line. A large excess of peroxydisulfuryl difluoride, $S_2O_6F_2$, was transferred to the flask by distillation, then the neck of the flask was sealed shut while the vessel was cold and evacuated. The flask was then allowed to stand at room temperature for 1 week. During the first part of this period the formation of bubbles of a gas (later shown to be oxygen) was observed. After the formation of bubbles had stopped, the vessel was held at 65° for 2 hr. while stirring. As the reaction occurred, the white I_2O_5 disappeared and was replaced by a solid powder having a light yellow color. Finally the reactor was attached to the vacuum line through the side arm and the excess of $S_2O_6F_2$ was distilled away through the break-seal into an evacuated cold trap. From 1.1056 g. of I_2O_5 the weight of the solid product obtained was 1.6995 g. (theoretical for IO_2SO_3F, 1.7080 g.). The oxidation state of iodine in the compound was found to be +5 (5.04 observed) as shown by a Volhard determination of iodine and an iodometric determination of the oxidizing capacity. *Anal.* Calcd. for IO_2SO_3F: I, 49.19; S, 12.43. Found: I, 48.9; S, 12.8.

The reaction involved in the preparation was

$$I_2O_5 + S_2O_6F_2 = 2IO_2SO_3F + {}^1/_2O_2$$

The IO_2SO_3F was a pale yellow, very hygroscopic powder which was stable up to 100°. At 120° it reacted slowly with the glass container producing SiF_4, SO_3, and a colorless oil (probably $IF_3(SO_3F)_2$) containing 32.6% I (theoretical for $IF_3(SO_3F)_2$, 32.2%.) The above products distilled away under vacuum as the reaction occurred. A bright yellow material remained behind in the reactor.

Iodyl fluorosulfate reacted with the solvent when dissolved in $CFCl_3$, $CHCl_3$, or CCl_4. Chlorine was produced even at room temperature and the color changed from yellow to orange to red. The resulting solution had absorption maxima at 4600 and 3300 Å. corresponding to ICl and Cl_2. An infrared spectrum of the volatile products indicated $S_2O_5F_2$, $COCl_2$, and CO_2. This behavior with the above solvents resembles that of ISO_3F and $I(SO_3F)_3$.[10] Iodyl fluorosulfate was substantially insoluble in fluorosulfuric acid but it dissolved readily with hydrolysis in water, the iodine remaining in the +5 oxidation state.

Finely crushed IO_2SO_3F was packed into a 0.5-mm. Lindemann glass capillary inside a drybox. The tube was sealed with Halcarbon wax and after removal from the drybox was mounted in a large standard Philips powder camera (radius 57.2956 mm.) having the conventional Straumanis arrangement. After a 12-hr. exposure using nickel-filtered copper X-radiation ($\lambda_{K\alpha}$ 1.54178 Å.), over 49 lines were observed and measured to within 0.05 mm. A second exposure of 2 hr. was also made. The camera was calibrated with a 30-min. exposure of a standard (sodium chloride, a = 5.63874 Å.). Calculations showed the camera to have an effective radius of 57.208 ± 0.027 mm. Using the now calibrated IO_2SO_3F intense lines in the 2-hr. exposure, the 12-hr. exposure powder spectrum was measured and the radius correction applied. The results are listed in Table I. A sample of solid I_2O_5 gave a different powder spectrum and agreed with ASTM Inorganic X-Ray Powder File 1962, p. 99, No. 1-0692.

TABLE I

d SPACINGS FROM LINES IN X-RAY POWDER PHOTOGRAPH

Å.	Intensity[a]	Å.	Intensity[a]	Å.	Intensity[a]	Å.	Intensity[a]
8.031	m	2.596	l	1.785	m	1.351	l
6.501	h	2.532	l	1.737	l	1.331	l
5.238	m	2.376	l	1.710	l	1.296	l
4.108	l	2.335	l	1.673	l	1.268	l
4.016	m	2.256	l	1.629	l	1.248	l
3.556	h	2.153	l	1.593	l	1.218	l
3.262	l	2.124	m	1.566	l	1.205	l
3.127	l	2.064	l	1.561	l	1.190	l
2.917	l	1.974	l	1.528	l	1.163	l
2.827	l	1.934	l	1.482	l	1.141	l
2.694	m	1.893	l	1.457	l	1.134	l
2.663	l	1.815	l	1.423	l	1.128	l
						1.078	l

[a] h, high intensity; m, medium intensity; l, light intensity.

Acknowledgment.—This work was supported in part under contract with the Office of Naval Research and in part by a grant from the National Institute of Health.

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[10] F. Aubke and G. H. Cady, *Inorg. Chem.*, in press.

CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES,
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Preparation of Bis(triphenylphosphine oxide) Complexes of Nickelous and Cobaltous Halides

BY W. E. DANIELS

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In this laboratory, it has been found that a useful method for the preparation of complexes of the type $MX_2 \cdot 2(C_6H_5)_3PO$[1] consists of oxidation of the corresponding phosphine complex, $MX_2 \cdot 2(C_6H_5)_3P$, with hydrogen peroxide.

To the writer's knowledge, no such simple oxidation has been reported as a synthetic method.

Experimental

Materials.—Bis(triphenylphosphine)nickel(II) bromide and iodide were prepared by the method of Venanzi.[2] Bis(triphenylphosphine)cobalt(II) bromide was prepared by the method of Chatt and Shaw.[3] Hydrogen peroxide was J. T. Baker's Reagent Grade 30% H_2O_2. Melting points are uncorrected.

Preparation of Bis(triphenylphenylphosphine oxide)nickel(II) Bromide.—A refluxing solution of $NiBr_2 \cdot 2(C_6H_5)_3P$ (7.4 g., 0.01 mole) in absolute ethanol (250 ml.) was treated with 30% hydrogen peroxide solution (2.5 ml., 0.024 mole) for 1 hr. The dark green solution became pale yellow after this time. The solution

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[1] F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771, 5774 (1960).

[2] L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

[3] J. Chatt and B. L. Shaw, *ibid.*, 285 (1961).

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 $NiBr_2 \cdot 2(C_6H_5)_3PO$ 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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Synthesis of Monochloropentaaquochromium(III) Ion by Displacement Ion Exchange

BY JAMES E. FINHOLT, KENNETH G. CAULTON,
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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).