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The Use of Chromium(IV) Diperoxo Amines in the Synthesis of Chromium(III) Amine Complexes. IV. Some Chloro and Bromo Ammineethylenediamine Complexes[1]

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Treatment of $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ with 7 *F* HBr yields an impure purple solid. Cation-exchange chromatography of a 0.01 *F* $HClO_4$ solution of this solid has resulted in the isolation of the new blue-green complex $Cr(en)(NH_3)(OH_2)Br_2^+$ in aqueous solution. Hydrolysis of this complex in 0.3 *F* $HClO_4$, followed by chromatography, yields aqueous solutions of the new purple-red complex $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and a pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ species; the latter possibly may be an isomer of the pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ recently reported as forming when $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ is decomposed in 1 *F* $HClO_4$. Hydrolysis of violet-blue $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$ gives a solution from which two red-violet isomers of $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$ may be isolated chromatographically. The geometric configurations of the new complexes are unknown. Maxima and minima of the visible and near-ultraviolet absorption spectra of the new complexes are reported.

Introduction

In a previous paper[2] of this series,[3] we described the synthesis of diperoxoammineethylenediaminechromium(IV) monohydrate, $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$,[4] and its use in the synthesis of the cations triaquoammineethylenediaminechromium(III), $Cr(en)(NH_3)(OH_2)_3^{3+}$ (pink isomer), and dichloroaquoammineethylenediaminechromium(III), $Cr(en)(NH_3)(OH_2)Cl_2^+$ (violet-blue isomer). In the current paper we report the use of this diperoxo compound to prepare the previously unreported bromo analog of the above chloro complex, namely, dibromoaquoammineethylenediaminechromium(III) cation, $Cr(en)(NH_3)(OH_2)Br_2^+$ (blue-green isomer). We also report the isolation and characterization of the products of hydrolysis of both the chloro and bromo complexes in 0.3 *F* $HClO_4$ at 20–25°.

Experimental Section

Blue-Green Dibromoaquoammineethylenediaminechromium(III) Cation.—Three grams of $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O^2$ was slurried with 5 ml of water and very slowly added to 15 ml of 9 *F* HBr at 20–25° with continual stirring (*caution!*[5]). Effervescence occurred, Br_2 was released, and the solution temperature rose to *ca.* 35°. The solution was stirred for 10 min and then the Br_2 was extracted with five 50-ml portions of $CHCl_3$ and finally with 50 ml of $(C_2H_5)_2O$. The remaining red-purple aqueous solution was evaporated to dryness at 25° on a vacuum line at 0.1 torr for 2 days; yield, 4 g of impure purple solid.

Ca. 0.1 g of this solid was dissolved in 25 ml of 0.01 *F* $HClO_4$ at 2°, and the solution was rapidly charged onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 2°. The column was eluted with 100 ml of 0.01 *F* $HClO_4$, followed by 50 ml each of 0.05 and 0.1 *F* $HClO_4$, which eluted no color. The latter eluent began to move a green band, which was then fully eluted with 75 ml of 0.3 *F* $HClO_4$ to give a blue-green effluent. The center half of this effluent (*ca.* 2.3 m*F* in complex) was kept iced for several minutes, then rapidly warmed to 20–25° for spectral scanning.

Analysis of the blue-green center cut yielded a Br:Cr atom ratio of 1.95, in acceptable agreement with the formula $Cr(en)(NH_3)(OH_2)Br_2^+$. *Ca.* 60–70% of the above purple solid consisted of this bromoaquo product.

Purple-Red Bromodiaquoammineethylenediaminechromium(III) Cation.—After the elution of the above column with 0.3 *F* $HClO_4$, a purple-red band was left on the column. This band was eluted as a purple-red effluent with 50 ml of 1.5 *F* $HClO_4$. This effluent was suspected of containing the new complex $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ but was too dilute to characterize well.

Hence, 0.1 g of the original impure purple solid was dissolved in 50 ml of 0.3 *F* $HClO_4$ and allowed to hydrolyze for 2–3 hr at 20–25°. The solution was then charged onto a second cation-exchange column (at 2°) of the kind referred to above. Some blue-green effluent came through the column and the remainder of the green band (unreacted $Cr(en)(NH_3)(OH_2)Br_2^+$) was eluted with 50 ml of 0.3 *F* $HClO_4$ plus 100 ml of 0.6 *F* $HClO_4$, leaving a purple-red band near the bottom of the column. This band was completely removed by 50 ml of 2 *F* $HClO_4$, giving a purple-red effluent. The center cut of this effluent (*ca.* 2.7 m*F* in complex) was collected at 0°, then warmed quickly to 20–25° for recording of its visible absorption spectrum (which was the same except for intensity as the spectrum of the purple-red effluent from the original cation-exchange column).

