spectra using at low magnetic field a Model HR-60 n.m.r. spectrometer. Molecular weights were measured in benzene using a Mechrolab vapor pressure osmometer (Elek Microanalytical Laboratories, Los Angeles, Calif., and at JPL). Dipole moments were obtained in benzene (Guggenheim Method) by Dr. H. Nöth, Munich, Germany.

Analyses.—Tungsten was weighed as WO_3 after treatment with HNO_3. Chlorine was titrated with $AgNO_3$ solution (Mohr) after dissolution in dilute H_2O_2 solution and neutralization. Elemental and alkoxyl (Zeisel) analyses were obtained by Elek Microanalytical Laboratories.

Studies of the Alcoholysis of WCl_6.—Samples of WCl_6 were transferred under nitrogen to a stoppered 50-ml. flask and weighed (0.2–13 g.). The flask with a funnel and trap was evacuated and all reactions were carried out in the absence of air. Alcohol or sodium alkoxide solution was run in onto WCl_6 held at −196° and reaction began on warming. From 1 g. of WCl_6 and 10 ml. of methanol or ethanol yellow solutions formed above 0° in an endothermic reaction. From 1 g. of WCl_6 and 3–5 ml. of methanol or ethanol brown solutions formed, turning blue; cooling to 0° was required. With strong cooling to −20° a black-brown solution was made from 13 g. of WCl_6 and 20 ml. of ethanol; reaction of 13 g. with 10 ml. was violent. All solutions turned blue on evaporation *in vacuo* and gave a blue solid residue. The distillate of alcohol, aldehyde, chlorine, and hydrogen chloride was diluted with water, reduced with H_2O_2, and titrated with base to give a value of 2.5 to 3HCl/W. Blue residues were hydrolyzed with water–alcohol or dissolved in H_2O_2; filtrate or solution gave 3HCl/W by base and $AgNO_3$ titration. Tungsten hexachloride dissolved to give a yellow solution above −70° in solutions of sodium alkoxide in the parent alcohol (1:6 molar ratio). Greenish evaporation residue in alcohol gave NaCl and a brown solution which, hydrolyzed, gave a partially tetravalent black-brown hydroxide (about 1.5 reducing equiv./W).

For oxidation studies WCl_6 (1 mmole) was treated with 2 ml. of alcohol or 10 ml. of alkoxide solution. Evaporation residues were dissolved in 2 ml. of methanol and hydrolyzed by adding water–methanol (1:1, 10 ml.). Blue tungsten hydroxide (or black-brown from alkoxide reaction) was filtered, washed with water–methanol, and oxidized by shaking with 20 ml. of 0.144 N ceric sulfate solution in 1 M H_2SO_4. Excess cerium(IV) was titrated in the filtrate from cerous tungstate, using ferrous ammonium sulfate solution and ferroin indicator. Air was excluded until the final filtration. Partial reoxidation occurred in methanol but venting to a cold trap removed the chlorine (change from 0.648 to 0.893 reducing equiv./W). In ethanol some reduction to W(IV) also occurred (1.04 to 1.17 reducing equiv./W).

Tungsten(V) Trichloride Dialkoxides.—Upon drying under vacuum the blue evaporation residues from the WCl_6 alcoholysis reached the compositions $WCl_3(OCH_3)_2$ (I) and $WCl_3(OC_2H_5)_2$ (II). The substances are extremely soluble in alcohol and CH_3CN. *Anal.* Calcd. for I: C, 6.81; H, 1.72; OCH_3, 17.61; W, 52.20. Found: C, 6.88; H, 1.98; OCH_3, 14.29; W, 53.80; ratio Cl/W, 3.0; red. equiv./W, 0.89. Found for II: ratio Cl/W, 3.0; red. equiv./W, 1.04.

Blue solutions of II in methanol show absorption maxima at 445 and 568 $m\mu$. N.m.r. spectra of I in methanol or ethanol show sharp proton signals from the alkyl groups of the solvent and a broad hydroxyl signal which narrows below −50° forming well-defined triplets at −70°. A strong e.p.r. signal was obtained from a blue 10^{-5} M solution of II in CH_3CN.

