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The Use of Chromium(IV) Diperoxo Amines in the Synthesis of Chromium(III) Amine Complexes. II. Some Ammineethylenediamine, Propylenediamine, and Isobutylenediamine Complexes[1]

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Three new chromium(IV) diperoxo compounds, $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$, $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$, and $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$, have been synthesized and unsuccessful attempts have been made to synthesize similar compounds with 29 other amines. Decomposition in 1 *F* $HClO_4$ produces the new burgundy-to-pink aquo ions, $Cr(en)(NH_3)(OH_2)_3{}^{3+}$, $Cr(pn)(OH_2)_4{}^{3+}$, and $Cr(ibn)(OH_2)_4{}^{3+}$. Violet-blue $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$ is formed by the action of concentrated HCl on $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$; the other two diperoxo compounds react to give impure solids. Ion-exchange chromatography of 0.01 *F* $HClO_4$ solutions of these impure solids has resulted in the isolation of six new chloroaquo complexes: magenta $Cr(pn)(OH_2)_3Cl^{2+}$, purple $Cr(pn)(OH_2)_2Cl_2{}^+$, green-blue $Cr(pn)(OH_2)Cl_3$, magenta $Cr(ibn)(OH_2)_3Cl^{2+}$, purple $Cr(ibn)(OH_2)_2Cl_2{}^+$, and green $Cr(ibn)(OH_2)Cl_3$; the geometric configurations are unknown. Maxima and minima of previously unreported visible absorption spectra are presented.

Introduction

The previous paper in this series[2] described the synthesis of some chromium(IV) diperoxo amines and their use in the preparation of some monoethylenediamine and monodiethylenetriamine complexes of chromium(III).

In the current paper we describe the preparation and characterization of three new diperoxo compounds, namely, diperoxoammineethylenediaminechromium(IV) monohydrate, $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$,[3] diperoxoaquopropylenediaminechromium(IV) dihydrate, $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$,[4] and diperoxoaquoisobutylenediaminechromium(IV) monohydrate, $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$, together with an extensive series of new aquo and chloroaquo complexes of chromium(III) made from them. Maxima and minima of the near-ultraviolet and visible absorption spectra of the new complexes are presented. These new chromium(III) complexes are of interest to us for kinetic investigations of their hydrolysis and anation[5] reactions for comparison with the extensively studied bisethylenediamine complexes of chromium(III) and cobalt(III).

In addition we report some unsuccessful attempts to make chromium(IV) diperoxo compounds with other amines.

Experimental Section

Diperoxoammineethylenediaminechromium(IV) Monohydrate.—Attempts to prepare this compound by mixing CrO_3 and H_2O_2 with mixtures of NH_3 and ethylenediamine gave only $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$. The ammine compound was successfully synthesized by dissolving 4.2 g of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$, made as described earlier,[2] in a mixture of 375 ml of 15 *F* NH_4OH and 300 ml of water, filtering, and then storing the filtrate at $-10°$ for 2 days. The greenish brown crystals were filtered off, washed with ice water, acetone, and ether, and air dried; yield, 2.2 g (52%). In repeated syntheses the crystals varied from flat lustrous plates to very small needles.

Anal. Calcd for $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$: C, 11.40; H, 6.16; N, 19.72; Cr, 24.6; oxidation equiv, 2.50; reduction equiv, 3.00. Found: C, 11.49; H, 6.23; N, 19.83; Cr, 25.3; oxidation equiv, 2.40; reduction equiv, 2.97.

The diperoxo compound showed no evidence of change within 1 day at 20–25° or 1 month at $-10°$. It charred at 114–115° when heated from 20–25° at 2°/min and exploded at 115° when heated at 10°/min. *Caution:* this compound is potentially explosive at 25°.

Diperoxoaquopropylenediaminechromium(IV) Dihydrate.—Aqueous solutions of CrO_3 (10 g of J. T. Baker Co. technical grade in 100 ml of water) and H_2O_2 (30 ml of 30%) were added from separate dropping funnels over a 30-min period to ice-cold aqueous propylenediamine (12 ml of Eastman Kodak White Label 90% in a slurry of 100 ml of water with 250 g of crushed ice). After 1–2 hr at *ca.* 5° a gray-green microcrystalline product was collected in *ca.* 1-g portions on Whatman No. 54 paper, washed with ice water, acetone, and ether, and air dried; yield, 6 g (25%). The product was stored at 0° in small portions in separate glass vials.

Anal. Calcd for $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$: C, 14.75; H, 6.55; N, 11.5; Cr, 21.3; oxidation equiv, 2.50; reduction equiv, 3.00. Found: C, 15.05; H, 6.62; N, 11.5; Cr, 21.3; oxidation equiv, 2.41; reduction equiv, 2.97.

The compound changed from gray-green to golden brown in 1–2 days at 20–25°, but can be kept at 0° for 1–2 weeks in the dark without apparent change. When heated from 20–25° at 2°/min, the compound exploded at 88–90°. *Caution:* several preparations of this compound have exploded spontaneously at 20–25°.

