TABLE VIII

CONCENTRATION DEPENDENCE OF LIFETIMES FOR METHYL GROUP EXCHANGE[a]

$Ti(acac)_2F_2$

Temp, °C	0.163 *M* $\tau \times 10^2$, sec	0.316 *M* $\tau \times 10^2$, sec
−59.1	8.3	7.8
−63.0	14	15
−67.1	21	19

$Ti(acac)_2Cl_2$

Temp, °C	0.173 *M* $\tau \times 10^2$, sec	0.315 *M* $\tau \times 10^2$, sec
−20.7	2.3	2.4
−24.7	3.6	3.6
−30.7	5.5	5.4

$Ti(acac)_2Br_2$

Temp, °C	0.088 *M* $\tau \times 10^2$, sec	0.154 *M* $\tau \times 10^2$, sec
−20.7	0.88	0.89
−31.0	2.3	2.3
−39.4	4.4	4.7

[a] In dichloromethane solution.

the halogen and (b) the dialkoxides, $Ti(acac)_2(OR)_2$, also exhibit methyl group exchange with activation energies very similar to those for the dihalides.[29] It is likely that there is some halide dissociation in dichloromethane since halide ligand exchange reactions occur; for example, $Ti(acac)_2F_2$ and $Ti(acac)_2Br_2$ give an equilibrium mixture of starting materials plus the mixed complex, Ti(acac)$_2$FBr. However, nmr spectra indicate that the rate of halide exchange is slow compared with the rate of exchange of methyl groups. Therefore, complete dissociation of halide ligands cannot be the mechanism for methyl group exchange.

Complete dissociation of an acetylacetonate ligand requires rupture of two M–O bonds. This mechanism, which seems less likely than the one-bond rupture mechanism, may be eliminated since exchange of acetylacetonate ligands with excess acetylacetone is not observed under conditions where exchange of $Ti(acac)_2X_2$ methyl groups is fast. At 37° dichloromethane solutions containing $Ti(acac)_2X_2$ and H(acac) (1:2 mole ratio) give two methyl resonances separated by 4 to 8 cps. The line width of the $Ti(acac)_2X_2$ resonance is the same as in the absence of excess H(acac). Dissociation of bidentate ligands has also been excluded in the case of $Sn(acac)_2Cl_2$, where tin–ring proton spin coupling is observed before, during, and after coalescence of the methyl resonances.[30]

Variable-temperature nmr studies of the bis-benzoylacetonato complexes, $Ti(bzac)_2X_2$, allow elimination of certain twisting mechanisms.[34] It appears that rupture of one M–O bond may be the preferred mechanism for these stereochemical rearrangements. We are continuing experiments designed to provide further evidence on this point.

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(34) N. Serpone and R. C. Fay, *Inorg. Chem.*, in press.

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The Use of Chromium(IV) Diperoxo Amines in the Synthesis of Chromium(III) Amine Complexes. III. Some Bromo, Phosphato, and Sulfato Ethylenediamine Complexes[1]

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Treatment of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ with 7 *F* HBr gave the new greenish purple compound $[Cr(en)(OH_2)_2Br_2]Br$ in *ca.* 90% purity. Cation-exchange chromatography of a 0.01 *F* $HClO_4$ solution of the solid resulted in isolation of the new green-blue complex $Cr(en)(OH_2)_2Br_2^+$, together with low yields of $Cr(en)(OH_2)_4^{3+}$ and a green polymer. Hydrolysis of green-blue $Cr(en)(OH_2)_2Br_2^+$ yielded the new magenta complex $Cr(en)(OH_2)_3Br^{2+}$. The action of 5 *F* H_3PO_4 on $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ gave a solution from which the new pink complex $Cr(en)(OH_2)_3HPO_4^+$ (or possibly $Cr(en)(OH_2)_2HPO_4^+$) was isolated chromatographically; species which may be $Cr(en)(OH\ )_3PO_4$ and $Cr(en)(OH_2)_3H_2PO_4^{2+}$ were also produced. Dissolution of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in 6 *F* H_2SO_4 gave a solution from which the new pink complex $Cr(en)(OH_2)_3SO_4^+$ (or possibly $Cr(en)(OH_2)_2SO_4^+$) was chromatographically isolated. No evidence of any nitrato complexes was found on treatment of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ with 7 *F* HNO_3, only $Cr(en)(OH_2)_4^{3+}$ being formed. The geometric configurations of these new diaquo and triaquo complexes are unknown. Maxima and minima of the visible absorption spectra of the new complexes are presented.