Solutions of II (ethanol, CH_3CN) dissolve NaF with a dark blue color. Solutions of I in methanol (0.2 M) dissolve NaCl up to a ratio 3NaCl/I (blue). Solid I was dissolved in methanol solutions of $LiOCH_3$ (dark brown), $NaOCH_3$, and $KOCH_3$ (dark blue-green) at a molar ratio of 1:3 without precipitation of NaCl or KCl.

Di-μ-chloro-dichlorohexaethoxoditungsten(V) (III).—WCl_6 (4.515 g.) was reduced with absolute ethanol (4.5 ml., 1 hr., cooling to 0°, venting to a cold trap). The dark brown reaction solution was evaporated for 1 hr.; the blue residue was taken up in 5 ml. of ethanol and evaporated until dry. The dark green residue gave in 10 ml. of ethanol a blue solution turning green, brown, and finally red. Red crystals of III separated in 2 days and were washed by decanting and distilling in the closed system. The solution was evaporated and the blue residue solvolyzed again for a total yield of 600 mg. of III, 13.5%. Reaction ended at 3.6HCl/W evolved and considerable reduction to unknown W(IV) compounds was observed.

Anal. Calcd. for $W_2Cl_4(OC_2H_5)_6$: C, 18.48; H, 3.88; OC_2H_5, 34.67; Cl, 18.18; W, 47.15; mol. wt., 779.9. Found: C, 18.34; H, 3.82; OC_2H_5, 32.70; Cl, 17.40; W, 47.28; mol. wt., 762; in this laboratory: Cl, 17.49; W, 47.03; mol. wt. (at 49 mg./ml.), 791.

III is soluble in chloromethanes, acetone, benzene, acetonitrile, dimethylformamide, diethyl ether, carbon disulfide; slightly soluble in heptane, methanol, propanol, glacial acetic acid; and insoluble in water and ethanol.

Spectra in $CHCl_3$ show absorption maxima at 301, 412, and 518 $m\mu$. Infrared absorption bands are (cm.$^{-1}$): 2975, 2928, 2860 (C–H stretch); 1435, 1364, 1338 (C–H bending); 1255 (w), 1131 (m), 1094 (s), 1078 (m), 1040 (vs), 984 (s), 922 (vs), 888 (s), 795 (m), and 612 (s). The C–O stretching modes center around 1040,[4] W–O stretching modes around 900 cm.$^{-1}$. N.m.r. spectra (CCl_4) show signals of methyl and methylene protons at 61.0 and 273.0 c.p.s. downfield from tetramethylsilane (internal standard) and, half as intense, at 82.6 and 347.8 c.p.s. (Figure 1). The dipole moment was found equal to 2.06 D. and was corrected (10% for atom polarization) to a value 1.85 D.

Heated in a sealed, evacuated tube, III darkens above 128°, melts partially at 196°, and at 213° forms blue-black solid and clear liquid. III is inert to ceric sulfate solution and 1 N $K_2Cr_2O_7$ in 12.5% H_2SO_4 (ethanol oxidation reagent[8]) but reacts with aqueous base and dissolves in alkaline H_2O_2 solution.

Ethanolic $NaOC_2H_5$ and III (6:1, 2 hr.) formed 4NaCl and a blue solution, turning green after 15 hr. N.m.r. spectra (CCl_4) of the evaporation residue were extremely complex. The same reaction at 4:1 ratio gave first the blue solution, which dissolved III forming 2NaCl and a red solution of a brown, acetone-soluble substance. Sodium iodide in acetone and III (4:1, 24 hr.) formed 3.54NaCl per mole under a green solution. Potassium iodide and III in methanol (6:1) formed no KCl in 4 days; recovery was 84%.

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CONTRIBUTION FROM THE CHEMICAL LABORATORY
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Preparation and Isolation of Ligandpentaaquochromium(III) Sulfate Monohydrate Compounds

BY PETER MOORE AND FRED BASOLO

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In the course of our work it has been necessary to isolate complexes of the type $[Cr(H_2O)_5X]^{2+}$ (X = F, Cl, Br, I, NO) as solids. This has been achieved using sulfate as the counterion and extracting water from aqueous solutions of these ions by the method described below. Although some of these complexes have been isolated previously, it is believed that the procedure described here is simpler and may be universally applicable to dipositive cations of aquochromium(III) complexes. The fluoro, bromo, and iodo complexes have been isolated in this way for the first time. They are green solids stable for months under dry nitrogen.