Diperoxoaquoisobutylenediaminechromium(IV) Monohydrate.—Conditions and amounts similar to those of the above propylenediamine compound preparation were used except that 12 ml of isobutylenediamine (Commercial Solvents Corp., New York, N. Y.) replaced the propylenediamine. Near the end of the addition of the CrO_3 and H_2O_2 solutions, considerable frothing usually occurred, together with the formation of a deep blue

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

(3) Abbreviations used: en = ethylenediamine, $H_2NCH_2CH_2NH_2$; pn = propylenediamine = 1,2-diaminopropane, $H_2NCH_2CH(CH_3)NH_2$; ibn = isobutylenediamine = 2-methyl-1,2-diaminopropane, $H_2NCH_2C(CH_3)_2NH_2$; dien = diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$; hexamine = hexamethylenetetramine, $(CH_2)_6N_4$.

(4) This compound was prepared independently in our laboratory by D. A. H. and C. S. G. and at University Chemical Laboratory, Cambridge, England, by Dr. E. A. V. Ebsworth and R. G. H., and its preparation and that of the other two new diperoxo complexes were briefly outlined by E. A. V. Ebsworth, C. S. Garner, D. A. House, and R. G. Hughes, *Inorg. Nucl. Chem. Letters*, **3**, 61 (1967).

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

precipitate.[6] The mixture was stirred for an additional 2 hr at 0° until the blue precipitate dissolved, the frothing ceased, and an olive-green microcrystalline solid formed, which was collected in *ca.* 1-g portions on Whatman No. 54 paper, washed with ice water, acetone, and ether (or 95% ethanol, methanol, and ether), and air dried; yield, 5–7 g (20–28%). The compound was stored in separate glass vials at 0°. It is somewhat difficult to obtain this compound in high purity, free from CrO_4^{2-}.

Anal. Calcd for $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$: C, 20.0; H, 6.71; N, 11.7; Cr, 21.6; oxidation equiv, 2.5; reduction equiv, 3.00. Found: C, 19.8; H, 6.02; N, 12.2; Cr, 21.3; oxidation equiv, 1.7 maximum; reduction equiv, 2.8 maximum. Determinations of both oxidation and reduction equivalents gave highly variable results, apparently due to thermal decomposition.

The olive-green solid turned golden brown in several hours at 20–25° but can be kept for several days at 0° in the dark. It exploded at 83–84° when heated from 20–25° at 2°/min. *Caution:* this compound is potentially explosive at 25°.

Diperoxotriamminechromium(IV).—The compound was made by the method of Kauffman and Acero,[7] for spectral comparison purposes. We have not determined its explosive properties quantitatively, but the compound is explosive.

Attempted Synthesis of Other Diperoxo Amines.—One or the other of the following two methods was used in unsuccessful attempts to prepare diperoxo complexes with the amines methylamine, dimethylamine, trimethylamine, diethylamine, *n*-butylamine, *t*-butylamine, *n*-hexylamine, cyclohexylamine, 1,3-diaminopropane, N-methylethylenediamine, N-ethylethylenediamine, N,N-dimethylethylenediamine, N,N′-dimethylethylenediamine, N,N-diethylethylenediamine, N,N′-diethylethylenediamine, N,N,N′,N′-tetraethylethylenediamine, N-acetylethylenediamine, 1,6-diaminohexane, stilbenediamine, 1,2-diaminocyclohexane (75% *trans*–25% *cis* mixture), 2-aminoethyl-1,3-propanediamine, dipropylenetriamine, triethylenetetramine, hexamethylenetetramine,[8] pyridine, 2-aminopyridine, 2,2′-dipyridyl, guanidine, and 2-(2-aminoethylamino)ethanol. Mention should be made that no diperoxo compound could be obtained with acetylacetone either.

In one method, solutions of CrO_3 (10 g in 100 ml of water) and H_2O_2 (30 ml of 30%) were slowly added from separate dropping funnels to a stirred slurry of water, crushed ice, and the amine. The mixture was then stirred at various temperatures for various intervals and finally placed in a refrigerator to crystallize. In many cases a blue precipitate formed which was allowed to decompose *in situ*. However, no diperoxo compounds could be isolated.

In the other method, aqueous solutions of CrO_3 and the amine were cooled to 0° and the precipitated amine chromate(VI) was filtered off. The filtrate was frozen, then 30% H_2O_2 was added, and the mixture was allowed to thaw and was then stored for 1–3 days at −10 or −20°. Blue solids or mixtures of blue solids and yellow chromates were often obtained, but diperoxo compounds were not isolated.

Triaquoammineethylenediaminechromium(III) Cation.—About 50 mg of $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ was dissolved in 100 ml of 1 *F* $HClO_4$ and the solution warmed to 50° for 1 hr. Substantially this same procedure was found earlier[2,9] to produce essentially quantitatively the aquo cations $Cr(en)(OH_2)_4^{3+}$ and $Cr(dien)(OH_2)_3^{3+}$ from $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ and $[Cr(dien)(O_2)_2]\cdot H_2O$, respectively. To verify the formation of $Cr(en)(NH_3)(OH_2)_3^{3+}$, we put half of the above solution on a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at 20–25°. The resulting red band was eluted with 100 ml of 3 *F* $HClO_4$, as expected for a 3+ ion of this size, giving a burgundy effluent having a visible absorption spectrum identical, except for 5% lower absorbancies, with the spectrum of the original solution. The configuration of the new triaquo complex is unknown.

Tetraaquopropylenediaminechromium(III) Cation.—This new complex was prepared from $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$ in the same way as described above for $Cr(en)(NH_3)(OH_2)_3^{3+}$, and its 3+ charge was similarly verified.

Anal. Calcd for $Cr(pn)(OH_2)_4^{3+}$: N/Cr atom ratio, 2.00. Found for chromatographed complex: N/Cr atom ratio, 1.99, 2.02.

