was evaporated to dryness with a rotary evaporator and the residual blue solid washed with a total of 100 ml. of diethyl ether. After vacuum drying 6.6 g. of product was obtained, m.p. 212–215°, mixture melting point with $NiBr_2 \cdot 2(C_6H_5)_2PO$ prepared by Cotton's method[1] undepressed.

**Preparation of Bis(triphenylphosphine oxide)nickel(II) Iodide.**—A slurry of $NiI_2 \cdot 2(C_6H_5)_3P$ (8.4 g., 0.01 mole) in absolute ethanol (50 ml.) was treated with 30% hydrogen peroxide (2.3 ml., 0.02 mole) with ice–water cooling. After an initial vigorous reaction the solution was warmed on a steam bath until a green solution resulted. On removal of solvent a red-brown oil was obtained. This crystallized on washing with diethyl ether (50 ml.) to a green solid, 6.5 g. after vacuum drying, m.p. 207–209°, lit.[1] 209.5°.

**Preparation of Bis(triphenylphosphine oxide)cobalt(II) Bromide.**—A slurry of $CoBr_2 \cdot 2(C_6H_5)_3P$ (7 4 g., 0.10 mole) in absolute ethanol (100 ml.) was treated at room temperature with 30% hydrogen peroxide (3.0 ml., 0.029 mole). Immediate warming to 50° ensued, and a deep blue solution resulted. The solvent was removed, and the bright blue solid was washed with diethyl ether (50 ml.). There was 6.5 g. of product obtained, m.p. 228–230°, lit.[4] 223°.

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[4] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

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# Synthesis of Monochloropentaaquochromium(III) Ion by Displacement Ion Exchange

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The synthesis of many inert transition metal species is complicated by the necessity of separating the desired species from a mixture of related species. Conventional elution ion-exchange column techniques can be used for such separations, but this procedure has several limitations. Usually, only small amounts of the desired species can be prepared, the desired species can only be obtained at low concentration, and the eluting ion is the principal ionic species in all fractions collected from the column. The displacement ion-exchange technique overcomes these handicaps. In conventional elution ion-exchange column techniques, the equilibrium

$$\frac{m}{c}C^{c+} + MR_m = M^{m+} + \frac{m}{c}CR_c$$

favors the ion in question $M^{m+}$ staying in the resin phase. This procedure generally yields a dilute solution of $M^{+m}$ in which the principal cationic species is the eluting ion. If, on the other hand, the ion $C^{c+}$ has a great affinity for the resin phase, this equilibrium is displaced far to the right, and the resulting effluent solution contains $M^{m+}$ at a high concentration and does not contain $C^{c+}$. Using the displacement technique quantities of 5 to 50 mmoles or more can be prepared easily at concentrations of 0.1 *M* or higher. In a separation of cations the effluent will usually contain the hydrogen ion in addition to the desired species, but the concentration of the hydrogen ion can be made as low as desired. The general procedure has been discussed by Helfferich,[1] and examples of its use can be found in the work of Connick and his students.[2]

In a displacement ion-exchange separation the top part of an ion-exchange column is loaded with a mixture of species to be separated. A solution containing an ion having a great affinity for the resin is then slowly passed into the column. All species of the mixture to be separated are displaced by the displacing ions. As the operation continues the species of the mixture gradually separate into a set of adjacent bands which can be collected separately at the bottom of the column.

The synthesis of solid monochloropentaaquochromium(III) chloride was described by Bjerrum[3] over 50 years ago. More recently, Gates and King[4] reported the preparation of an aqueous solution of the monochloropentaaquochromium(III) ion by means of an elution ion-exchange procedure. This method suffers from the usual handicaps of elution techniques. Elving and Zemel[5] claimed to have prepared the ion by mixing stoichiometric quantities of silver ion and dichlorotetraaquochromium(III) ion. In our attempts to repeat their work we always obtained a mixture of monochloro and dichloro species or else a mixture of monochloro and hexaaquo species. The displacement ion-exchange procedure reported here gives a highly purified product in large enough quantities to permit the preparation of a solid salt.