Introduction

The previous papers of this series[2,3] described the synthesis of some chromium(IV) diperoxo amines and their use in the preparation of some ethylenediamine, ammineethylenediamine, propylenediamine, isobutylene-

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(2) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).

(3) D. A. House, R. G. Hughes, and C. S. Garner, *ibid.*, **6**, 1077 (1967).

diamine, and diethylenetriamine complexes of chromium (III).

In the current paper we describe the use of diperoxoaquoethylenediaminechromium(IV) monohydrate, $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$,[4] in the preparation of some bromoaquo, phosphatoaquo, and sulfatoaquo ethylenediamine complexes of chromium(III). Maxima and minima of the near-ultraviolet and visible absorption spectra of the new complexes are reported. These new complexes are of interest to us for kinetic investigations of their hydrolysis and anation[5] reactions. In addition, we report an unsuccessful attempt to prepare a nitrato complex by the action of nitric acid on the diperoxo compound.

Experimental Section

Greenish Purple Dibromodiaquoethylenediaminechromium(III) Bromide.—A slurry of 6 g of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$[6] with 5 ml of water was slowly added to 20 ml of 9 *F* HBr with continuous stirring (*caution*[7]); Br_2 was produced and the solution temperature rose to *ca.* 40°. After cooling to 20–25°, the solution was shaken with ten 50-ml portions of $CHCl_3$ until no further Br_2 color was extracted. The resulting purple solution was evaporated at 35° in an air stream to give white crystals, presumably enH_2Br_2 formed by a side reaction, which were filtered off; continued evaporation to dryness gave a greenish purple solid. This was leached with 5 ml of water for 2–5 min, and the resulting purple extract was evaporated at 25° and 0.01 torr to dryness (*ca.* 16 hr); yield, 3 g (40%).

Anal. Calcd for $[Cr(en)(OH_2)_2Br_2]Br$: C, 6.18; H, 3.09; N, 7.22; Cr, 13.41; Br, 61.8. Found: C, 6.31; H, 3.35; N, 6.54; Cr, 13.85; Br, 62.9.

Since the analyses, although in near accord with the theoretical values, indicate the solid is not 100% pure, we dissolved 100 mg of the solid in 10 ml of 0.01 *F* $HClO_4$ and charged it onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 2° and eluted with 100 ml of 0.3 *F* $HClO_4$; the blue isomer of $Cr(en)(OH_2)_2Cl_2^+$ is known[2] to be quantitatively eluted under these conditions, and we would expect the dibromo analog to be eluted here. The resulting green-blue effluent had a Br:Cr atom ratio of 2.04, and its visible absorption spectrum further supports the assignment of this new species as green-blue $Cr(en)(OH_2)_2Br_2^+$; the effluent was *ca.* 5 m*F* in the complex. A faint red band left on the column was eluted by 100 ml of 3 *F* $HClO_4$ and was characterized by its visible absorption spectrum[2] as $Cr(en)(OH_2)_4^{3+}$. A very faint green band remaining on the column presumably represents a highly charged polymer of some kind. The chromatography suggests that the original solid was *ca.* 90% $[Cr(en)(OH_2)_2Br_2]Br$.

Magenta Bromotriaquoethylenediaminechromium(III) Cation.—A solution of 100 mg of the above solid in 20 ml of 0.3 *F* $HClO_4$ was warmed to 40° for 30 min, then cooled to 2°, and adsorbed on an ion-exchange column at 2° as above. Successive elution with $HClO_4$ solutions yielded four bands as follows.

The first band was eluted by 100 ml of 0.8 *F* $HClO_4$ to give a green effluent whose visible absorption spectrum indicates that it is $Cr(OH_2)_5Br^{2+}$; spectral changes with time show this species aquates slowly. We estimate that *ca.* 10% of the adsorbed Cr species was in this form.