Tetraaquoisobutylenediaminechromium(III) Cation.—This new complex was made in the same way as $Cr(en)(NH_3)(OH_2)_3^{3+}$ above except that $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$ was used; chromatography verified the 3+ charge of the species. Like $Cr(pn)(OH_2)_4^{3-}$, moderately concentrated (0.05 *F*) solutions of $Cr(ibn)(OH_2)_4^{3+}$ have a burgundy color which becomes reddish pink on dilution 10–1000 times.

Violet-Blue Dichloroaquoammineethylenediaminechromium(III) Chloride.—Six grams of $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$ was slurried with 10 ml of water and poured in *ca.* 50-mg portions into 20 ml of 12 *F* HCl. After effervescence ceased, the resulting solution was saturated with HCl gas at 60°, then cooled to 0°, and resaturated with HCl. After the mixture stood 10–12 hr at −10°, it was filtered and the violet-blue crystals obtained were washed with 1:1 ethanol–water, then with acetone and ether; yield, 3 g (42%).

Anal. Calcd for $[Cr(en)(NH_3)(OH_2)Cl_2]Cl$: C, 10.2; H, 4.71; N, 16.5; Cr, 20.52; Cl, 42.0. Found: C, 9.7; H, 5.06; N, 16.1; Cr, 20.50; Cl, 41.7.

Despite the generally good chemical analyses above, chromatography as follows suggests that the material is not 100% pure. Dissolution in 0.01 *F* $HClO_4$ and adsorption on a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 20–25°, followed by elution with 100 ml of 0.3 *F* $HClO_4$ (which quantitatively elutes the blue isomer of $Cr(en)(OH_2)_2Cl_2^+$, as reported earlier,[2] and which would be expected to elute quantitatively the analogous isomer of $Cr(en)(NH_3)(OH_2)Cl_2^-$), left two very faint bands on the column. One of these bands was eluted by 150 ml of 3 *F* $HClO_4$ and may represent $Cr(en)(NH_3)(OH_2)_3^{3+}$; the solution was too dilute to obtain a visible absorption spectrum. The remaining faint band was green. The geometric configuration of the new dichloro complex is unknown but probably is the same as that (also unknown) of the blue isomer of $Cr(en)(OH_2)_2Cl_2^+$ (see Results).

Green-Blue Trichloroaquopropylenediaminechromium(III).—Six grams of $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$ was added in 50-mg portions to 10 ml of 12 *F* HCl. Effervescence occurred and the temperature of the solution rose to 35–40°. The violet solution was evaporated nearly to dryness on a water bath at 35° under a stream of air, then transferred to a vacuum line for 24 hr at 0.01 torr for final evaporation to a purple solid; yield, 7 g (100%). Since chemical analyses for C, H, and Cr did not correspond to a single pure compound, 100 mg of the solid was dissolved in 10 ml of 0.01 *F* $HClO_4$, adsorbed on a 20-cm × 2-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh), and subjected to successive elutions with increasing concentrations of $HClO_4$, yielding five bands.

The band eluted first (100 ml of 0.01 *F* $HClO_4$) gave a greenish blue effluent of a neutral or anionic species. Passage through a 6-cm × 1-cm diameter column of NO_3^- Dowex AG2-X8 anion-exchange resin (100–200 mesh) without any adsorption of color

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[6] Probably the chromium(VI) complex, $Cr(ibn)(O_2)_2O$; compounds of this type are dangerously explosive, and no attempt should be made to isolate the blue compound without adequate safety precautions.

[7] G. B. Kauffman and G. Acero, *Inorg. Syn.*, **8**, 132 (1966).

[8] In our attempted synthesis, orange crystals of what was probably hexamethylenetetraammonium tetraperoxochromate(V), possibly $[(CH_2)_6(NH)_4]_3[Cr(O_2)_4]_4$, were formed and recrystallized from water, then washed with methanol; as the material was being sucked dry on a filter funnel, the crystals began to glow as the cake was touched with a stirring rod, and within seconds exploded mildly. For this reason, further study of the reaction was abandoned. K. A. Hoffman, *Ber.*, **39**, 3181 (1906), has reported isolating by a similar method a "reddish brown-yellow" diperoxochromium compound with hexamethylenetetramine. E. A. V. Ebsworth and R. G. Hughes, unpublished research, have similarly synthesized a red material which gave C, H, and N analyses in reasonably good agreement with the formula $Cr(hexamine)(O_2)_2$; however, its magnetic moment is much lower than expected for a true diperoxochromium(IV) compound, and it seems doubtful whether such a compound of hexamethylenetetramine has yet been made.

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

showed the complex was not anionic and also served to remove free Cl^- so that a meaningful Cl/Cr atom ratio could be determined; a ratio of 3.06 was found, in good agreement with the value 3.00 expected for the neutral complex $Cr(pn)(OH_2)Cl_3$. The geometric configuration of the new complex is unknown. About 30% of the original solid appears to be this neutral complex.

Following elution of the green-blue $Cr(pn)(OH_2)Cl_3$, 200 ml of 0.03 *F* $HClO_4$ was passed through the column without the appearance of color in this effluent. Then 100 ml of 0.1 *F* $HClO_4$ gave a green effluent having a Cl/Cr atom ratio of 2.06 and a visible absorption spectrum apparently identical with that reported[10] for *cis*-$Cr(OH_2)_4Cl_2^+$; moreover, the complex aquated with about the rate reported for the *cis*-dichloro cation. This species was present to the extent of *ca.* 5% of the Cr in the original purple solid.