A Br:Cr atom ratio of 0.93 was found for this center cut, in acceptable accord with the formula $Cr(en)(NH_3)(OH_2)_2Br^{2+}$. *Ca.* 60–70% of the hydrolyzed solution was in this form.

Pink Triaquoammineethylenediaminechromium(III) Cation.—Elution of both of the columns was continued with 100 ml each of 3 *F* $HClO_4$. In each case a pink effluent was obtained which had a visible absorption spectrum somewhat like that of the burgundy-to-pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ produced when $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ is decomposed with 1 *F* $HClO_4$,[2] but the spectra were sufficiently different to suggest that the above pink effluent possibly may be an isomer of the $Cr(en)(NH_3)(OH_2)_3^{3+}$ species prepared earlier. Alternatively, the chromatography may have permitted some other species possibly present, such as $Cr(en)(OH_2)_4^{3+}$, to coelute with the $Cr(en)(NH_3)(OH_2)_3^{3+}$ and alter the apparent spectrum. Since we were interested mainly in the chloro and bromo complexes, we did not pursue this point further.

After the above elution perhaps 5% of the total chromium remained on each column as a faint green band even after passage

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[1] (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and this university. This paper constitutes Report No. UCLA-34P12-66 to the USAEC. (b) Presented before the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 30–Nov 1, 1967.

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

[3] Part III: R. G. Hughes and C. S. Garner, *ibid.*, **6**, 1519 (1967).

[4] Abbreviation en = ethylenediamine, $H_2NCH_2CH_2NH_2$.

[5] The solid diperoxo compound itself decomposes slowly at 25° and explodes when heated to 115° at 10°/min.[2] Effervescence in the treatment with HBr can be violent if the rate of addition is too great, and minor explosions may occur if the solid is added to the HBr without first forming a slurry with water.

of 100 ml of 6 *F* $HClO_4$ through each column. The band presumably arises from a polymer of high charge.

Red-Violet Isomers of Chlorodiaquoammineethylenediaminechromium(III) Cation.—*Ca.* 0.1 g of impure violet-blue $[Cr(en)(NH_3)(OH_2)Cl_2]Cl^2$ was hydrolyzed in 50 ml of 0.3 *F* $HClO_4$ for 2 days at 20–25°, then charged onto a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 2°. Unhydrolyzed $Cr(en)(NH_3)(OH_2)Cl_2^+$ was eluted with 50 ml of 0.3 *F* $HClO_4$, leaving what appeared to be two partly separated red-violet bands. Clear separation into two red-violet bands was achieved by passing 500 ml of 0.3 *F* $HClO_4$ through the column at 2.5 ml/min (the flow rate must be this low in order to separate the two isomers). A further 100 ml of 0.3 *F* $HClO_4$ eluted the lower band (isomer I) as a faint red-violet solution 0.2 m*F* in the complex and brought the upper band (isomer II) near the bottom of the column. This latter band was then eluted with 100 ml of 0.6 *F* $HClO_4$ to give a red-violet effluent (center half) *ca.* 3 m*F* in isomer II (in a second experiment, 200–300 ml of 0.3 *F* $HClO_4$ in place of the 100 ml of 0.6 *F* $HClO_4$ was found to elute isomer II).

Analyses of these two effluents gave Cl:Cr atom ratios of 1.05 (isomer I) and 0.96 (isomer II), in acceptable agreement with the formula $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$. The proportions of the two isomers were found to vary when the hydrolysis times or temperatures were changed; for the conditions given above, *ca.* 5% of the total chromium was isomer I and *ca.* 70% was isomer II.

Chemical Analyses and Spectrophotometry.—These were carried out as described earlier.[2,3]

Results

Bromoaquo Complexes.—The new blue-green complex $Cr(en)(NH_3)(OH_2)Br_2^+$ has been synthesized by the action of 7 *F* HBr on $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ and isolated in pure form in aqueous solution. This reaction is analogous to the reaction between 7 *F* HBr and $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ reported earlier.[3] Characterization of the new complex was based on its Br:Cr atom ratio, its chromatographic behavior (see Experimental Section; the complex is eluted under conditions where the blue isomer of the analogous $Cr(en)(OH_2)_2Cl_2^+$ is known[6] to be quantitatively eluted), and its visible absorption spectrum (see Table I and Discussion). The complex hydrolyzes in 0.3 *F* $HClO_4$ with an estimated half-life of *ca.* 1 hr at 20–25°.