The second band was eluted by 100 ml of 1 *F* $HClO_4$, giving a magenta effluent with a Br:Cr atom ratio of 1.07 and a visible absorption spectrum suggesting it is the new complex $Cr(en)(OH_2)_3Br^{2+}$ (magenta isomer, unknown configuration). This effluent was *ca.* 2 m*F* in the complex; we estimate that *ca.* 85% of the adsorbed Cr species was present as this complex.

The third band was eluted by 100 ml of 3 *F* $HClO_4$ and was found to contain no Br. Its visible absorption spectrum was identical with that[2] of $Cr(en)(OH_2)_4^{3+}$. Less than 5% of the Cr was apparently present in this form.

A fourth faint green band remained on the column; presumably it was a polymer of high charge.

Phosphatoaquoethylenediaminechromium(III) Complexes.—A slurry of 3 g of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$[6] with 10 ml of water was slowly added to 20 ml of 7 *F* H_3PO_4 with stirring (*caution*[7]). The resulting purple solution was cooled to *ca.* −10°; since no crystallization occurred, 5 ml of this solution was poured into *ca.* 500 ml of 95% ethanol, but no solid was obtained. Ten milliliters of the aqueous solution (4.2 *F* in H_3PO_4, as found by titration with standard NaOH) was diluted with water to 50 ml and charged onto a 12-cm × 2-cm diameter column of Crystalab Deeminite L-10[8] mixed-bed cation–anion-exchange resin at 20–25°. Less than 30% of the color was adsorbed. The column was washed with 3 l. of water until the effluent came through colorless (these effluents were discarded); then the column was subjected to successive elution with $HClO_4$ solutions as follows. A faint pink effluent was obtained with 100 ml of 0.05 *F* $HClO_4$, and 100 ml each of 0.1, 0.2, and 0.3 *F* $HClO_4$ gave successively more deeply pink effluents. The total 400 ml of effluents was diluted to 800 ml with water and passed through a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 20–25°; all color was adsorbed. Elution with 50 ml of 0.3 *F* $HClO_4$ gave a pink effluent, but elution with 50 ml each of 0.45 and 0.6 *F* $HClO_4$ did not give more deeply colored effluents, and indeed the color of the latter effluent was less than that of the 0.3 *F* $HClO_4$ effluent (see Results section for consideration of the proton equilibria probably involved here). Accordingly, 150 ml more of 0.3 *F* $HClO_4$ eluent was used, giving a pink effluent *ca.* 1 m*F* in what we believe is $Cr(en)(OH_2)_3HPO_4^+$ or $Cr(en)(OH_2)_2HPO_4^+$ (see below and Results section). All color remaining on the column was eluted with 100 ml of 3 *F* $HClO_4$, giving an effluent with a visible absorption spectrum similar to that of $Cr(en)(OH_2)_4^{3+}$ but sufficiently different to suggest contamination with one or more phosphato complexes.

Since the 0.3 *F* $HClO_4$ pink effluent above was contaminated with excess phosphate owing to its incomplete removal by the earlier washings and a meaningful PO_4:Cr ratio could not be obtained for it, 2 g of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$ was slurried with water and dissolved in *ca.* 15 ml of 7 *F* H_3PO_4 (*caution*[7]); the solution was diluted fivefold with 0.1 *F* $HClO_4$ and then charged onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 20–25°; some of the color was adsorbed and the column was then subjected to five successive elutions with 50 ml each of 0.1 *F* $HClO_4$. Because of the large excess of phosphate, the PO_4:Cr mole ratios of the 0.1 *F* $HClO_4$ were all greater than unity, the last such effluent having a ratio of 1.42 (lowest ratio). Then the top 1 cm of resin was transferred to a similar new column and eluted with three 50-ml portions of 1 *F* $HClO_4$, and the PO_4:Cr ratios and visible absorption spectra of the effluents were determined. The PO_4:Cr mole ratios of the 1 *F* $HClO_4$ effluents were, successively, 1.01, 1.19, and 0.87, with essentially identical spectra (see Table II) with absorption maxima and minima only several mμ different from those of the 0.3 *F* $HClO_4$ effluent of the above paragraph. The pink complex of the last 50 ml of 0.1 *F* $HClO_4$ effluent and of the 1 *F* $HClO_4$ effluent is apparently $Cr(en)(OH_2)_3HPO_4^+$ or $Cr(en)(OH_2)_2HPO_4^+$.