Purple Dichlorodiaquopropylenediaminechromium(III) Cation.—After elution of *cis*-$Cr(OH_2)_4Cl_2^+$ in the above synthesis, 100 ml of 0.3 *F* $HClO_4$ was passed through the column, giving a purple effluent with a Cl/Cr atom ratio of 2.07. This elution behavior is that expected for at least one isomer of $Cr(pn)(OH_2)_2Cl_2^+$, presumably the analog of the blue isomer of $Cr(en)(OH_2)_2Cl_2^+$, originally prepared as the Cl^- salt by Weinmann[11] using an unrelated method and later made by House and Garner[2,9] by dissolution of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in 12 *F* HCl and evaporation to dryness. The new complex $Cr(pn)(OH_2)_2Cl_2^+$, of unknown geometric configuration, constitutes about 30% of the original purple solid.

Following elution of this complex, 100 ml of 1 *F* $HClO_4$ was passed through the column without color appearing in the effluent.

Magenta Chlorotriaquopropylenediaminechromium(III) Cation.—Following the elution with 1 *F* $HClO_4$ above, 100 ml of 3 *F* $HClO_4$ was passed through the column. This effluent was magenta and had a Cl/Cr atom ratio of 1.02. The elution behavior is compatible with the species being an isomer of the new complex $Cr(pn)(OH_2)_3Cl^{2+}$. The mode of formation and the visible absorption spectrum (see Results) are similar to those of a magenta isomer of $Cr(en)(OH_2)_3Cl^{2+}$ and the spectrum is substantially different from that of the other (purple) isomer of $Cr(en)(OH_2)_3Cl^{2+}$.[12] The new complex appears to be about 20% of the original solid, depending upon the particular batch prepared. After elution of the new complex, 100 ml of 6 *F* $HClO_4$ was passed through the column without the appearance of color in the effluent; a green band (presumably some polymeric species) was left on the column.

Green Trichloroaquoisobutylenediaminechromium(III).—A purple solid, evidently impure as judged from C, H, and Cr analyses, was obtained in *ca.* 100% yield from $[Cr(ibn)(OH_2)(O_2)_2]\cdot 2H_2O$ and 12 *F* HCl by a procedure analogous to the one used above in making the green-blue trichloroaquopropylenediaminechromium(III). A similar chromatographic separation was made. The first band, eluted with 150 ml of 0.01 *F* $HClO_4$, gave a green effluent, which after passage through an NO_3^- Dowex AG2-X8 column (no adsorption of color) gave a Cl/Cr atom ratio of 2.92. Thus this species is a new neutral complex, $Cr(ibn)(OH_2)Cl_3$, an analog, but not necessarily of the same geometric configuration, of the green-blue $Cr(pn)(OH_2)Cl_3$. About 30–40% of the original solid appeared to be this species.

Further elution, with 100 ml of 0.05 *F* $HClO_4$, gave a colorless effluent but left on the column one band which was subsequently developed into five bands. Green *cis*-$Cr(OH_2)_4Cl_2^+$ (Cl/Cr atom ratio of 2.01 and visible absorption spectrum identification) was then eluted with 200 ml of 0.075 *F* $HClO_4$, after which 100 ml of 0.1 *F* $HClO_4$ passed through the column gave a colorless effluent.

Purple Dichlorodiaquoisobutylenediaminechromium(III) Cation.—Following the last eluent above, 100 ml of 0.3 *F* $HClO_4$ was used to elute the next band. This effluent was purple, had a Cl/Cr atom ratio of 2.07, and contained about 35–40% of the Cr in the original solid taken for chromatography. This species appears to be the new complex $Cr(ibn)(OH_2)_2Cl_2^+$, probably of the same (unknown) geometric configuration as the purple isomer of $Cr(pn)(OH_2)_2Cl_2^+$ and the blue isomer of $Cr(en)(OH_2)_2Cl_2^+$.

Subsequent passage of 100 ml of 0.5 *F* $HClO_4$ through the column failed to elute any color, but 100 ml of 1 *F* $HClO_4$ eluted a greenish blue band, giving an almost colorless effluent which was too dilute to characterize but which may be $Cr(OH_2)_5Cl^{2+}$.

Magenta Chlorotriaquoisobutylenediaminechromium(III) Cation.—After elution of the apparent $Cr(OH_2)_5Cl^{2+}$ above, 100 ml of 3 *F* $HClO_4$ was used to elute a dark magenta band, giving a magenta effluent having a Cl/Cr atom ratio of 1.12 and containing about 20–25% of the Cr in the solid taken for chromatography. This species appears to be a magenta isomer of the new complex $Cr(ibn)(OH_2)_3Cl^{2+}$, possibly of the same (unknown) geometric configuration as the magenta isomers of $Cr(pn)(OH_2)_3Cl^{2+}$ and $Cr(en)(OH_2)_3Cl^{2+}$ (*vide ante* and Results).

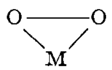
A very faint green band (polymeric species) was left on the column after the passage of 200 ml of 6 *F* $HClO_4$, which eluted no color.

