3 *F* $HClO_4$	22.6	16.4
trans-$Cr(NH_3)_3(OH_2)Cl_2^+$ [f]	0.6 *F* $HClO_4$	~280	
trans-$Cr(NH_3)_3(OH_2)Br_2^+$ [f]	0.6 *F* $HClO_4$	~15	~18
cis-$Cr(en)_2Cl_2^+$ [g]	0.1 *F* $HClO_4$	35	
cis-$Cr(en)_2Br_2^+$ [c]	0.1 *F* $HClO_4$	4.12	8.5
cis-$Cr(dien)(OH_2)Cl_2^+$ [f,h]	0.6 *F* $HClO_4$	~37	

[a] Hydrolysis rate ratio for the dibromide relative to the dichloride. [b] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961). [c] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964); A. M. Weiner and J. A. McLean, Jr., *ibid.*, **3**, 1469 (1964). [d] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *ibid.*, **6**, 1524 (1967). [e] R. G. Hughes and C. S. Garner, *ibid.*, **7**, 1988 (1968). [f] This research. [g] J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957); I. Bratushko and P. Nazarenko, *Russ. J. Inorg. Chem.*, **12**, 1118 (1967) [h] S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, in press.

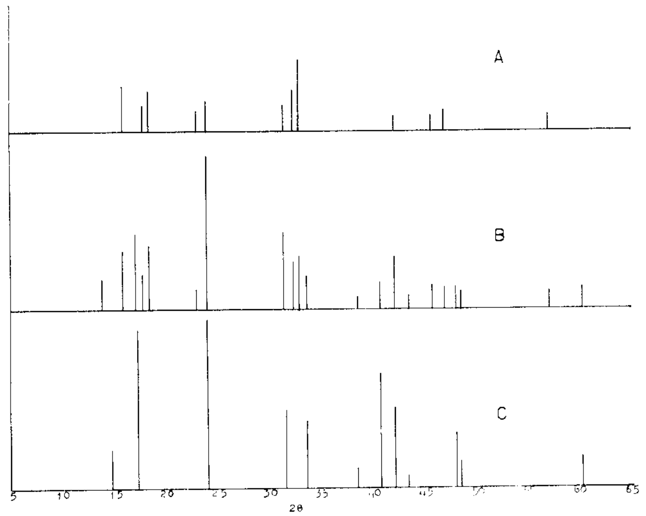

Figure 3.—X-Ray powder diffraction patterns of (A) green $Cr(NH_3)_3Cl_3$, (B) green $Cr(NH_3)_3Cl_3$–$[Cr(NH_3)_3(OH_2)Cl_2]Cl$ mixture, and (C) violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ ($2\theta = 4$–$65°$). Vertical lines represent the positions and intensities (arbitrary units) of the major peaks.

triammine configuration, assuming no isomerization in the hydrolysis process. That we get the same triaquo cation by both Hg^{2+} catalysis and base hydrolysis of the *trans*-dichloro, -monochloro, and -monobromo cations would suggest that isomerization to a *cis*-triaquo cation is unlikely, unless this is a very rapid process. Thus we suggest that the $Cr(NH_3)_3(OH_2)_3^{3+}$ cation described here and also generated by decomposition of $Cr(NH_3)_3(O_2)_2$ in $HClO_4$ has the *trans* rather than the *cis* configuration.

Chloroaquo Cations.—Decomposition of $Cr(NH_3)_3(O_2)_2$ in HCl gives green $Cr(NH_3)_3Cl_3$–$[Cr(NH_3)_3(OH_2)Cl_2]Cl$ mixtures or violet $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ depending on the reaction conditions.[2–7] This parallels the analogous reactions of the chromium(IV) diperoxides $Cr(dien)(O_2)_2 \cdot H_2O$[14] and $Cr(en)(NH_3)(O_2)_2 \cdot H_2O$[15] which give *trans*-$Cr(dien)Cl_3$[9,16,17] and $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$,[15] respectively, under similar conditions.

