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The Use of Chromium(IV) Diperoxo Amines in the Synthesis of Chromium(III) Amine Complexes. I. Some Monoethylenediamine and Monodiethylenetriamine Complexes[1]

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The chromium(IV) diperoxo compound $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ reacts with concentrated HCl to give blue $[Cr(en)(OH_2)_2Cl_2]Cl$ and with NH_4HF_2 in 2 *F* HF solution to give sky-blue $NH_4[Cr(en)F_4]$. In 0.5–3 *F* $HClO_4$ this diperoxo compound decomposes to give the pink $Cr(en)(OH_2)_4{}^{+3}$ ion, and magenta $NH_4[Cr(en)(C_2O_4)_2]\cdot NH_4HC_2O_4\cdot H_2O$ can be obtained by addition of $(NH_4)_2C_2O_4\cdot H_2O$. The chromium(IV) diperoxo compound $[Cr(dien)(O_2)_2]\cdot H_2O$ reacts with concentrated HCl to give mauve, water-insoluble $Cr(dien)Cl_3$ and decomposes in 1 *F* $HClO_4$ at 40° to give the pink $Cr(dien)(OH_2)_3{}^{+3}$ ion (probably the *cis* form). Maxima and minima of previously unreported visible absorption spectra are presented.

The synthesis of chromium(III) polyamine complexes is remarkably difficult when compared to the ease with which the corresponding cobalt(III) compounds can be obtained. The reactions between the anhydrous amines and anhydrous chromium(III) chloride have been extensively investigated, $[Cr(en)_3]X_3$,[2,3] $[Cr(pn)_3]X_3$,[3] $[Cr(dien)_2]I_3$,[4] *cis*-α-$[Cr(trien)Cl_2]Cl$,[4,5] $[Cr(tmd)_3]X_3$,[6] $[Cr(dpt)_2]I_3$,[4] $Cr(ibn)_3{}^{+3}$ cation,[7] and polymeric $\{[Cr(H_2N(CH_2)_nNH_2)_2Cl_2]Cl\}_x$,[8] where n = 4, 5, 6, and 7, having been prepared by this method, but only the complexes with six chromium–nitrogen bonds (or four nitrogens plus two chlorines bonded to the chromium atom, in the case of the trien complex) have been obtained, as excess amine is required. An alternative synthetic route *via* air oxidation of the chromium(II) complexes has received little attention, but may become more popular now that chromium(II) complexes and salts can be relatively easily prepared.[9–15]

We describe in this paper our attempts to exploit the method first used by Werner[16,17] in his preparation of the neutral trichlorotriamminechromium(III) and the three isomers of dichloroaquotriamminechromium(III) cation,[18–22] namely, by reaction of diperoxotriamminechromium(IV)[23] with hydrochloric acid.

We have found that diperoxoaquoethylenediaminechromium(IV) monohydrate, $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$,[24–27] reacts readily with concentrated hydrochloric acid to give blue dichlorodiaquoethylenediaminechromium(III) chloride, $[Cr(en)(OH_2)_2Cl_2]Cl$, a compound previously isolated by Weinmann[28,29] from the reaction between oxalatobis(ethylenediamine)chromium(III) dioxalatoethylenediaminechromate(III), $[Cr(en)_2C_2O_4][Cr(en)(C_2O_4)_2]$, and concentrated hydrochloric acid. We report here also the use of this diperoxo compound in the synthesis of the ammonium salts of tetrafluoroethylenediaminechromate(III) and dioxalatoethylenediaminechromate(III) anions, as well as in the preparation of tetraaquoethylenediaminechromium(III) cation.

In addition we report the use of the recently synthesized diperoxodiethylenetriaminechromium(IV) monohydrate[30] to prepare trichlorodiethylenetriaminechromium(III) and triaquodiethylenetriaminechromium(III) cation.

Experimental Section

Diperoxoaquoethylenediaminechromium(IV) Monohydrate.—This compound was synthesized originally by Hoffman.[24] We have repeated Hoffman's synthesis with some modifications on a 6–8-g scale and adapted the method for the production of larger quantities.

Technical grade (J. T. Baker Co.) CrO_3 (10 g) was dissolved in 250 ml of water and 250 ml of ice in an 800-ml beaker, and 10 ml of 95–100% ethylenediamine (Eastman Kodak Co.) was added. The beaker was placed in an ice–salt bath and 30 ml of

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(2) Abbreviations used: en = ethylenediamine, $H_2NCH_2CH_2NH_2$; pn = propylenediamine, $H_2NCH_2CH(CH_3)NH_2$; ibn = isobutylenediamine, $H_2NCH_2C(CH_3)_2NH_2$; dien = diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$; trien = triethylenetetramine, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$; tmd = trimethylenediamine, $H_2NCH_2CH_2CH_2NH_2$; dpt = dipropylenetriamine, $H_2NCH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$.