Monohalogenopentaaquochromium(III) complexes are best prepared either by heating hexaaquochromium(III) perchlorate with the halide ion[1] (fluoride or chloride) or by allowing chromium(II) perchlorate to react with bromine or iodine[1,2] (bromide or iodide). The nitroso complex, $[Cr(H_2O)_5NO]^{2+}$, is obtained by the reaction of chromium(II) perchlorate with perchloric acid solutions saturated with nitric oxide.[3] All of these procedures yield as by-products hexaaquochromium(III) and traces of a hydrolytic dimer. The required monosubstituted derivative is separated by ion exchange; in some cases displacement ion exchange, using cerous ion as the displacing agent, has been used to give more concentrated aqueous solutions of the required complex.[4]

Another way of concentrating the dilute aqueous solutions eluted from the ion-exchange column and for eventually precipitating the product is described here. To the dilute solution (*e.g.*, 0.02 *M* complex) is added absolute ethanol (half the original volume) and *dry* ether (5 volumes). The mixture is shaken well and allowed to settle into an aqueous and an ether layer. The upper, ether layer is discarded and the procedure repeated several times adding a little less ethanol each time. In this way water is extracted into the ether–alcohol and the aqueous layer containing the complex becomes concentrated. If sulfuric acid is added, the complexes may be isolated eventually as solid sulfates. The procedure is carried out at 0° to avoid possible exchange of coordinated water molecules with the ethanol.[5] Care must also be taken to avoid adding any impurities such as alkali metal salts at any stage in the preparations, since these may then be present in the final products. Provided the ion-exchange extraction is clean, pure products are obtained. If too much ethanol is added, mixing of the solutions may occur and no separation is possible. However, should this happen a little water is added until a boundary is obtained and addition of more ethanol is omitted subsequently.

Experimental

Materials.—Because of the method of extracting the final products, it is necessary to use pure starting materials. Hexaaquochromium(III) perchlorate was prepared by adding 30% hydrogen peroxide (180 ml.) dropwise, with cooling and stirring, to a solution of chromium trioxide (40 g.) in water (100 ml.) and 70% perchloric acid (104 ml.). The mixture was boiled to decompose excess hydrogen peroxide and the volume reduced to *ca.* 200 ml. by evaporation. The volume was further reduced by vacuum distillation until crystallization just commenced. The solution was then cooled to below room temperature and filtered. The crystals of hexaaquochromium(III) perchlorate were recrystallized once from water.

Other materials were reagent grade.

Preparation of Iodopentaaquochromium(III) Sulfate Monohydrate, $[Cr(H_2O)_5I]SO_4\cdot H_2O$.—The procedure was essentially that described by Taube and Myers.[2] However, to facilitate extraction and subsequent purification of the products some modifications were used. A strong solution of chromium(II) perchlorate was prepared under nitrogen by electrolysis of chromium(III) perchlorate (*ca.* 46 g.) in water (40 ml.) and 70% perchloric acid (1 ml.) at a mercury pool cathode (area 30 cm.^{2}, 4 v., 0.3 amp.) for 20 hr.[6,7] This chromous solution was cooled in an ice bath and the cold solution passed dropwise, under nitrogen and with stirring, into iodine (25 g.) in concentrated (47%) HI (20 ml.) and water (10 ml.) cooled to −5° in an ice–salt bath. The mixture was kept below 0° at all times to avoid hydrolysis of the product, and solvents which were added afterward were precooled in an ice bath. An equal volume of ethanol was added followed by ether (2 volumes) and then concentrated H_2SO_4 (4 ml.) was added dropwise with caution and vigorous stirring. The volume was increased to 1 l. with ether, and upon shaking green crystals separated. These were collected on a filter and washed to remove excess iodine with ether (300 ml.) followed by ethanol–ether (1:1, 200 ml.) and then ether (100 ml.); yield 20 g. Analysis for iodide ion on a sample of this crude product indicated that it contained 90% of the desired material. The product was purified by dissolving in 0.2 *M* $HClO_4$ at 0° and placing on a Dowex 50W-X8 (100–200 mesh) cation-exchange column cooled to below 1°. The iodo complex was eluted with 1 *M* $HClO_4$ and collected below 0° as described by Ardon.[7] To the eluent, cooled in an ice–salt bath, was added dropwise and with stirring concentrated H_2SO_4 (3 ml.) and then ethanol–ether as described previously. Successive treatments with ethanol–ether finally gave the pure product as green crystals. These were dried in a vacuum desiccator over $CaCl_2$; yield 12 g. The product was analyzed for iodide ion gravimetrically as AgI, for sulfate ion as $BaSO_4$ after adding sodium acetate to avoid complex sulfate formation,[8] and for chromium by oxidation to chromate with sodium peroxide followed by spectrophotometric determination of the chromate.[1]