A Pink Sulfatoaquoethylenediaminechromium(III) Complex.—A slurry of 3 g of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$[6] with 10 ml of water was slowly added with stirring to 20 ml of 9 *F* H_2SO_4 (*caution*[7]), giving a solution 6 *F* in H_2SO_4 as found by titration of an aliquot

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(4) Abbreviations used: en = ethylenediamine, $H_2N(CH_2)_2NH_2$; pn = propylenediamine = 1,2-diaminopropane, $H_2NCH_2CH(CH_3)NH_2$; ibn = isobutylenediamine = 2-methyl-1,2-diaminopropane, $H_2NCH_2C(CH_3)_2NH_2$.

(5) Anation is the replacement of ligand water in a complex by an anion.

(6) Prepared and characterized as in ref 2.

(7) The solid diperoxo compound itself decomposes slowly at 25° and violently when heated at 2°/min to 96–97°;[2] see ref 3 for general comments about the explosive properties of such diperoxo compounds.

(8) Crystal Research Laboratories, Inc., Hartford, Conn.

with standard NaOH. Cooling to −10° failed to give a solid, as did mixing 5 ml of the solution with 500 ml of 95% ethanol. Hence, 5 ml of the aqueous solution was diluted with water to 100 ml (to give a solution 0.6 F in H^+) and passed through a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 20–25°; no color was adsorbed, showing the absence of species of charge 2+ or greater. A second 5 ml of the parent solution was diluted with water to 1 l. (to give a solution 0.06 F in H^+) and charged onto a 10-cm × 2-cm diameter column of Crystalab Deeminite L-10[8] mixed-bed cation–anion-exchange resin at 20–25°; all of the color was adsorbed, showing the absence of neutral complexes. This column was then eluted with 100 ml of 0.3 F $HClO_4$, and the resulting pink effluent was diluted threefold with water (to give a solution 0.1 F in H^+); the solution was charged onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 20–25°; all of the color was adsorbed. Elution with 100 ml of 0.3 F $HClO_4$ gave a pink effluent *ca.* 2 mF in $Cr(en)(OH_2)_3SO_4^+$ or possibly $Cr(en)(OH_2)_2SO_4^+$ (see below). A faint pink band left on the column was eluted with 100 ml of 4.5 F $HClO_4$, giving an effluent having a visible absorption spectrum identical with that[2] of $Cr(en)(OH_2)_4^{3+}$ and containing an estimated 5% of the Cr put on the column.

Because the above pink effluent contained excess sulfate owing to its incomplete removal by the earlier washings, 5 ml of the original solution was diluted with water to 50 ml and passed through a 6-cm × 1-cm diameter column of Cl^- Dowex AGI-X8 anion-exchange resin (50–100 mesh) to remove free HSO_4^- and SO_4^{2-}; no color was adsorbed, and 50 ml of pink effluent was obtained which was passed through two more such columns. The final pink effluent had a SO_4:Cr mole ratio of 0.94 (5% accuracy) and a visible absorption spectrum the same as that of the pink complex in the 0.3 F $HClO_4$ effluent above, namely, an isomer of the new complex $Cr(en)(OH_2)_3SO_4^+$ or possibly $Cr(en)(OH_2)_2SO_4^+$.

Attempt to Synthesize a Nitratoethylenediaminechromium(III) Complex.—A slurry of 3 g of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$[6] with 10 ml of water was added slowly with stirring to 20 ml of 11 F HNO_3 (*caution*[7]). The resulting red solution was diluted with water until it was 1 F in H^+ and charged onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 20–25°; the color was completely adsorbed. The column was then washed with 100 ml of 1 F $HClO_4$ without apparent effect and then with 100 ml of 2 F $HClO_4$, which slowly moved the pink band down the column. Elution with 100 ml of 3 F $HClO_4$ eluted all color giving an effluent having a visible absorption spectrum the same as that[2] of $Cr(en)(OH_2)_4^{3+}$. Thus, no evidence of a nitrato complex was found.