(3) C. L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **65**, 250 (1943); *Inorg. Syn.*, **2**, 196 (1946).

(4) O. Kling and H. L. Schläfer, *Z. Anorg. Allgem. Chem.*, **313**, 187 (1961).

(5) D. A. House and C. S. Garner, to be published.

(6) H. L. Schläfer and O. Kling, *Z. Anorg. Allgem. Chem.*, **302**, 1 (1959).

(7) K. G. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **81**, 2615 (1959).

(8) H. L. Schläfer and O. Kling, *Z. Anorg. Allgem. Chem.*, **309**, 245 (1961).

(9) H. Lux and G. Illmann, *Ber.*, **91**, 2143 (1958).

(10) H. Lux, L. Eberle, and D. Sarre, *ibid.*, **97**, 503 (1964).

(11) R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

(12) R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

(13) R. L. Pecsok, R. A. Garber, and L. D. Shields, *Inorg. Chem.*, **4**, 447 (1965).

(14) J. P. Fackler and D. G. Holah, *ibid.*, **4**, 954 (1965).

(15) D. G. Holah, *J. Chem. Educ.*, **42**, 561 (1965).

(16) A. Werner, *Ber.*, **43**, 2286 (1910).

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

(18) A. Werner, *Ber.*, **39**, 2656 (1906).

(19) E. H. Riesenfeld and F. Seemann, *ibid.*, **42**, 4222 (1909).

(20) F. Frowein, *Z. Anorg. Allgem. Chem.*, **110**, 107 (1920).

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

(22) See ref 17, p 1358.

(23) O. F. Wiede, *Ber.*, **30**, 2178 (1897).

(24) K. A. Hoffman, *ibid.*, **39**, 3181 (1906).

(25) R. Stomberg, *Arkiv Kemi*, **24**, 47 (1965).

(26) R. Stomberg, *ibid.*, **24**, 282 (1965).

(27) R. Stomberg, *Nature*, **207**, 76 (1965).

(28) E. Weinmann, Thesis, Zurich, 1919.

(29) E. Weinmann in "Nouveau Traité de Chimie Minérale," Vol. 14, P. Pascal, Ed., Masson Co., Paris, 1959, p 479.

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

30% H_2O_2 was added over 20 min from a dropping funnel while the solution was stirred mechanically. The color changed from the lemon-yellow of ethylenediamine chromate to an olive-green, and after 1–2 hr at 0–10°, olive-green crystals of the product had formed. These were collected by filtration through a coarse-porosity sintered-glass funnel and washed with ice water, 95% ethanol, and finally methanol, then air dried; yield 6–8 g (30–40%). The crystals were stored in a refrigerator. Technical grade CrO_3 gave a satisfactory yield of product but reagent grade (Baker Analyzed) CrO_3 failed to react until we added small amounts of Cu^{+2} (0.5 g of $CuSO_4 \cdot 5H_2O$ per 10 g of CrO_3) to catalyze the reaction.

The amount of product that can be formed by the above method is limited by the low solubility of ethylenediamine chromate in water. The formation of this compound can be avoided by adding the CrO_3 solution (30 g of technical grade or 30 g of reagent grade and 1 g of $CuSO_4 \cdot 5H_2O$, in 50 ml of water) and the H_2O_2 (100 ml of 30%) from separate dropping funnels to a cooled, stirred solution of ethylenediamine (25 ml of 95–100% in 100 ml of water plus 250 g of ice). The olive-green crystalline product was filtered, washed, and dried as above; yield 18–27 g (30–43%).

Anal. Calcd for $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$: C, 11.32; H, 5.70; N, 13.4; Cr, 24.5. Found (first preparative method): C, 11.8; H, 6.0; N, 13.7; Cr, 24.0. Found (second preparative method): C, 11.50; H, 5.92; Cr, 24.1.

The diperoxo compound is light- and heat-sensitive. At room temperature the color changes from olive-green to golden brown over a period of several days, although the compound can be kept without change at *ca.* −2° for *ca.* 1 month. When heated to 96–97°, at a heating rate of 2°/min, the compound decomposes violently.