Anal. Calcd. for $[Cr(H_2O)_5I]SO_4\cdot H_2O$: I, 33.1; SO_4, 25.1; Cr, 13.6. Found: I, 32.6; SO_4, 25.7; Cr, 13.6.

Preparation of Bromopentaaquochromium(III) Sulfate Monohydrate, $[Cr(H_2O)_5Br]SO_4\cdot H_2O$.—The procedure and analysis was identical with that described for the iodo complex except that in the preparation bromine (7 ml.) replaced iodine (25 g.); yield 16 g.

Anal. Calcd. for $[Cr(H_2O)_5Br]SO_4\cdot H_2O$: Br, 23.8; SO_4, 28.6; Cr, 15.5. Found: Br, 23.7; SO_4, 27.9; Cr, 15.5.

Preparation of Chloropentaaquochromium(III) Sulfate Monohydrate, $[Cr(H_2O)_5Cl]SO_4\cdot H_2O$.—The complex was prepared[9] by refluxing chromium(III) perchlorate (*ca.* 26 g.) with 2 *M* hydrochloric acid (50 ml.) followed by ion-exchange extraction[1] and separation by the method described for the iodo complex. The product was dried and analyzed as described before; yield 4 g.

Anal. Calcd. for $[Cr(H_2O)_5Cl]SO_4\cdot H_2O$: Cl, 12.2; SO_4, 32.8; Cr, 17.8. Found: Cl, 11.7; SO_4, 32.4; Cr, 17.5.

Preparation of Fluoropentaaquochromium(III) Sulfate Monohydrate, $[Cr(H_2O)_5F]SO_4\cdot H_2O$.—The complex was prepared by refluxing a solution of hexaaquochromium(III) perchlorate (*ca.*

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[9] Compare ref. 1. Here HCl was used instead of KCl to avoid the possibility of contamination of the final product with K_2SO_4.

52 g.) and potassium fluoride (11.6 g.) in water (50 ml.) for 3 hr. ($KClO_4$ was removed on a filter first). This preparation and the subsequent ion-exchange extraction have been described by Swaddle and King.[1] The required complex was eluted from the ion-exchange resin with sulfuric acid (0.5 *M*) and precipitated as the sulfate by the method described before. The product contained a considerable amount of potassium sulfate and was purified by extracting the complex with the minimum of ice-cold perchloric acid (1 *M*) and removing the residue of potassium perchlorate on a filter while the solution was cooled below −5°. The fluoro complex was reprecipitated as the sulfate by adding absolute ethanol to the saturated filtrate with vigorous stirring. The product was collected on a filter, washed with ether, and dried by sucking air through it and then in a vacuum desiccator over $CaCl_2$; yield 3 g. A better yield would probably be obtained if hydrofluoric acid was used instead of potassium sulfate. However, Pyrex glassware could not then be used.

Anal. Calcd. for $[Cr(H_2O)_5F]SO_4 \cdot H_2O$: Cr, 18.9. Found: Cr, 18.9. Fluoride ion interferes with the sulfate ion analysis.

Preparation of the Complex $[Cr(H_2O)_5NO]SO_4 \cdot H_2O$.—The complex was prepared essentially by the method of Ardon and Herman.[3] A solution (50 ml.) of 0.1 *M* $Cr(ClO_4)_2$ was added dropwise, in portions of 10 ml., under nitrogen and with stirring to a saturated solution of nitric oxide in 0.2 *M* $HClO_4$ (500 ml.) cooled in an ice bath (to increase the solubility of the nitric oxide). After each addition of $Cr(ClO_4)_2$ the solution was resaturated with nitric oxide gas. The products were separated by ion exchange and the desired red-brown product precipitated as the sulfate by the methods described for the iodo complex. This method of separation gave a monohydrated product rather than the anhydrous salt isolated by previous workers[3]; yield 0.7 g.