The blue $Cr(NH_3)_3(OH_2)Cl_2^+$ and magneta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cations have been isolated from the impure solids in pure forms in aqueous solution by ion-exchange chromatography and characterized by Cr:Cl ratios and visible absorption spectra. The visible absorption spectrum of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation (Table I, Figure 1) is quite similar to those of the blue $Cr(en)(NH_3)(OH_2)Cl_2^+$,[15] pink *trans*-$Cr(dien)(OH_2)Cl_2^+$,[9] and blue $Cr(en)(OH_2)_2Cl_2^+$ [16] cations. The latter is known to have a *trans*-dichloro structure from X-ray crystal studies of the solid chloride salt[18] and the spectral similarity and related mode of formation suggest a *trans*-dichloro arrangement is common to all. The absorption spectrum of the blue *cis*-$Cr(dien)(OH_2)Cl_2^+$ cation, where the chloride ligands are in the *cis* positions, is quite different in shape.[9] The *trans*-dichloro *trans*-triammine configuration for the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ ion is also supported by the observation that the primary hydrolysis rate in acid solution at 25° is of the same order as those of *trans*-$Cr(en)(OH_2)_2Cl_2^+$ and *trans*-$Cr(en)_2Cl_2^+$ (see Table II). These rates are about ten times slower than the primary hydrolysis rates of *cis*-$Cr(en)_2Cl_2^+$ and *cis*-$Cr(dien)(OH_2)Cl_2^+$ under the same conditions (Table II).

Additional support for the *trans*-dichloro configuration of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ cation comes from the elution behavior of this complex. It seems well established that *trans*-dichloro ions are removed from cation-exchange columns with similar volumes of more dilute eluting agents than the corresponding *cis*-dichloro isomers.[9–11] We have found that the $Cr(NH_3)_3(OH_2)Cl_2^+$ cation is effectively eluted with 0.3 *F* $HClO_4$, with an efficiency similar to that of the *trans*-dichloro $Cr(en)(OH_2)_2Cl_2^+$ ion, suggesting a similar *trans*-dichloro configuration.

The primary hydrolysis product of the blue $Cr(NH_3)_3(OH_2)Cl_2^+$ ion is the magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ cation which has been separated from the parent and the triaquo ion using ion-exchange chromatography. The visible absorption spectrum of this complex (Table I, Figure 1) is similar to that of the $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$ (isomer II) cation,[1] the major product from the hydrolysis of the blue $Cr(en)(NH_3)(OH_2)Cl_2^+$ cation, and these monochloro cations probably have similar *trans*-chloroaquo-*trans*-triammine configurations. The subsequent hydrolysis of the magenta $Cr(NH_3)_3(OH_2)_2Cl^{2+}$ ion to the pink $Cr(NH_3)_3(OH_2)_3^{3+}$ ion is slow at room temperature and even in the presence of Hg^{2+}; about 1 day is required for complete conversion.

Bromoaquo Cations.—When $Cr(NH_3)_3(O_2)_2$ is de-

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(18) R. Stomberg, personal communication.

composed in 63% HBr, an impure solid mixture of green $[Cr(NH_3)_3(OH_2)Br_2]Br$ and red-violet $[Cr(NH_3)_3(OH_2)_2Br]Br_2$ is formed.[2,3] The bromoaquo cations were isolated in a pure form in aqueous solution by dissolving this impure solid in 0.05 F $HClO_4$ and using ion-exchange chromatography to separate the various products. Characterization was effected by Cr:Br ratios and visible absorption spectra.

The green $Cr(NH_3)_3(OH_2)Br_2^+$ cation has an absorption spectrum (Table I, Figure 2) very similar to those of the related blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ and blue-green $Cr(en)(OH_2)_2Br_2^+$ cations[1,19,20] and probably has a similar *trans*-dibromo configuration. The facts that the primary hydrolysis rate of the green $Cr(NH_3)_3(OH_2)Br_2^+$ cation is of the same order as that of the blue-green *trans*-dibromo $Cr(en)(OH_2)_2Br_2^+$ cation[21] and that the rate ratio of $Cr(NH_3)_3(OH_2)Br_2^+$:$Cr(NH_3)_3(OH_2)Cl_2^+$ is about 18, similar to those of other *trans*-dihalochromium(III)–amine systems (Table II), support this assignment.