Oxidation of KI in 0.5 *F* H_2SO_4 with weighed amounts (*ca.* 0.2 g) of the freshly prepared diperoxo compound and titration of the liberated I_2 with 0.1 *N* $Na_2S_2O_3$ gave values of 2.45 and 2.46 moles of I_2/fwt of diperoxo compound. The reaction

$$2[Cr(en)(OH_2)(O_2)_2] \cdot H_2O + 10I^- + 16H^+ = 5I_2 + 2Cr(en)(OH_2)_4{}^{+3} + 8H_2O$$

requires 2.5 moles I_2/fwt of diperoxo compound.

Weighed amounts (20–50 mg) of the diperoxo compound were added to 20 ml of acidified (1.5 *F* H_2SO_4) 0.1 *N* $KMnO_4$ solution and, when gas evolution ceased (3 min), 20 ml of 0.1 *F* $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (an excess) was added. The unreacted Fe^{+2} was determined by titration with 0.1 *N* $KMnO_4$. The reaction

$$5[Cr(en)(OH_2)(O_2)_2] \cdot H_2O + 3MnO_4{}^- + 24H^+ = 5Cr(en)(OH_2)_4{}^{+3} + 3Mn^{+2} + 10O_2 + 2H_2O$$

requires 3 reduction equiv/fwt of diperoxo compound. The freshly prepared diperoxo compound gave 2.85 and 2.87 reduction equiv/fwt.

Diperoxodiethylenetriaminechromium(IV) Monohydrate.—This was prepared and characterized as previously described;[30] yield 20%. It should be noted that the compound explodes when heated at 2°/min to 109–110°, although the solid and its aqueous solution are both stable for at least 24 hr at 25° in laboratory light.

Anal. Calcd for $[Cr(dien)(O_2)_2] \cdot H_2O$: C, 20.26; H, 6.37; Cr, 21.92; N, 17.72. Found: C, 20.51; H, 6.34; Cr, 21.95; N, 17.80.

Trichlorodiethylenetriaminechromium(III).—Two grams of $[Cr(dien)(O_2)_2] \cdot H_2O$ was added in *ca.* 0.2-g portions to 20 ml of concentrated HCl. Effervescence occurred and the mauve crystals that precipitated were collected by filtration and washed with methanol; yield 2 g. (90%). This previously unreported compound is insoluble in cold water.

Anal. Calcd for $Cr(dien)Cl_3$: C, 18.4; H, 5.0; Cr, 19.9; N, 16.0; Cl, 40.7. Found: C, 18.5; H, 5.1; Cr, 19.8; N, 16.0; Cl, 40.6.

Triaquodiethylenetriaminechromium(III) Cation.—*Ca.* 0.2 g of freshly prepared $[Cr(dien)(O_2)_2] \cdot H_2O$ was dissolved in 250 ml of 1 *F* $HClO_4$ and heated at 40° for 2 hr until the effervescence ceased. Its visible absorption spectrum was taken, then 100 ml of the solution was put on a 6-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) and the $ClO_4{}^-$ washed off with 30 ml of 0.1 *F* H_2SO_4 (to avoid interference of $ClO_4{}^-$ in the Kjeldahl nitrogen analysis made on the 1.5 *F* H_2SO_4 effluent below). The single red band was *ca.* 15% eluted with 100 ml of 1.5 *F* H_2SO_4 at *ca.* 25°. This elution behavior, together with an N/Cr atom ratio of 3.04 in the effluent, is in agreement with the formula $Cr(dien)(OH_2)_3{}^{+3}$. The visible absorption spectrum of this pink effluent was identical within 3% error with the spectrum of the unchromatographed complex in 1 *F* $HClO_4$, showing that the previously unreported $Cr(dien)(OH_2)_3{}^{+3}$ ion is essentially quantitatively formed in the above reaction. The H_2O ligands are probably *cis* to each other (see Results).

Blue Dichlorodiaquoethylenediaminechromium(III) Chloride.—Weinmann's method[28,29] was used as follows. One hundred grams of the red oxalato double salt,[31] $[Cr(en)_2C_2O_4][Cr(en)(C_2O_4)_2]$, was added to 150 ml of concentrated HCl and the solution warmed to 35–40° to dissolve the double salt; the solution was then stored at 0° for 2 days and filtered. The filtrate was treated with a slow stream of HCl gas for 2 hr at −20 to −12° and then stored at −5°. After 2 days, 0.5–1.5 g of green powder formed (so far our attempts to characterize this material have given ambiguous results); the green material was removed by filtration and after 4 days at −5° blue crystals were deposited from the filtrate. The mother liquor was decanted and the blue crystals were washed with 1:1 2-propanol–concentrated HCl, then with 2-propanol, and dried over silica gel at *ca.* 25°; yield 6–10 g (15–25%).