Anal. Calcd. for $[Cr(H_2O)_5NO]SO_4 \cdot H_2O$: Cr, 18.2. Found: Cr, 18.0.

Spectra.—A Cary Model 14 spectrophotometer was used. The spectra of all the complexes in 1 *M* $HClO_4$ were obtained to check the molar absorbancy indices and peak positions with the reported values.[1-3] Good agreement was observed in all cases. The observed peak positions (in mμ), shoulders (sh), and corresponding molar absorbancy indices (in parentheses) were: fluoro complex 268 (5.0), 417 (12.4), 594 (12.9), *ca.* 667 (sh, *ca.* 5.1); chloro complex 428 (21.9), 608 (17.4), *ca.* 674 (sh, *ca.* 7.5); bromo complex 432 (23.7), *ca.* 470 (sh, *ca.* 15), 622 (21.3), *ca.* 675 (sh, *ca.* 12); iodo complex 474 (32.8), 649 (unsymmetric peak, 36.5); $[Cr(H_2O)_5NO]^{2+}$ 325 (91.7), *ca.* 399 (sh, *ca.* 90.5), 451 (120.9), 562 (28.5).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Modified Friedel-Crafts Preparation of 2,2,4,4-Tetrachloro-6,6-diphenylcyclotriphosphazatriene[1]

BY E. T. MCBEE, K. OKUHARA, AND C. J. MORTON

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The title compound was first prepared[2] by refluxing a benzene solution of hexachlorocyclotriphosphazatriene with aluminum chloride for 2 days. The yield (40%) is not improved substantially either by increasing the proportion of aluminum chloride or by extending the reaction time.[3,4] The low yields and slow reaction rates are unexpected and have not hitherto been explained satisfactorily.

We noted that hydrogen chloride, formed as a coproduct, could protonate $P_3N_3Cl_6$, thereby obstructing the formation of the quasi-phosphonium ion, $P_3N_3Cl_5^+$, which is the probable species[4] attacking benzene. The liberated chloride (as $AlCl_4^-$) could also react with this electrophile, stabilize the protonated species in the form of a complex, and, to a lesser extent, decrease the effective concentration of aluminum chloride.

$$P_3N_3Cl_6 + C_6H_6 \xrightarrow{AlCl_3} P_3N_3Cl_4(C_6H_5)_2 + 2HCl$$

$$HCl + P_3N_3R_6 + AlCl_3 \longrightarrow P_3N_3R_6 \cdot H^+ AlCl_4^-$$

$$(R = Cl_6,\ Cl_4(C_6H_5)_2,\ \text{etc.})$$

The original Friedel-Crafts reaction was modified in the three following ways: (A) Repetition of the reaction using fresh catalyst after decomposition of the complex (no. 3 and 4). (B) Addition of aluminum[5] to the reaction mixture (no. 5 and 6). (C) Addition of amines to the reaction mixture (no. 7, 8, and 9). The results are given in Table I together with those (no. 1 and 2) obtained for unmodified conditions.

All three methods are designed to reduce the effect of hydrogen chloride. Since each gives high yields of phenylated product, the contention that this coproduct is responsible for adversely influencing the reaction is confirmed. When the removal of hydrogen chloride is particularly efficient, as in methods (A) and (B) or when the reaction is doubly modified (no. 10), tetraphenylation is more prevalent, especially when compared with the result for the unmodified reaction. Hence, the possibility that the rate of phenylation of the 2,2,4,4-tetrachloro-6,6-diphenyl compound is greater than that of hexachlorocyclotriphosphazatriene cannot be ignored.

Since some amines are known to complex with aluminum chloride,[6] an excess of the latter is required in method (C). Nonetheless, using triethylamine or pyridine, high yields (up to 77%) of the diphenyl derivative are obtained. Although advantageous, the yields of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene are unexpectedly small. Possibly, the major product though not the starting material competes successfully with these amines for the protons of hydrogen chloride.

Experimental

Aluminum chloride (anhydrous, granular), a product of Baker Chemical Co., and technical benzene were used without further purification or drying. Separation of the products was generally carried out by chromatography on acid-washed alumina (Merck).

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