Chemical Analyses.—Cr, C, H, and N were determined as described earlier.[2] Bromide was determined by the same method used earlier[2] for chloride. Phosphate was determined with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $N_2H_4\cdot 2HCl$,[9] and sulfate was determined by titration with 0.01 F $BaCl_2$ using a Sargent-Jensen Model HF high-frequency titrator.

Spectrophotometry.—Visible absorption spectra were obtained as described earlier.[2] The wavelengths are accurate to ±2 mμ.

Results

Bromoaquo Complexes.—Greenish purple $[Cr(en)(OH_2)_2Br_2]Br$ has been synthesized in *ca.* 90% purity by the action of 7 F HBr on $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$, and the new complex $Cr(en)(OH_2)_2Br_2^+$ (green-blue isomer) was isolated in pure form in aqueous solution. The ion-exchange behavior strongly suggests that this compound and $Cr(en)(OH_2)_3Br^{2+}$ are isomerically pure, as the isomers of the chloro analogs are easily separable by ion exchange. The geometric configuration is unknown; the action of 12 F HCl on the diperoxo compound produces blue $[Cr(en)(OH_2)_2Cl_2]Cl$,[2] and the visible absorption band intensities of the new dibromo complex (Table I) are much more similar to those of the blue dichloro complex than to those of the green dichloro analog. Comparison of these spectra with the spectra of *cis*-$Cr(en)_2X_2^+$ and *cis*-$Cr(en)_2(OH_2)X^{2+}$ (X = Br, Cl)[10] does not give a clear answer to whether the band wavelengths of the new complex correspond better to the configuration of the blue or the green dichloro analog.

TABLE 1

ABSORPTION MAXIMA AND MINIMA IN THE 335–700 mμ RANGE OF BROMOAQUO- AND CHLOROAQUOETHYLENEDIAMINECHROMIUM(III) COMPLEXES IN AQUEOUS $HClO_4$ AT 20–25°

Complex	$[HClO_4]$, F	λ, mμ	a_M, M^{-1} cm^{-1} [a]
Green-blue $Cr(en)(OH_2)_2Br_2^+$ [b–d]	0.3	470 (max)	23
		630 (max)	35
Blue $Cr(en)(OH_2)_2Cl_2^+$ [b,e]	0.1	420 (max)	22.7
		475 (min)	16.3
		550 (sh)	37.6
		580 (max)	39.1
Green $Cr(en)(OH_2)_2Cl_2^+$(?) [b,d,f]	2	440 (max)	46
		502 (min)	21
		590 (max)	67
Magenta $Cr(en)(OH_2)_3Br^{2+}$ [b,c]	1	405 (max)	25.6
		455 (min)	15.4
		485 (sh)	15.7
		532 (max)	30.2
Magenta $Cr(en)(OH_2)_3Cl^{2+}$ [b,g]	3	402 (max)	31
		455 (min)	14
		535 (max)	40
Purple $Cr(en)(OH_2)_3Cl^{2+}$ [b,g]	2	335 (min)	3
		420 (max)	46
		480 (min)	19
		567 (max)	72

[a] Molar absorbancy index (molar extinction coefficient ε), defined by $A = \log (I_0/I) = a_M cd$, where c = molarity of absorbing complex, d = optical path in centimeters. [b] Geometric configuration unknown. [c] This research. [d] Obtained by extrapolation to $t = 0$ of a spectrum of a fairly rapidly hydrolyzing complex. [e] Reference 2. [f] Unpublished experiments of D. A. House, C. S. Garner, and G. A. Rogers, this laboratory; the species has not been obtained in high purity and the spectrum is therefore tentative. [g] Reference 11.