We have developed a new and much more efficient synthesis of this blue compound as follows. Six grams of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$ was added in 0.2–0.3 g. portions to 20 ml of concentrated HCl at *ca.* 25°. Effervescence occurred and the solution temperature increased to 35–40°. The resulting blue solution was set aside to evaporate under a slow stream of air. After *ca.* 2 days the blue crystalline product was collected on a sintered-glass filter, washed with 1:1 2-propanol–concentrated HCl, then with 2-propanol, and dried over silica gel at *ca.* 25°; yield 7 g (95%).

Anal. Calcd for $[Cr(en)(OH_2)_2Cl_2]Cl$: C, 9.42; H, 4.75; N, 11.0; Cr, 20.3; Cl, 41.8. Found (Weinmann's method): C, 9.62; H, 4.88; N, 10.9; Cr, 20.0; Cl, 42.0. Found (new method): C, 9.68; H, 4.75; Cr, 20.1; Cl, 41.9.

The salt is readily soluble in water (>60 g/100 ml at 25°), dilute acids, methanol, and ethanol, but insoluble in 2-propanol. The configuration is unknown.

Ammonium Tetrafluoroethylenediaminechromate(III).—Three grams of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$ was added to 5 g of NH_4HF_2 in 15 ml of water and 1 ml of 49% HF in a polyethylene beaker. Mild effervescence occurred and after warming at 30° for 15–20 min, the resulting clear blue solution was filtered to remove a small amount of green $(NH_4)_3[CrF_6]$ and the filtrate was slowly poured into 300 ml of methanol. The sky-blue crystalline product readily formed on cooling and was collected by filtration, washed with methanol, and air dried; yield 2.5 g (80%). The salt can be recrystallized by dissolving in a minimum volume of 1 *F* NH_4HF_2 and adding *ca.* 15 volumes of methanol; yield almost quantitative.

Anal. Calcd for $NH_4[Cr(en)F_4]$: C, 11.65; H, 5.87; N, 20.38; Cr, 25.2. Found: C, 11.55; H, 5.90; N, 20.23; Cr, 25.0.

Ammonium Dioxalatoethylenediaminechromate(III) Mono-(ammonium hydrooxalate) Monohydrate.—Four grams of $[Cr(en)(OH_2)(O_2)_2] \cdot H_2O$ was added slowly to 20 ml of 3 *F* $HClO_4$ at *ca.* 25° and the red solution heated at 70° on a water bath for about 10 min. $(NH_4)_2C_2O_4 \cdot H_2O$ (4.5 g) was dissolved in 30 ml of 70° water and added to the red solution when it gave no more gas evolution on swirling.[32] The combined solutions were heated at 70° for 5 min, the color changing from red to red-violet, and then 200 ml of methanol was added and the solution allowed to cool slowly overnight at *ca.* 25°. Reddish purple crystals of the

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(31) A. Werner, *Ber.*, **44**, 3132 (1911).

(32) If the $(NH_4)_2C_2O_4 \cdot H_2O$ is added before all gas evolution has ceased, the major product will be $Cr(C_2O_4)_3{}^{-3}$ ion.

hydrated product, which formed as a layer on the walls of the beaker, were scraped off, collected on a filter, washed well with methanol to remove any $H_2C_2O_4$, and dried by suction; yield 2.5–3.0 g (40–50%). The product can be recrystallized by dissolving in a minimum volume of water and adding *ca.* 2 volumes of methanol. If an attempt is made to recrystallize from water alone, an unknown purple insoluble material is deposited on standing.

Anal. Calcd for $NH_4[Cr(en)(C_2O_4)_2]\cdot NH_4HC_2O_4\cdot H_2O$: C, 22.2; H, 4.44; N, 13.0; Cr, 12.0; H_2O, 4.2. Found: C, 21.7; H, 4.26; N, 13.2; Cr, 11.9; H_2O, 4.2.