Chemical Analyses.—Chromium was determined by spectrophotometric analysis of CrO_4^{2-} at 372 mμ after decomposition of the complexes and oxidation with hot alkaline peroxydisulfate or alkaline peroxide. Chloride was determined on the decomposed complexes gravimetrically as the Ag^+ salt or by potentiometric microtitration with $AgNO_3$. Oxidation and reduction equivalents of the diperoxo compounds were determined as described earlier.[2] Standard microanalytical procedures, mainly carried out by Miss Heather King, were used to determine C, H, and N on the solids. A micro-Kjeldahl method was used in determining N of one solution.

Spectrophotometry.—Visible absorption spectra were measured at 20–25° with a Cary Model 15 or Model 11 recording spectrophotometer, using matched 10.00-cm quartz cells, with the reference cell filled with water; spectra of the diperoxo compounds were also run in KBr disks *vs.* air. A Beckman DU spectrophotometer was used for Cr analyses. Infrared spectra were determined in KBr disks using a Perkin-Elmer Model 421 spectrophotometer.

Results

Diperoxoaminechromium(IV) Compounds.—Three new chromium(IV) diperoxoamines have been synthesized and characterized, namely, $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$, $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$, and $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$; this brings the total number of such nonsalt-like chromium(IV) compounds to six (seven, if the doubtful hexamethylenetetramine compound[8] is included). The Cr(IV) state of these new compounds was established by determination of oxidation and reduction equivalents. The presence of peroxo ligands is also indicated by infrared spectra recorded in KBr disks. The bands at *ca.* 900 cm^{-1} (Table I) have previously been assigned in other peroxo compounds to an O–O stretching vibration.[13] In the light of the work of Vaska[14] and Ibers[15] on O_2 adducts of iridium compounds, these bands must now be assigned to a concerted vibration of the



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[10] E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

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

[12] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.*, in press.

[13] W. P. Griffith, *J. Chem. Soc.*, 3948 (1962).

[14] S. Vaska, *Science*, **140**, 809 (1963).

[15] S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965); also personal communication.

TABLE I

INFRARED BANDS IN THE 800–900-CM^{-1} REGION FOR DIPEROXOAMINECHROMIUM(IV) COMPOUNDS (KBr DISK)

Compound	$\tilde{\nu}$, cm^{-1}
$Cr(NH_3)_3(O_2)_2$[a]	887
$[Cr(en)(NH_3)(O_2)_2] \cdot H_2O$[b]	860, 875, 885 (triplet)
$[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$[b]	885
$[Cr(pn)(OH_2)(O_2)_2] \cdot 2H_2O$[b,c]	880
$[Cr(ibn)(OH_2)(O_2)_2] \cdot H_2O$[b]	865
$[Cr(dien)(O_2)_2] \cdot H_2O$[d]	870, 885 (doublet)
"$[Cr(hexamine)(O_2)_2]$"[a,e]	830, 850

[a] E. A. V. Ebsworth and R. G. Hughes, unpublished research. [b] This research. [c] Reference 4. [d] D. A. House and C. S. Garner, *Nature*, **208,** 776 (1965). [e] See footnote 8.

group as a whole. Hence, the triplet in the infrared spectrum of $[Cr(en)(NH_3)(O_2)_2] \cdot H_2O$ given in Table I is not anomalous. A moderately strong band was found at 930 cm^{-1} in the infrared spectra of all preparations of $[Cr(ibn)(OH_2)(O_2)_2] \cdot H_2O$, apparently from Cr=O stretching vibrations in a CrO_4^{2-} impurity present.

The near-ultraviolet and visible absorption spectra of the new diperoxo compounds were recorded in freshly prepared 1 *F* NH_4OH solutions (Table II) since these spectra did not vary appreciably with time at 20–25°, whereas in water (except for the diethylenetriamine compound and, to a lesser extent, the propylenediamine compound) the spectra changed with time. The spectra of $Cr(NH_3)_3(O_2)_2$, $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$, and $[Cr(dien)(O_2)_2] \cdot H_2O$ are included for comparison purposes. Proton loss from the water ligand of the diperoxoaquoamine compounds probably was negligible in 1 *F* NH_4OH, inasmuch as spectra taken in KBr disks were very similar to the spectra in 1 *F* NH_4OH, although not as well resolved. The visible absorption spectrum of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$ was also taken in a KCl disk, giving a spectrum identical, except for poorer resolution, with that in a KBr disk; after the spectrum was taken in KBr, the disk was dissolved in 1 *F* NH_4OH, giving a spectrum nearly the same as that of the parent diperoxo compound directly dissolved in 1 *F* NH_4OH. This suggests the compounds did not appreciably decompose in either fresh 1 *F* NH_4OH solution or in KBr disks. The low symmetry of the compounds splits the d levels into unknown configurations and would make assignment of the bands especially difficult. The band at *ca.* 250 mμ is probably due to charge transfer from the peroxo groups to the metal. The similarity of the spectra further supports the close chemical relationship among these compounds.