At 25° green-blue $Cr(en)(OH_2)_2Br_2^+$ hydrolyzes in 0.3 F $HClO_4$ with a half-life of *ca.* 0.5 hr; considering the fact that bromoaquo complexes of Cr(III) are more labile than their chloroaquo analogs,[10] we regard this as additional circumstantial evidence that the new dibromo complex more likely is the geometric isomeric analog of the blue dichloro complex, since the green dichloro complex appears to have about the same hydrolysis rate (see Table I, footnote *f*) and the blue dichloro complex under essentially the same conditions hydrolyzes with a 370-min half-life.[11]

The product of this hydrolysis is the new complex $Cr(en)(OH_2)_3Br^{2+}$ (magenta isomer), the visible absorption maxima and minima of which are given in Table I. The band wavelengths and intensities suggest

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(9) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 810.

(10) See Table V and references therein: L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

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

the geometric configuration of the new complex is the same as that of magenta $Cr(en)(OH_2)_3Cl^{2+}$. An exploratory experiment indicates that magenta $Cr(en)(OH_2)_3Br^{2+}$ hydrolyzes to $Cr(en)(OH_2)_4^{3+}$ in 2 *F* $HClO_4$, with a half-life of the order of several hours at 25°; the same product is formed in the hydrolysis of magenta $Cr(en)(OH_2)_3Cl^{2+}$,[11] but at a lower rate ($t_{1/2} = 17.4$ hr at 50°), as expected.

Phosphatoaquo Complexes.—Dissolution of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in 5 *F* H_3PO_4 produces one or more phosphatoaquo complexes. The ion-exchange behavior (see Experimental Section) strongly suggests that the species present are undergoing protonation in increasingly acidic solutions and deprotonation in more basic solutions. Elution with 0.1, 0.3, and 1 *F* $HClO_4$ would be expected to elute cations of charge 1+ (for ions of the size involved) under the conditions used, and since the visible absorption spectra of these effluents were nearly the same and the PO_4:Cr mole ratio was close to unity (see Experimental Section), the pink species involved appears to be $Cr(en)(OH_2)_3HPO_4^+$ at these acidities with the phosphato ligand monodentate, though not necessarily isomerically pure. Alternatively, although less likely, we think the phosphato ligand could be acting as a bidentate ligand, giving $Cr(en)(OH_2)_2HPO_4^+$. Since the acid dissociation constants of H_3PO_4 are $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, and $K_3 = 4.8 \times 10^{-13}$ at 25°,[12] we would expect that appreciable percentages of the phosphato complex species would be existing as $Cr(en)(OH_2)_3H_2PO_4^{2+}$, and perhaps even $Cr(en)(OH_2)_3H_3PO_4^{3+}$, accounting for the observed decreasing yield of effluent color with increasing acid concentration of eluent (see Experimental Section). These ideas are given general support by the changes in spectra noted when the pink singly charged complex, which we shall refer to as $Cr(en)(OH_2)_3HPO_4^+$, is placed in media of varying acidity (see Table II). Protonation of the apparently bidentate phosphato ligand of $Co(NH_3)_4PO_4$ to give $Co(NH_3)_4HPO_4^+$ shifts the *ca.* 520-mμ absorption band to slightly higher wavelength, as indicated in Table II; for the phosphatoaquoethylenediaminechromium(III) complexes considered here, the shift appears to be in the opposite direction, although in both cases the effect is small and direct comparison of the two types of complex is complicated by the difference in transition metal, in symmetry, and in chromophores other than the phosphato ligand. The data do not seem to warrant speculation on the position of monodentate and bidentate phosphato ligand in the spectrochemical series.

In 1 *F* $HClO_4$ at 20–25°, $Cr(en)(OH_2)_3HPO_4^+$ slowly changes spectrum, but the reaction product has not been identified.