Tetraaquoethylenediaminechromium(III) Cation.—Varying amounts (40–90 mg) of freshly prepared $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ were dissolved in 100 ml each of 0.5, 1, 2, and 3 *F* $HClO_4$ and the solutions kept at 40° for 1 hr. Gas (presumably O_2) was evolved and pink solutions formed. Measurements of the visible absorption spectra of these solutions gave the same spectrum, including the same molar absorbancy indices at the absorption maxima and minima within *ca.* 4% error. Samples (50 ml of the 0.5 and 1 *F* $HClO_4$ solutions) were adsorbed on 6-cm × 1-cm diameter columns of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) at *ca.* 25°, and the resulting red band was 96% eluted with 100 ml of 3 *F* $HClO_4$ (1 *F* $HClO_4$ did not move the red band). The effluents gave visible absorption spectra, including molar absorbancy indices based on Cr analyses, which were identical (within 4%) with those of the original solutions which were based on the weight of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ used. Analyses of the N/Cr atom ratio in solutions of the cation eluted with 1.5 *F* H_2SO_4 gave 1.96 and 1.98, in acceptable agreement with the formula $Cr(en)(OH_2)_4{}^{+3}$. This formula is further supported by the elution behavior, which is typical for a +3 ion of this size. Attempts to obtain the perchlorate salt of this cation, using more concentrated solutions (3 g of diperoxo compound in 15 ml of 3 *F* $HClO_4$) and evaporation over P_2O_5 gave only a red syrup.

Results

Blue $[Cr(en)(OH_2)_2Cl_2]Cl$.—A blue compound of this composition had been obtained by Weinmann[28, 29] from the decomposition of $[Cr(en)_2C_2O_4][Cr(en)(C_2O_4)_2]$ with concentrated hydrochloric acid. The blue compound obtained by us from the decomposition of $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ in concentrated hydrochloric acid is identical with Weinmann's blue salt as evidenced from ultimate analysis and identical visible and infrared spectra. The new synthesis method is simpler and gives a much higher yield. Weinmann[28] has shown that both $[Cr(en)(OH_2)_2(OH)_2]X$ (X = Cl, Br, I, NCS, ClO_4, $^1/_2S_2O_6$) and $M[Cr(en)(NCS)_4]$ (M = NH_4, K, Na, Cs) can be obtained from blue $[Cr(en)(OH_2)_2Cl_2]Cl$ in aqueous solution by addition of ammonium hydroxide (plus the proper anion) or M^+ thiocyanate, respectively.

When a freshly prepared solution of the blue compound in 0.1 *F* $HClO_4$ was put on a H^+ Dowex AG50W-X8 cation-exchange column (100–200 mesh) at *ca.* 1° all the color was adsorbed; elution with 50 ml of 0.01 *F* $HClO_4$ removed no color, but 50 ml of 0.3 *F* $HClO_4$ eluted all the color and gave an effluent with a Cl/Cr atom ratio of 1.98 and a visible absorption spectrum identical with that obtained when the blue compound was dissolved directly in 0.1 *F* $HClO_4$ (see Table I). The elution behavior is that expected for a singly-charged cation of this size and rules out the possibility that the blue compound is a polymer.

Theoretically there are three possible geometric isomers for the $Cr(en)(OH_2)_2Cl_2{}^+$ ion, but it is not yet possible to assign a configuration to the blue salt. We are currently investigating the kinetics of aquation of the $Cr(en)(OH_2)_2Cl_2{}^+$ ion in acid solution in the hope that the kinetic data and identification of the aquation products may help to characterize the geometric configuration.

A pink cation of apparently this same formula has been chromatographically isolated from *trans*-$Cr(en)_2Cl_2{}^+$ aquation-reaction solutions,[33, 34] but the relation of this pink cation to Weinmann's blue cation has not yet been established. Efforts in this laboratory to characterize the pink cation more fully have not been successful to date.

$NH_4[Cr(en)F_4]$.—This salt has not been reported in the literature, although recently Vaughn and Krainc[35] reported the synthesis of *cis*-$[Cr(en)_2F_2][Cr(en)F_4]\cdot H_2O$ by heating anhydrous chromium(III) fluoride with anhydrous ethylenediamine, and Dahme[36, 37] has isolated $Na[Cr(en)F_4]\cdot 0.5NaClO_4$ and $(en{-}H_2)[Cr(en)F_4]ClO_4$ by reaction of $[Cr(en)_3](ClO_4)_3$ with hydrofluoric acid. Dahme[36] also describes the synthesis of $[Cr(en)(OH_2)_2F_2]Cl$ (unknown configuration) from $Na[Cr(en)F_4]\cdot 0.5NaClO_4$.

The synthesis of $NH_4[Cr(en)F_4]$ from $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ is simple and occurs with high yield. The previously unreported spectrum of $Cr(en)F_4{}^-$ is given in Table I.

The $Cr(en)F_4{}^-$ anion is slowly aquated in dilute acid at 25°, the color of the solution changing from sky-blue to violet.