TABLE II

ABSORPTION MAXIMA AND MINIMA IN THE 220–700-mμ RANGE OF DIPEROXOAMINECHROMIUM(IV) COMPOUNDS IN 1 *F* NH_4OH AT 20–25°

Compound	λ, mμ	a_M, M^{-1} cm^{-1} [a]
$Cr(NH_3)_3(O_2)_2$[b]	256 (max)	5380
	370 (max)	549
$[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$[c]	230 (min)	4110
	250 (max)	4960
	340 (min)	441
	370 (max)	504
	500 (min)	24.4
	525 (max)	25.2
	590 (sh)	22.2
$[Cr(en)(NH_3)(O_2)_2] \cdot H_2O$[c]	230 (min)	4080
	252 (max)	4970
	355 (min)	362
	382 (max)	432
	495 (min)	28.8
	510 (sh)	26.7
	620 (sh)	17.0
$[Cr(pn)(OH_2)(O_2)_2] \cdot 2H_2O$[d]	235 (min)	4480
	255 (max)	5060
	342 (min)	430
	370 (max)	457
	498 (min)	24.4
	525 (max)	25.3
	590 (sh)	23.4
$[Cr(ibn)(OH_2)(O_2)_2] \cdot H_2O$[c]	235 (min)	3860
	252 (max)	4520
	335 (min)	392
	373 (max)	460
	515 (sh)	24.0
	590 (sh)	17.9
$[Cr(dien)(O_2)_2] \cdot H_2O$[e]	235 (min)	4880
	250 (max)	5400
	355 (min)	415
	382 (max)	460
	485 (min)	38.8
	520 (max)	41.5
	570 (min)	38.5
	610 (max)	38.6

[a] Molar absorbancy index (extinction coefficient ε), defined by $A = \log (I_0/I) = a_M dc$, where c is the molarity of absorbing complex and d is the optical path in centimeters. [b] E. A. V. Ebsworth and R. G. Hughes, unpublished research; spectrum invariant in 0.1–15 *F* NH_4OH. [c] This research. [d] Reference 4. [e] D. A. House and C. S. Garner, *Nature*, **208,** 776 (1965); spectrum in H_2O.

Aquo Complexes.—Dissolution of the new diperoxo compounds in 1 *F* $HClO_4$, followed by gentle warming, produces the corresponding chromium(III) aquo complexes apparently quantitatively. When $[Cr(ibn)(OH_2)(O_2)_2] \cdot H_2O$ was dissolved in 0.1 *F* $HClO_4$, however, only about 30% of the Cr was found as $Cr(ibn)(OH_2)_4^{3+}$, most of the Cr being present as CrO_4^{2-}. Like $Cr(en)(OH_2)_4^{3+}$ [2,16] and *trans*-$Cr(dien)(OH_2)_3^{3+}$,[17] $Cr(pn)(OH_2)_4^{3+}$, $Cr(ibn)(OH_2)_4^{3+}$, and $Cr(en)(NH_3)(OH_2)_3^{3+}$ all aquate very slowly in 0.1–3 *F* $HClO_4$ at 25°.

The maxima and minima of the near-ultraviolet and visible absorption spectra of these new aquo ions are tabulated in Table III, along with values for the previously known analogs. All of these spectra are similar to one another, as would be expected from ligand field theory. The spectrum of $Cr(en)(NH_3)(OH_2)_3^{3+}$ resembles the spectra of the 1,2,3-triaquo complexes of Table III more than it does the spectrum of 1,2,6-$Cr(dien)(OH_2)_3^{3+}$; however, since we have no information on the visible absorption spectrum of the other theoretically possible geometric isomer of $Cr(en)(NH_3)(OH_2)_3^{3+}$, we prefer to regard as unknown the geometric configuration of the isomer we have synthesized.

Chloroaquo Complexes.—Various chloroaquo complexes of chromium(III) were obtained, in most cases

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(16) R. F. Childers, K. G. Vander Zyl, Jr., D. A. House, and C. S. Garner, unpublished research.

(17) D. K. Lin and C. S. Garner, unpublished research.

TABLE III

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

Complex	$[HClO_4]$, F	λ, mμ	a_M, M^{-1} cm^{-1} [a]
1,2,3-$Cr(NH_3)_3(OH_2)_3^{3+}$ [b,c]	2	375 (max)	22.2
		432 (min)	6.5
		518 (max)	34.5
$Cr(en)(NH_3)(OH_2)_3^{3+}$ [d,e]	1	380 (max)	29.0
		428 (min)	13.9
		502 (max)	41.5
1,2,3-$Cr(dien)(OH_2)_3^{3+}$ [b,f]	2	375 (max)	39
		430 (min)	17
		510 (max)	73
1,2,6-$Cr(dien)(OH_2)_3^{3+}$ [f,g]	1	390 (max)	31
		440 (min)	16
		518 (max)	53
$Cr(en)(OH_2)_4^{3+}$ [h]	1	387 (max)	22.0
		428 (min)	10.7
		517 (max)	32.0
$Cr(pn)(OH_2)_4^{3+}$ [d]	1	383 (max)	24.4
		438 (min)	11.6
		515 (max)	36.0
$Cr(ibn)(OH_2)_4^{3+}$ [d]	1	390 (max)	11.9
		440 (min)	9.7
		518 (max)	29.0
Purple $Cr(en)(OH_2)_3Cl^{2+}$ [e,i]	2	335 (min)	3
		420 (max)	46
		480 (min)	19
		567 (max)	72
Magenta $Cr(en)(OH_2)_3Cl^{2+}$ [e,i]	2	402 (max)	30.5
		458 (max)	14.1
		535 (max)	38.9
Magenta $Cr(pn)(OH_2)_3Cl^{2+}$ [d,e]	3	405 (max)	23.4
		450 (min)	10.7
		540 (max)	31.8
Magenta $Cr(ibn)(OH_2)_3Cl^{2+}$ [d,e]	3	402 (max)	33.5
		460 (min)	13.7
		535 (max)	35.6
Violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^{+}$ [d,e]	0.3	420 (max)	32.1
		460 (min)	22.8
		510 (max)	31.3
		560 (min)	25.0
		585 (max)	26.4
Blue $Cr(en)(OH_2)_2Cl_2^{+}$ [h,e]	0.1	420 (max)	22.7
		475 (min)	16.3
		550 (sh)	37.6
		580 (max)	39.1
Purple $Cr(pn)(OH_2)_2Cl_2^{+}$ [d,e]	0.3	420 (max)	29.5
		480 (min)	15.8
		555 (sh)	38
		580 (max)	39.6
Purple $Cr(ibn)(OH_2)_2Cl_2^{+}$ [d,e]	0.3	420 (max)	30.3
		480 (min)	19.3
		560 (max)	42.9
		585 (sh)	40
Green-blue $Cr(pn)(OH_2)Cl_3$ [d,e]	0.01	454 (max)	42.6
		510 (min)	28
		591 (max)	55.5
Green $Cr(ibn)(OH_2)Cl_3$ [d,e]	0.01	450 (max)	26.9
		530 (min)	8.3
		625 (max)	18.4