Sulfatoaquochromium(III) Complex.—The pink singly charged sulfatoaquo complex eluted with 0.3 *F* $HClO_4$ appears to be either $Cr(en)(OH_2)_3SO_4^+$ (monodentate sulfato), though not necessarily isomerically pure, or possibly $Cr(en)(OH_2)_2SO_4^+$ (bidentate sulfato). Inasmuch as Barraclough and Tobe[13] obtained $Co(en)_2SO_4^+$ with bidentate sulfato ligand by heating at 110° $Co(en)_2(OH_2)SO_4^+$ (monodentate sulfato), which was prepared in aqueous solution, the method of preparation used by us for our sulfato complex probably would give the monodentate sulfato complex. This supposition is further supported by the infrared studies of Finholt, *et al.*,[14] on $Cr(OH_2)_5SO_4^+$ and by their rationalization of the monodentate nature of the sulfato ligand in this complex in terms of bond distances and angles. Our attempts to obtain a meaningful infrared spectrum of our complex were thwarted by our inability to obtain a solid salt and by interference from free SO_4^{2-} and HSO_4^- in aqueous H_2SO_4 in which we tried to record the spectrum.

The visible absorption maxima and minima of our pink complex, which we shall refer to as $Cr(en)(OH_2)_3SO_4^+$, in solutions of various acidities are given in Table II, along with the other sulfato complexes referred to above. Since the acid dissociation constant of HSO_4^- is $K_2 = 1.2 \times 10^{-2}$ at 25°,[12] and though this varies with ionic strength, some change in protonation of $Cr(en)(OH_2)_3SO_4^+$ might be expected in media of varying acidity. The spectra of Table II suggest such an effect (the apparently abnormal wavelengths of the complex in 16 *F* H_2SO_4 may be related to outer-sphere complexing with sulfate ion, since Posey and Taube[15] have found that the presence of sulfate ions can substantially alter the visible absorption spectra of cobalt(III) ammine complexes due to outer-sphere complexing), similar to the shifts noted above for the phosphato complex, though the protonation affect would be difficult to separate from changes due to ion pairing at high ionic strengths. If we compare the spectrum of $Cr(en)(OH_2)_3SO_4^+$ in 0.1 *F* $HClO_4$–0.2 *F* H_2SO_4 with that of $Cr(en)(OH_2)_4^{3+}$ in 0.5 *F* $HClO_4$ (namely, bands at 387 and 517 mμ, with respective molar absorbancy indices of 21.7 and 32.0 M^{-1} cm^{-1}),[2] we see substitution of SO_4^{2-} for an H_2O ligand shifts the d–d bands to lower energies by *ca.* 700–900 cm^{-1}. The corresponding shift calculated from the spectra of $Cr(OH_2)_5SO_4^+$ [14] and $Cr(OH_2)_6^{3+}$ [16] is *ca.* 300–600 cm^{-1}.

Discussion

The production of pink $Cr(en)(OH_2)_4^{3+}$ by the dissolution of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in 0.1–3 *F* $HClO_4$ was reported earlier.[2] Dissolution of the diperoxo compound in 7 *F* HNO_3 has now been found to form the tetraaquo complex, without evidence for the presence of any nitrato complex.

Dissolution of the diperoxo compound in 7 *F* HBr produces primarily greenish purple $[Cr(en)(OH_2)_2Br_2]Br$, in analogy with the formation of blue $[Cr(en)(OH_2)_2Cl_2]Cl$ on dissolution of the diperoxo compound in 12 *F* HCl.[2] Hydrolysis of the dibromo com-

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[12] N. A. Lange, Ed., "Handbook of Chemistry," 9th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1956, pp 1201–1202.

[13] C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

[14] J. Finholt, R. Anderson, J. Fyfe, and K. Caulton, *Inorg. Chem.*, **4**, 43 (1965).

[15] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

[16] R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957).

TABLE II

ABSORPTION MAXIMA AND MINIMA IN THE 350–700 mμ RANGE OF SOME PHOSPHATO AND SULFATO COMPLEXES OF CHROMIUM(III) AND COBALT(III) IN AQUEOUS SOLUTION AT 20–25°