$NH_4[Cr(en)(C_2O_4)_2]\cdot NH_4HC_2O_4\cdot H_2O$.—The potassium salt of the $Cr(en)(C_2O_4)_2{}^-$ anion has been prepared by Werner[38] from $[Cr(en)_2C_2O_4][Cr(en)(C_2O_4)_2]$ and by Bushra and Johnson[39] from $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and ethylenediamine, but in both cases the syntheses were difficult. The ammonium salt has been found to be readily prepared in reasonable yield from $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$. The visible absorption spectrum of the ammonium salt in 0.1 *F* $HClO_4$ is identical except for small differences in intensities with that obtained by Schläfer, Kling, Mähler, and Opitz[40] for $K[Cr(en)(C_2O_4)_2]\cdot 2H_2O$, prepared from $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and measured in 0.1 *F* $HClO_4$–0.06 *F* $NaClO_4$ (see Table I).

$Cr(en)(OH_2)_4{}^{+3}$ Cation.—We have found that this cation is quantitatively formed when $[Cr(en)(OH_2)(O_2)_2]\cdot H_2O$ is dissolved in 0.5–3 *F* $HClO_4$ and heated to 40° for 1 hr. The cation-exchange chromatographic behavior is consistent with that expected for a triply-charged cation of this size (see Experimental Section). The visible absorption spectrum is reported in Table I.

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

(34) 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.

(35) J. W. Vaughn and B. J. Krainc, *Inorg. Chem.* **4**, 1077 (1965).

(36) W. Dahme, Thesis, Berkakademie Clausthal, 1957.

(37) "Gmelins Handbuch der anorganischen Chemie," Chrom, Teil C, Vol. 52, 1965, p 274.

(38) A. Werner, *Ann.*, **406**, 261 (1914).

(39) E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1937 (1939).

(40) H. L. Schläfer, O. Kling, L. Mähler, and H. P. Opitz, *Z. Physik. Chem.* (Frankfurt), **24**, 307 (1960).

TABLE I

ABSORPTION MAXIMA AND MINIMA IN THE 320–700 mμ RANGE OF Cr(III) en AND dien COMPLEXES AT 20–25°

Complex	$HClO_4$, *F*	λ, mμ	a_M, M^{-1} cm^{-1}[a]
Blue $Cr(en)(OH_2)_2Cl_2^+$ [b]	0.1	420 (max)	22.7
		475 (min)	16.3
		550 (sh)	37.6
		580 (max)	39.1
$Cr(en)(OH_2)_4^{+3}$ [b]	1.0	387 (max)	22.0
		428 (min)	10.7
		517 (max)	32.0
	0.5	387 (max)	21.7
		438 (min)	10.5
		517 (max)	32.0
	0.1	387 (max)	23.8
		438 (min)	11.1
		517 (max)	37.1
"$Cr(en)(OH_2)_4^{+3}$"[c]	0.1	378 (max)	27.4
		430 (min)	12.0
		505 (max)	49.8
"$Cr(en)(OH_2)_4^{+3}$"[d]	*Ca.* 0.01–0.1?	398 (max)	33.0
		440 (min)	25.0
		515 (max)	48.6
$Cr(en)F_4$ [b]	0.1	410 (max)	14.5
		470 (min)	5.6
		571 (max)[e]	32.9
$Cr(en)(C_2O_4)_2^-$ [b]	0.1	341 (min)	24.9
		395 (max)	98.3
		452 (min)	22.7
		530 (max)	87.3
		685 (min)	1.8
		690 (max)	2.3
$Cr(en)(C_2O_4)_2^-$ [f]	0.1	341 (min)	17.7
		395 (max)	94.4
		452 (min)	19.4
		530 (max)	88.0
		685 (min)	1.6
		690 (max)	2.1
$Cr(dien)(OH_2)_3^{+3}$ [b]	1.0	388 (max)	24.3
		440 (min)	12.0
		518 (max)	38.8

[a] Molar absorbancy index, defined by $\log (I_0/I) = A = a_M cd$, where c = molarity of absorbing complex, d = optical path in cm. [b] This research. [c] Read off spectral curve deduced in ref 41; see text regarding the possible presence of hydroxoaquo forms. [d] Read off spectral curve deduced in ref 42; see text regarding the possible presence of hydroxoaquo forms. [e] Ref 35 states that a blue complex anion, presumably $Cr(en)F_4^-$, eluted from an anion-exchange column has an absorption peak at 572 mμ. [f] Ref 40; spectrum in 0.1 *F* $HClO_4$–0.06 *F* $NaClO_4$.