## Experimental

**Reagents.**—Dowex AG 50W X8, 200–400 mesh resin obtained from Bio Rad Laboratories, Richmond, Calif., was used in all experiments. This is a cation resin and was used in the hydrogen form. All other chemicals were analytical reagent grade. Ordinary distilled water was used for all solutions.

**Analytical Methods.**—Chromium was determined spectrophotometrically after oxidation to chromate by alkaline peroxide. Chloride was determined by adding excess silver nitrate solution, allowing all bound chloride to be released to the silver, and carrying out a potentiometric back titration with potassium chloride solution using a Ag–AgCl electrode *vs.* a glass electrode.

**Preparation of Ion-Exchange Columns.**—A glass column having an inside diameter of 2.2 cm. and 40 cm. long with a fritted glass bottom was used in this work. Columns were packed by closing off the bottom of the column, filling it about one-third full of water, and adding a slurry containing one part resin and three parts water by volume. After the resin had settled, the bottom was opened and several column volumes of water passed through the column.

**Preparation of $[Cr(OH_2)_5Cl]Cl_2 \cdot 5H_2O$.**—A solution containing a mixture of chlorochromium(III) species was prepared by dissolving 15 g. of $CrCl_3 \cdot 6H_2O$ in 300 ml. of water. The solution was allowed to stand for 2 hr. to allow partial transformation of dichlorotetraaquochromium(III) into monochloropentaaquochromium(III). The dichloro species is reported to be the principal

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[1] F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., New York N. Y., 1962, pp. 437, 438.

[2] H. W. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958); J. E. Finholt, Lawrence Radiation Lab. Rept., UCRL 8879, University of California, Berkeley, 1960.

[3] N. Bjerrum, *Z. physik. Chem.*, **59**, 581 (1907).

[4] H. S. Gates and E. L. King, *J. Am. Chem. Soc.*, **80**, 501 (1958).

[5] P. J. Elving and B. Zemel, *ibid.*, **79**, 1281 (1957).

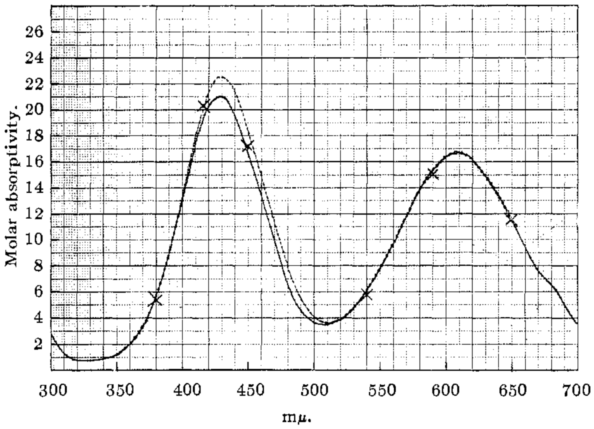

Fig. 1.—Molar absorptivity of 0.04 *M* $[Cr(OH_2)_5Cl](ClO_4)_2$ at 25° in 0.1 *M* perchloric acid (———) and in 6 *M* perchloric acid (– – – –). Points reported by Gates and King[3] are denoted by × symbols.

species in solid chromic chloride.[6] Next, 5 ml. of concentrated perchloric acid was added to inhibit decomposition of the monochloro species to the hexaaquo species. The solution was added to a resin column 14 cm. long. The column was then rinsed with 20 ml. of 0.001 *M* perchloric acid. At this point the top of the column, from 0.0 to 1.0 cm., was dark violet, from 1.0 to 5.5 cm. the column was dark green, and from 5.5 to 14 cm. the column was light green. Displacement was begun by adding a solution of 0.1 *M* cerous perchlorate and 0.1 *M* perchloric acid at a flow rate of 0.5 drop/sec. After 20 min., the top part of the column was a very light green, next came a band of dark violet, then a band of dark green, and the rest of the column was white. A volume of 140 ml. was collected from the dark green band, the monochloro band. Two drops of the collected solution was added to two drops of saturated sodium oxalate solution. No precipitate was observed, indicating the absence of cerous ion. Two more drops of the solution was added to two drops of 0.1 *M* silver nitrate solution and no precipitate was observed. This indicated the absence of any free chloride ion.