Complex	Medium	λ, mμ	a_M, M^{-1} cm^{-1} [a]
Pink "$Cr(en)(OH_2)_3HPO_4^+$"(?)[b–d]	10 F in $HClO_4$, 0.4 F in H_3PO_4	405 (max)	24
		455 (min)	13
		535 (max)	38
		~670 (sh)	4
	1 F $HClO_4$	399 (max)	24
		450 (min)	13
		536 (max)	40
		~670 (sh)	~4
	0.4 F in H_3PO_4	410 (max)	24
		468 (min)	12
		552 (max)	42
		~670 (sh)	5
	Phosphate buffer, pH 1.6[e]	412 (max)	24
		470 (min)	11
		552 (max)	42
		670 (min)	4.7
		675 (max)	5.2
	Phosphate buffer, pH 5.9[e]	415 (max)	32
		475 (min)	13
		562 (max)	49
		675 (min)	6.5
		680 (max)	7.2
$Co(NH_3)_4PO_4$[f]	0.01 F H_3PO_4	365 (max)	23
		522 (max)	37
$Co(NH_3)_4HPO_4^+$ [f]	12 F H_3PO_4	526 (max)	73
Pink "$Cr(en)(OH_2)_3SO_4^+$"(?)[b–d]	16 F H_2SO_4	405 (max)	20
		455 (min)	12
		528 (max)	39
		665 (min)	3.4
		672 (max)	3.6
	10 F in $HClO_4$, 0.2 F in H_2SO_4	395 (max)	14
		442 (min)	12
		515 (max)	32
		~665 (sh)	3
	0.1 F in $HClO_4$, 0.2 F in H_2SO_4	400 (max)	26
		450 (min)	13
		535 (max)	43
		~670 (sh)	2
	Phosphate buffer, pH 1.5[g]	400 (max)	26
		450 (min)	12
		532 (max)	43
		~670 (sh)	2
$Co(en)_2SO_4^+$ [h]	H_2O	337 (min)	53
		367 (max)	72
		427 (min)	17
		505 (max)	100
		~600 (sh)	~23
$Co(en)_2(OH_2)SO_4^+$ [h]	H_2O	326 (min)	30
		361 (max)	71
		421 (min)	17
		500 (max)	100
$Cr(OH_2)_5SO_4^+$ [i]	0.1 F $HClO_4$	417 (max)	18.8
		587 (max)	19.0
		671 (sh)	5.3

[a,b,c] Same as footnotes *a*, *b*, and *c* of Table I. [d] See Results section for discussion of extent of protonation and number of water ligands. [e] Neutralization of 4.2 F H_3PO_4 solution of complex with NaOH to indicated measured pH. [f] S. S. Daniel and J. E. Salmon, *J. Chem. Soc.*, 86 (1961). [g] Beckman pH 7 phosphate buffer added to 6 F H_2SO_4 solution of complex until measured pH was 1.5. [h] Reference 13. [i] Reference 14; the molar absorbancy indices are *ca.* 20% greater than reported by N. Fogel, J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962).

plex in acidic solution forms the magenta isomer of $Cr(en)(OH_2)_3Br^{2+}$, which appears to be the analog of magenta $Cr(en)(OH_2)_3Cl^{2+}$ [11] formed similarly from blue $Cr(en)(OH_2)_2Cl^+$. These complexes are analogs also of violet-blue $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$, purple $Cr(pn)(OH_2)_2Cl_2^+$, purple $Cr(ibn)(OH_2)_2Cl_2^+$, magenta $Cr(pn)(OH_2)_3Cl^{2+}$, and magenta $Cr(ibn)(OH_2)_2Cl_2^+$, similarly synthesized by dissolution of the appropriate diperoxo compound in 12 F HCl and by hydrolysis of the directly formed products of the dissolution.[3]

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

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

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

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

Introduction

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

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

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

Experimental Section

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

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

[3] E. Weinmann, Thesis, Zurich, 1919.

[4] D. A. House and C. S. Garner, *Inorg. Nucl. Chem. Letters*, **1**, 137 (1965).

[5] D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 840 (1966).

[6] D. A. House, R. G. Hughes, and C. S. Garner, *ibid.*, **6**, 1077 (1967).

[7] J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

[8] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

[9] C. S. Garner and D. J. MacDonald, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 266–275.

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

[11] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

[12] D. C. Olson and C. S. Garner, *ibid.*, **2**, 414 (1963).

[13] V. Holba, M. Dillinger, and C. Skoršepa, *Collection Czech. Chem. Commun.*, **30**, 1331 (1965).

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

[15] J. M. Veigel and C. S. Garner, *ibid.*, **4**, 1569 (1965).