[a] Footnote *a*, Table II. [b] The *cis*, or facial, isomer in which all three like ligands are *cis* to one another. [c] C. E. Shäffer and P. Andersen, "Proceedings of the Wroclaw Symposium," Pergamon Press Ltd., London, 1964, pp 571–582. [d] This research. [e] Geometric configuration unknown. [f] The 1,2,3 and 1,2,6 isomers of $Cr(dien)(OH_2)_3^{3+}$ were synthesized from green 1,2,3- and 1,2,6-$Cr(dien)Cl_3$, respectively, by D. A. House, *Inorg. Nucl. Chem. Letters*, **3**, 67 (1967), and unpublished research; the purple $Cr(dien)Cl_3$ is the same compound described in ref 2 as mauve $Cr(dien)Cl_3$, and the $Cr(dien)(OH_2)_3^{3+}$ species obtained from $[Cr(dien)(O_2)_2]\cdot H_2O$ and tentatively characterized as the *cis* isomer in ref 2 appears to be the 1,2,6 or *trans* isomer, or possibly a mixture of the *cis* and *trans* isomers with the latter predominating. [g] The *trans*, or peripheral, isomer in which two of the three like ligands are *trans* to one another. [h] Reference 2. [i] Reference 12.

by chromatographic separation, by treatment of the new diperoxo complexes with hydrochloric acid.

Two new chlorotriaquo complexes were synthesized, namely, the magenta $Cr(pn)(OH_2)_3Cl^{2+}$ and $Cr(ibn)(OH_2)_3Cl^{2+}$. Their colors and visible absorption spectra (Table III) are very similar to those of magenta $Cr(en)(OH_2)_3Cl^{2+}$ [12] and substantially different from those of the purple isomer of $Cr(en)(OH_2)_3Cl^{2+}$.[12] One might be led from this to postulate that all three magenta chlorotriaquo complexes have the same geometric configuration; however, although the ethylenediamine complex can exist in only two geometric configurations, the propylenediamine and isobutylenediamine complexes can exist theoretically in four geometric configurations, so without kinetic or other evidence we cannot exclude the possibility that the latter complexes could be mixtures of two or more isomers. The magenta $Cr(ibn)(OH_2)_3Cl^{2+}$ in 3 F $HClO_4$ hydrolyzes to $Cr(ibn)(OH_2)_4^{3+}$ in 2–3 days at 20–25°.

Three new dichloro complexes were obtained, namely, the violet-blue $Cr(en)(NH_3)(OH_2)Cl_2^+$, purple $Cr(pn)(OH_2)_2Cl_2^+$, and purple $Cr(ibn)(OH_2)_2Cl_2^+$. Their visible absorption spectra (Table III) are similar to the spectrum[2] of blue $Cr(en)(OH_2)_2Cl_2^+$. Since the latter can theoretically exist in three geometric isomeric forms and the former in four, six, and six geometric configurations, respectively, it is not possible without kinetic or other evidence to decide that these all represent the same geometric configuration. The ammine complex undergoes appreciable spectral change in 0.3 F $HClO_4$ within 24 hr at 20–25°. The isobutylenediamine complex in 0.3 F $HClO_4$ changes its spectrum to that of magenta $Cr(ibn)(OH_2)_3Cl^{2+}$ in several hours at 20–25°, with the existence of isosbestic points, and hence is probably not a mixture of isomers.

Two new neutral trichloroaquo complexes were synthesized, namely, green-blue $Cr(pn)(OH_2)Cl_3$ and green $Cr(ibn)(OH_2)Cl_3$. Their visible absorption spectra are indicated in Table III; these are sufficiently different so as to suggest that these complexes either are not isomerically pure or do not have the same geometric configuration. Both spectra represent an extrapolation to zero time. The former complex rapidly hydrolyzes in 0.01 F $HClO_4$ at 20–25°, an estimated half-life being about 20 min. The latter complex hydrolyzes under the same conditions with a half-life estimated as *ca.* 1

hr; isosbestic points were observed except for the first spectral scan at 5 min and a much later scan taken after 24 hr, so the complex may be a mixture of isomers.