This tetraaquo species had been hypothesized[41,42] as an intermediate in the aquation of *cis*-$Cr(en)_2(OH_2)_2^{+3}$, and attempts were made to calculate its visible absorption spectrum from the spectral changes observed during the aquation. Since the hypothesized complex was not isolated from its precursor or its decomposition products and since we find that the spectrum of our $Cr(en)(OH_2)_4^{+3}$ (Table I) changes negligibly in going from 3 *F* $HClO_4$ to 0.5 *F* $HClO_4$ but changes molar absorbancy indices by 10–15% in going to 0.1 *F* $HClO_4$, possibly from partial loss of one or more protons at hydrogen ion concentrations below *ca.* 0.5 *M* (the cited aquation studies were made in *ca.* 0.01–0.1 *M* H^+), it is clear that the $Cr(en)(OH_2)_4^{+3}$ cation has not previously been well characterized and that the visible absorption spectra deduced[41,42] for this ion (Table I) were not reliable.

We are currently investigating the kinetics of the aquation of $Cr(en)(OH_2)_4^{+3}$ to $Cr(OH_2)_6^{+3}$ in $HClO_4$ solutions and endeavoring to isolate the reaction intermediate.

$Cr(dien)Cl_3$.—This previously unreported neutral complex is easily prepared in 90% yield from $[Cr(dien)(O_2)_2]\cdot H_2O$. Theoretically, this complex can exist in two stereoisomeric forms, with the three chloro ligands in a plane either bisecting the octahedron (*trans* form) or coincident with one face of the octahedron (*cis* form). The configuration of the mauve isomer is not known. The compound is insoluble in water, methanol, and dimethylformamide; hence, we have been unable to obtain a meaningful visible absorption spectrum of it in solution. The deep brown $Co(dien)Cl_3$[43–45] has been reported[44] to be readily soluble in water, but to hydrolyze, so that its visible absorption spectrum is not known either.

***cis*-$Cr(dien)(OH_2)_3^{+3}$.**—This new complex cation is obtained essentially quantitatively when $[Cr(dien)(O_2)_2]\cdot H_2O$ is heated in 1 *F* $HClO_4$ at 40° for 2 hr. The visible absorption maxima and minima in 1 *F* $HClO_4$ at *ca.* 25° are given in Table I; the molar absorbancy indices are constant within 4% between 1.8 and 4.5 m*M* in the complex. The shape of this spectrum, the wavelengths, and the molar absorbancy indices are similar to those reported for *cis*-$Cr(NH_3)_3(OH_2)_3^{+3}$ ion[46] in 2 *F* $HClO_4$, as would be expected if the pink $Cr(dien)(OH_2)_3^{+3}$ made by us has a *cis*-triaquo configuration. Tentatively, therefore, we assign this complex a *cis* configuration.

Visible Absorption Spectra.—The wavelengths of the maxima and minima in the visible absorption spectra (aqueous perchloric acid solution at 20–25°) and the corresponding molar absorbancy indices are listed in Table I for the complexes synthesized in this study.

Discussion

The use of chromium(IV) diperoxo compounds, which are readily obtained from inexpensive commercially available chromium compounds, opens up a new synthetic pathway for the preparation of chromium(III) amine compounds. In concentrated hydrochloric acid, the aquo–en and dien diperoxo compounds are easily reduced with replacement of the four peroxo oxygens by two and three chloro ligands, respectively. Probably other halide and pseudo-halide ligands can be similarly introduced. In perchloric acid these diperoxo

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(41) H. L. Schläfer and R. Kollrack, *Z. Physik. Chem.*, (Frankfurt), **18**, 348 (1958).

(42) M. Ohta, H. Matsukawa, and R. Tsuchiya, *Bull. Chem. Soc. Japan*, **37**, 692 (1964).

(43) P. Job and J. Brigando, *Compt. Rend.*, **210**, 438 (1940).

(44) P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960).

(45) P. H. Crayton, *Inorg. Syn.*, **7**, 207 (1963).

(46) C. E. Schäffer and P. Andersen, "Proceedings of the Wroclaw Symposium," Pergamon Press, 1964, pp 571–582; spectrum reported: 375 mμ (max, a_M = 22.2 M^{-1} cm^{-1}), 432 mμ (min, a_M = 6.5 M^{-1} cm^{-1}), 518 mμ (max, a_M = 34.5 M^{-1} cm^{-1}).

compounds generate the aquo complexes, which in turn can probably be substituted with appropriate ligands by anation. We are investigating the extent to which other diamines and triamines will form chromium(IV) diperoxo compounds and the products that form on addition of these to acids.