Hydrolysis of blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ in 0.3 *F* $HClO_4$ at 20–25° yields the previously unreported purple-red $Cr(en)(NH_3)(OH_2)_2Br^{2+}$, which has been chromatographically isolated in pure form in aqueous solution and characterized in the same way as the dibromo complex. In 1 *F* $HClO_4$ at 20–25° the monobromo complex hydrolyzes slowly ($t_{1/2} \sim$ 0.5–2 days).

Chloroaquo Complexes.—As reported earlier,[2] decomposition of $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ in 12 *F* HCl produces violet-blue $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$, isolated as a slightly impure solid. We have now found that this dichloro complex can be hydrolyzed in 0.3 *F* $HClO_4$ at 20–25° to yield two new red-violet complexes which are isomeric forms of $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$. The isomers were quantitatively separated by cation-exchange chromatography and obtained in aqueous solution in pure form. Their characterization is based on their mode of formation, their Cl:Cr atom ratios, their chromatographic behavior,[7] and their visible absorption spectra (Table I). It is not known which of the four theoretically possible geometric isomers of $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$ these two red-violet isomers represent, nor is it known whether both are directly formed hydrolysis products or if instead one of the two isomers arises as a result of isomerization. Isomer II of the monochloro complex appears to change spectrum slowly in 0.6 *F* $HClO_4$ at 20–25°. Isomer I was

TABLE I

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

Complex	$[HClO_4]$, *F*	λ, mμ	a_M, M^{-1} cm^{-1} [a]
Blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ [b,c]	0.3	405 (sh)	26
		450 (max)	33
		500 (sh)	30
		560 (min)	19
		620 (max)	38
Purple-red $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ [b,c]	1	400 (max)	38.5
		450 (min)	23.8
		475 (sh)	28.3
		510 (max)	34.7
		570 (sh)	26
Violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$ [c,d]	0.3	420 (max)	32.1
		460 (min)	22.8
		510 (max)	31.3
		560 (min)	25.0
		585 (max)	26.4
Red-violet $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$, isomer I[b,c]	0.3	400 (max)	36
		450 (min)	17
		535 (max)	46
Red-violet $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$, isomer II[b,c]	0.6	396 (max)	38.4
		445 (min)	18.4
		503 (max)	36.5
		670 (sh)	1
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$, isomer I[c,d]	1	380 (max)	29.0
		428 (min)	13.9
		502 (max)	41.5
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$, isomer II? [b,c]	3	375 (max)	34
		425 (min)	15
		492 (max)	37
1,2,3-$Cr(NH_3)_3(OH_2)_3^{3+}$ [e]	2	375 (max)	22.2
		432 (min)	6.5
		518 (max)	34.5
1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$ [f]	3	373 (max)	25.6
		428 (min)	8.0
		502 (max)	25.6
		680 (sh)	1

[a] Molar absorbancy index a_M (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 in cm. [b] This research. [c] Geometric configuration unknown. [d] Reference 2. [e] Reference 8. [f] Reference 9.

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

(7) We would not expect 0.3 *F* $HClO_4$, in the volumes and at the flow rates we normally have used, to elute effectively a complex ion of charge 2+ and of the size involved. The separation of the isomers required abnormally large volumes of 0.3 *F* $HClO_4$ at an abnormally low flow rate (see Experimental Section) and is consistent with the 2+ charge of the complexes.

isolated in too dilute a solution to allow meaningful observations on its reaction.

Kinetic studies of the new bromoaquo and chloroaquo complexes are underway.

Triaquo Complexes.—Chromatography of hydrolyzed blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ led to isolation of what appeared to be a pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ species. This complex may be an isomer (isomer II) of the burgundy-to-pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ (isomer I) obtained earlier[2] by treatment of $[Cr(en)(NH_3)(O_2)_2] \cdot H_2O$ with 1 *F* $HClO_4$. Although we are not certain the chromatographed fraction was pure (see Experimental Section), comparison (see Table I) of the visible absorption spectrum of the apparent new isomer II with the spectrum of 1,2,6-$Cr(NH_3)_3(OH_2)_3^{3+}$ [8] and of the isomer I spectrum with that of 1,2,3-$Cr(NH_3)_3(OH_2)_3^{3+}$ [9] suggests that isomers I and II may have, respectively, two H_2O ligands *trans* to each other and all three H_2O ligands *cis* to one another. Definite assignments are not possible without further evidence.