The primary hydrolysis product of the green $Cr(NH_3)_3(OH_2)Br_2^+$ ion is the magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ cation which is apparently similarly related to the magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and $Cr(en)(OH_2)_3Br^{2+}$ cations.[1,19,20] The final hydrolysis product ($t_{1/2}$ = 0.5–1 day at room temperature) is the $Cr(NH_3)_3(OH_2)_3^{3+}$ cation, identical with the *trans*-triaquo ion obtained from the chloro analog. Thus we suggest that the green $Cr(NH_3)_3(OH_2)Br_2^+$ cation has the *trans*-dibromo-*trans*-triammine configuration and the magenta $Cr(NH_3)_3(OH_2)_2Br^{2+}$ cation derived from it, the *trans*-bromoaquo-*trans*-triammine configuration.

Discussion

There are potentially three geometric isomers for a $Cr(NH_3)_3(OH_2)X_2^+$ complex and three for a $Cr(NH_3)_3(OH_2)_2X^{2+}$ (X = Cl, Br) complex. Although it has been suggested in the literature that the three isomers of the $Cr(NH_3)_3(OH_2)Cl_2^+$ cation (of unknown configuration) have been obtained,[21,22] we have been able to isolate only one cation corresponding to this formula and we have assigned to it the *trans*-dichloro-*trans*-triammine configuration.

The reactions of six different diperoxochromium(IV)–amine complexes with hydrohalic acids have now been investigated using ion-exchange chromatography to separate and characterize the products.[1,15,19] From these studies it appears that *trans*-dihalochromium(III)–amine complexes are generated as the major product. When the $CrN_3(O_2)_2$ complexes are used, the N atoms adopt the 1,2,6-*trans* or peripheral arrangement in the octahedral chromium(III) complex. This is not unexpected, as the N atoms in the diperoxochromium(IV) complexes that have been investigated structurally[13] are nearly at the 1,2,6 positions of an octahedron in the distorted pentagonal bipyramid. This geometry is apparently conserved in the decomposition reaction. The apparently exclusive formation of a *trans*-dihalo (or -trihalo) configuration is more difficult to rationalize and no adequate explanation can be advanced here. Anation studies of the aquo complexes, with due regard for the complication of Cr–N bond rupture in acid solution, are required to decide whether the configuration of the chromium(IV)–diperoxo complex provides the stereochemical template necessary to form the *trans*-dihalochromium(III) configuration. We can note with regard to this point that the *trans*-dichloro $Cr(en)(OH_2)_2Cl_2^+$ cation can also be generated by the decomposition of the $Cr(en)(ox)_2^-$ cation (ox = oxalate) in HCl,[16,23] presumably *via* aquo intermediates, and it is possible that the *trans*-dihalo configuration is thermodynamically more stable in the monoethylenediamine complexes than in the bisethylenediamine complexes.

The only other chromium(III) complex that has an analog in the diperoxo decomposition series and has been prepared from chromium(III) starting materials is $Cr(dien)Cl_3$. In this case, the diperoxide decomposition forms the *trans* isomer, and the conventional perparation, the *cis* form.[9,17]

The chromium(III) complexes formed by the diperoxide decomposition are also remarkably free from amine isomerization in their hydrolysis reactions.[11,20] This appears to be characteristic of chromium(III) complexes, in general, as the recently investigated *trans*-$Cr(NH_3)_4X_2^{n+}$ complexes[24,25] are also free from isomerization to the *cis* forms. When isomerization does occur, as in the *trans*-$Cr(en)_2X_2^{n+}$ and *cis*-α-$Cr(trien)X_2^{n+}$ systems, it is usually accompanied by competitive Cr–N bond rupture.[26]

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