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Crystalline Complex of Acrolein with Copper(I) Chloride

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Yellow crystalline complex of acrolein with copper(I) chloride, $(CH_2CHCHO)CuCl$, was synthesized through the direct reaction of acrolein with copper(I) chloride at room temperature in a vacuum system. The equilibrium vapor pressure data at various temperatures and the electronic and infrared absorption spectra were determined. The frequency of C=C stretching is shifted about 90 cm^{-1} to the lower frequency side by the ligation, but that of the C=O stretching shows only a small decrease, indicating that acrolein coordinates to copper(I) mainly with the double bond.

Introduction

Acrolein seems to be a very interesting substrate in catalytic reactions since the molecule is composed of two reactive parts, formyl and vinyl groups. With the object of searching for fundamental aspects concerning the prospective homogeneous catalytic reactions, we are trying to synthesize the acrolein complexes of various metals.

Schrauzer[1] obtained bis(acrolein)nickel(0), $(C_3H_4O)_2Ni$, by the reaction of acrolein with nickel carbonyl. Acroleiniron(0) tetracarbonyl,[2] $(C_3H_4O)Fe(CO)_4$, and bis(acrolein)molybdenum(0) dicarbonyl,[3] $(C_3H_4O)_2Mo(CO)_2$, have also been synthesized by the reactions of acrolein with diiron enneacarbonyl and tris(acetonitrile)molybdenum(0) tricarbonyl, respectively. This paper reports the preparation of copper(I) chloride complex of acrolein by the direct combination of both components. The reduction of copper(II) in the presence of appropriate ligands is frequently effective in preparing copper(I) complexes, and Haight, *et al.*,[4] obtained crystalline copper(I) complexes of various cyclic olefins by this means. In the present case, acrolein can dissolve copper(I) chloride and reacts easily, depositing a crystalline compound. The yellow solution is very sensitive to air, and the whole procedure of synthesis was performed in a vacuum system.

Experimental Section

Starting Materials.—Copper(I) chloride was prepared by reducing copper(II) sulfate solution containing sodium chloride with sulfur dioxide. The fine, white, crystalline product thus obtained was filtered, then washed with water containing sulfur dioxide and with acetic acid without exposing to air. Copper(I) chloride was dried and kept *in vacuo*. The specimen for the spectroscopic study was specially purified by the distillation *in vacuo*.

Acrolein was purchased from Wakamatsu Chemicals Co. and purified by the fractional distillation through a 30-cm Widmer column after drying with Molecular Sieves, Type 3A, Linde Co. In each experiment the freshly distilled sample was used.

Synthesis of Acrolein–Copper(I) Chloride Complex.—The ampoule system employed for the synthesis and analysis of the complex is illustrated in Figure 1. A freshly distilled sample of acrolein was charged in ampoule C, deaerated completely, and distilled into ampoule B containing copper(I) chloride. The apparatus was sealed off at E from the vacuum line. Acrolein readily reacts with copper(I) chloride forming yellow crystals, which dissolve in acrolein itself (to about 10^{-2} *M*) yielding a yellow solution. The yellow solid might contain unreacted copper(I) chloride as the nucleus. To obtain a pure product, the yellow solution was passed through a glass filter D into an empty ampoule A. The solvent was distilled back to B by keeping A at 10° and B at 0°. The saturated solution was again transferred into A, and the solvent was distilled back to B. This procedure was repeated until the desired amount of crystalline product was accumulated in A. Finally, the solvent acrolein was distilled from B into A to wash the solid product, and the solution was transferred back to B through D. The solid complex was then kept at 5° and the ampoule B at 0° for more than 30 hr. As will be shown by the vapor pressure data, the complex can be dried safely without any accompanying decomposition at this temperature difference.

Analysis of the Complex.—The crystalline complex, which had been prepared and dried in ampoule A as described in the preceding section, was kept at 0°, and the empty vessel A′ was cooled to $-78°$ after ampoule B was sealed off at F. The complex was decomposed at this temperature difference, and finally A was heated up to 50° to make sure of the complete decomposition. The volatile material gathered in the cold vessel A′ was identified as acrolein by means of the infrared assay in another experiment. After ampoule A′ was sealed off and weighed, the quantity of acrolein was determined by brominating with the bromide–bromate reagent and then titrating the excess bromine iodometrically.[5] Nonvolatile copper(I) chloride left in ampoule A was added with aqueous ammonia after weighing the sealed vessel. After copper (I) was oxidized completely to copper (II),

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[1] G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); **82**, 1008 (1960); *Chem. Ber.*, **94**, 642 (1961).

[2] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[3] D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965).

[4] H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *ibid.*, **2**, 1301 (1963).

[5] C. W. Smith, Ed., "Acrolein," John Wiley and Sons, Inc., New York, N. Y., 1962, p 244.