Discussion

In general the preparation of the four new chloroaquo and bromoaquo ammineethylenediamine complexes described in this paper parallels the syntheses of magenta and purple $Cr(en)(OH_2)_3Cl^{2+}$,[10] magenta $Cr(en)(OH_2)_3Br^{2+}$,[3] and green-blue $Cr(en)(OH_2)_2Br_2^+$.[3] Moreover, two geometric isomers are known for both of the monochloro complexes, $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$ (four isomers theoretically possible) and $Cr(en)(OH_2)_3Cl^{2+}$ (two isomers theoretically possible), but only one geometric isomer each has been prepared for the monobromo complexes, $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ and $Cr(en)(OH_2)_3Br^{2+}$.

It is interesting to compare the electronic spectrum of the new blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ (Table I) with that of violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$ reported earlier.[2] Splitting of band I[11] occurs to a large extent in both complexes, whereas splitting of band II[11] is noticeable only in the dibromo complex (shoulder at 405 mμ). Except for *trans*-$Cr(en)_2Cl_2^+$, such splitting of both bands has not been observed until the recent observations of Baker and Phillips,[12] who carefully examined the electronic spectra of *trans*- and *cis*-$Cr(en)_2X_2^{n+}$ complexes (X = Cl, Br, NCS, OH, OH_2) in solution. They report splitting of both bands of these *trans* complexes (excepting the diisothiocyanato complex), but none for the *cis* complexes (despite the prediction from theory of significant splitting of the first band in the dichloro and dibromo complexes and the second band in the dihydroxo and hydroxoaquo complexes). The extent of the splitting for our dibromo complex is greater than for any of their complexes. Since Baker and Phillips state that the magnitude of the splitting for such lower symmetry complexes cannot necessarily be predicted on the basis of differences in ligand field strengths as represented by Dq values for octahedral complexes, we do not pretend to understand why the splitting is so large for our dibromo complex. However, since in the *trans*-$Cr(en)_2X_2^{n+}$ complexes the splitting is not greatly different for the dichloro and dibromo complexes and since splitting is unobservable in the *cis* analogs, we are inclined to think that our blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ and violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$ species do not have the same configuration, and that probably the dibromo complex has the *trans*-dibromo configuration (although the latter hypothesis is shaky in view of the lower symmetry of our dibromo complex compared with *trans*-$Cr(en)_2Br_2^+$ and the presence of somewhat different chromophores). This possibility is supported by preliminary approximate values of the hydrolysis rates of our dichloro and dibromo complexes at 20–25°, for which we find a ratio of k_{Br}/k_{Cl} *ca.* one-fifth the ratio we would expect (from analogy with the $Cr(en)_2Cl_2^+$ and $Cr(en)_2Br_2^+$ complexes) if our dibromo and dichloro complexes were to have the same configuration. Circumstantial evidence in favor of a *trans*-dibromo assignment of blue-green $Cr(en)(NH_3)(OH_2)Br_2^+$ also comes from the fact that only one hydrolysis product has been observed, whereas two isomeric products are found for violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$. This latter evidence is weak, however, because the finding of only one monobromo product in hydrolysis of the dibromo complex may be due to the greater difficulty of separating bromo isomers by cation-exchange chromatography than their chloro analogs or to rapid isomerization of one of the monobromo products, and the appearance of the two red-violet isomers of $Cr(en)(NH_3)(OH_2)_2Cl^{2+}$ in the hydrolysis of violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$ could be a result of isomerization. We hope to answer some of these questions through kinetic and stereochemical studies of these complexes now getting underway.

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[8] The *trans,* or peripheral, isomer in which two of the three like ligands are *trans* to each other: R. G. Hughes, E. A. V. Ebsworth, and C. S. Garner, to be published.

[9] The *cis,* or facial, isomer in which all three like ligands are *cis* to one another: C. E. Schäffer and P. Andersen, "Proceedings of the Wroclaw Symposium," Pergamon Press Ltd., London, 1964, pp 571–582.

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

[11] Bands I and II refer, respectively, to the low- and high-energy bands. In spin-free d^3 complexes of octahedral symmetry these bands are associated with ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions, respectively.

[12] W. A. Baker, Jr., and M. G. Phillips, *Inorg. Chem.,* **5**, 1042 (1966).