Discussion

Two of the new diperoxo compounds, $[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O$ and $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$, are strict analogs of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$.[2] The third, $[Cr(en)(NH_3)(O_2)_2]\cdot H_2O$, is a strict analog of $[Cr(dien)(O_2)_2]\cdot H_2O$.[18] As judged from their explosion temperatures, the order of decreasing stability of these compounds is $en(NH_3) \sim dien > en(OH_2) >> pn(OH_2) \sim ibn(OH_2)$. Spontaneous explosions have occurred at 20–25° with the propylenediamine compound, and the isobutylenediamine compound is very difficult to obtain free of CrO_4^{2-}.

No further compounds of this type could be obtained with various primary, secondary, or tertiary aliphatic amines, N-substituted ethylenediamines, diamines not capable of forming five-membered rings, or aromatic amines (see Experimental Section). Blue solids, presumably analogs of $Cr(amine)(O_2)_2O$, were often formed in the course of the attempted syntheses, but these were not isolated since they are highly explosive. Attempts to enhance the decomposition of the presumed $Cr(ibn)(O_2)_2O$ and $Cr(1,2\text{-diaminocyclohexane})(O_2)_2O$ to desired products, by the action of CrO_3 or H_2O_2 in the former case and by dissolution in acetone and addition of excess amine in the latter case, failed; in the latter case only the amine chromate(VI) was obtained.

The crystal structures[19] of $Cr(NH_3)_3(O_2)_2$ and $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ show that considerable hydrogen bonding occurs. This addition to the lattice energy may be vital to the stabilization of these compounds in the solid state. Modification of the amine can considerably reduce the opportunity for this hydrogen bonding, so that some of these compounds are much less stable than others or are not formed at all. It is especially interesting that the 1,2-diaminocyclohexane compound was not obtained in spite of repeated attempts, nor the stilbenediamine compound in one attempt.

The decomposition of $Cr(NH_3)_3(O_2)_2$ at slightly elevated temperatures has been shown[20] to occur about 95% *via* the reaction

$$Cr(NH_3)_3(O_2)_2(s) = {}^1/_2Cr_2O_3(s) + 3NH_3(g) + {}^5/_4O_2(g) \quad (1)$$

With the aid of a rough calculation of 100 ± 100 kcal/mole for the standard enthalpy of formation of $Cr(NH_3)_3(O_2)_2(s)$ at 298°K, we estimate $\Delta H^\circ_{298} = 200 \pm 100$ kcal for reaction 1. The other diperoxoamines are probably even less stable than $Cr(NH_3)_3(O_2)_2$.

The reactions by which a variety of chloroaquo complexes of chromium(III) amines have been produced from the treatment of the diperoxoaminechromium(IV) compounds with hydrochloric acid are not well understood. The apparent presence of *cis*-$Cr(OH_2)_4Cl_2^+$ in certain chromatographed fractions in the isolation of chloroaquo complexes of the propylenediamine and isobutylenediamine complexes (see Experimental Section) probably originates from side reactions in which some CrO_4^{2-} is formed in the dissolution of the diperoxo compounds in hydrochloric acid; *e.g.*

$$2[Cr(pn)(OH_2)(O_2)_2]\cdot 2H_2O = 4H^+ + 2CrO_4^{2-} + 2pn + O_2 + 4H_2O \quad (2)$$

$$16H^+ + 2CrO_4^{2-} + 10Cl^- = 2\textit{cis}\text{-}Cr(OH_2)_4Cl_2^+ + 3Cl_2 \quad (3)$$

Support for possible reactions of this kind is found in the fact that Cl_2 was detected, as well as an odor of amine after removal of the Cl_2 and HCl. The possible presence of $Cr(OH_2)_5Cl^{2+}$ in one chromatographed faction could be accounted for by fairly rapid aquation of the *cis*-$Cr(OH_2)_4Cl_2^+$. Moreover, dissolution of $[Cr(ibn)(OH_2)(O_2)_2]\cdot H_2O$ in 0.1 *F* $HClO_4$ gives largely CrO_4^{2-}.

In the first paper of this series,[2] we expressed the hope that diperoxoaminechromium(IV) compounds might become useful precursors of numerous chromium(III) amine complexes. To some extent this hope has been fulfilled. However, the number of possible diperoxoaminechromium(IV) compounds now appears to be rather limited, and such compounds must be handled with great caution because of their potential explosive properties. Moreover, except for the aquo ions, the various chromium(III) amine complexes synthesized to date by this general method of dissolution of the diperoxo compounds in hydrochloric acid have usually not been pure and have required somewhat tedious ion-exchange chromatographic techniques for separation into pure species, which have then been present only in dilute solutions.

Nevertheless, these complexes are now available in a form suitable for kinetic study of their hydrolysis and anation reactions, and it is our plan to investigate such kinetics.

We are also investigating the interaction of other acids with the less explosive of these diperoxo compounds.

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[18] D. A. House and C. S. Garner, *Nature*, **208**, 776 (1965).

[19] R. Stomberg, *Arkiv Kemi*, **22**, 29, 49 (1964); **23**, 401 (1965); **24**, 47, 111 (1965). The structures have been described as deformed pentagonal bipyramids, with the two peroxo groups and one nitrogen atom forming the base of the pyramid while the two remaining nitrogen atoms of the ammine complex, or one remaining nitrogen atom and the ligand water oxygen atom of the ethylenediamine complex, occupy the apical positions; the question of the coordination number of Cr(IV) in such complexes remains unresolved.

[20] E. A. V. Ebsworth and R. G. Hughes, unpublished research.