The 140 ml. of solution collected from the ion-exchange column was placed on a vacuum line and 130 ml. of water was removed Hydrogen chloride gas was bubbled through 5 ml. of the concentrated solution at 0°. No precipitate appeared at first, but after 2 hr. at 0° a dark solid formed. The precipitate was separated by filtration, washed with diethyl ether, and stored in a desiccator. The yield was 0.3 g. The product was very hygroscopic.

**Spectra.**—Spectral measurements were made at 25° on solutions containing about 0.04 *M* monochloropentaaquochromium(III) perchlorate and 0.1 *M* perchloric acid. The results reported here are an average of four determinations, three using a Cary Model 15 spectrophotometer and one using a Beckman DU spectrophotometer. The positions and molar absorptivities of spectral peaks are as follows[7]: shoulder at 675 mμ, 7.0 cm.$^{-1}$ mole$^{-1}$ l.; 608 mμ, 16.7 cm.$^{-1}$ mole$^{-1}$ l.; 428 mμ, 21.0 cm.$^{-1}$ mole$^{-1}$ l.

One determination was made on a solution containing about 0.04 *M* monochloropentaaquochromium(III) perchlorate in 6 *M* perchloric acid at 25°. The Beckman DU spectrophotometer was used. The positions and molar absorptivities of spectral peaks are as follows: shoulder at 675 mμ, 7.0 cm.$^{-1}$ mole$^{-1}$ l.; 608 mμ, 16.7 cm.$^{-1}$ mole$^{-1}$ l.; 428 mμ, 22.6 cm.$^{-1}$ mole$^{-1}$ l.

**Characterization.**—A solution obtained directly from the ion-exchange column was analyzed for chromium and chloride. The Cl:Cr ratio was 1.00 ± 0.1. An aliquot was reabsorbed on a second ion-exchange column and eluted with 0.5 *M* perchloric acid. Only one band was observed. Measurements of the total charge concentration of the displacing solution, together with the pH and the chromium concentration of the solution from the dark green band, allowed the average charge per chromium atom to be determined as 2.02 ± 0.02. The procedure is described elsewhere.[2]

The spectrum of solid monochloropentaaquochromium(III) chloride dissolved in 0.1 *M* perchloric acid agreed within experimental error with that of material isolated in solution directly from an ion-exchange column. A solution made by dissolving some solid in 0.1 *M* perchloric acid was passed into an ion-exchange column in the hydrogen form. When the column was eluted with 0.1 *M* perchloric acid only a single band was observed. These results are taken to indicate that the solid contained the $Cr(OH_2)_5Cl^{2+}$ ion in pure form.

The solid was analyzed for chromium and chloride.

*Anal.* Calcd. for $[Cr(OH_2)_5Cl]Cl_2 \cdot 5H_2O$: Cr, 15.4; Cl, 31.5. Found: Cr, 15.4; Cl, 31.0.

## Discussion

The spectrum of the material obtained in this synthesis is shown in Fig. 1. The results reported here are in good agreement with those of Gates and King,[3] but differ from those of Elving and Zemel.[4] The change in media from 0.1 *M* perchloric acid to 6 *M* perchloric acid produces a small, but distinct, effect on the spectra.

In designing displacement operations a few precautions should be observed. The resin beads should be as small as possible. Low flow rates should be used. The fraction of the column occupied by the mixture of ions to be separated should be small enough to allow complete separation as displacement takes place. Generally, all of the ions of the mixture should be in the top half of the column initially.

The displacement ion-exchange technique is quite general in application. In the case reported here it was used to separate ions of charge +2 from +1 and +3 ions, but the procedure can be used to separate ions of the same charge, even if they have similar hydrated radii. For example, we have made successful separations of mixtures containing $Cu^{2+}$ and $Ca^{2+}$. Of course, the method can only be applied to the separation of nonlabile species. The ease with which separations can be accomplished, the high purity of the product, and the large yields make the displacement ion-exchange technique a valuable synthetic tool.

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

(7) A tabulation of the molar absorptivity values in both 0.1 and 6 *M* perchloric acid has been deposited as Document No. 8092 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $1.25 for photoprints, or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.