calomel electrode (-0.2680 v.),[5] $E_2°$ is the standard oxidation potential of the mercury–mercurous cobalticyanide electrode, $m\gamma_{\pm}$ refers to $K_3Co(CN)_6(aq)$, and $m'\gamma_{\pm}'$ refers to KCl(aq). From the observed cell voltages, the above stated molalities, and the mean molal activity coefficients of $K_3Co(CN)_6$[3] and KCl,[7] the standard oxidation potential of the mercury–mercurous cobalticyanide electrode is calculated to be

$$6Hg(l) + 2Co(CN)_6^{3-}(aq,\ a = 1) = (Hg_2)_3[Co(CN)_6]_2(s) + 6e^- \quad E° = -0.427 \pm 0.001 \text{ v.}$$

In the calculation of this $E°$ the solid phase was assumed to be anhydrous salt, although it is probably the tetrahydrate. This introduces no significant uncertainty in $E°$, however, since the correction for the activity of water is within the experimental error.

Silver Cobalticyanide.—The potential of the silver–silver cobalticyanide electrode was determined in the cell

$$Ag(s)|Ag_3Co(CN)_6(s)|K_3Co(CN)_6(aq)|(Hg_2)_3[Co(CN)_6]_2(s)|Hg(l)$$

If the solid phases controlling the activities of Ag^+ and Hg_2^{2+} ions in solution are those represented in the cell diagram the observed cell voltage should be independent of the $K_3Co(CN)_6$ concentration and $E = E°$. For $K_3Co(CN)_6$ molalities of 0.10, 0.20, and 0.50 the observed cell voltages were (silver negative): 0.130 ± 0.001, 0.128 ± 0.001, and 0.129 ± 0.001 v., respectively. This cell came to equilibrium in about 1 day and had a constant voltage for as long as it was followed (6–8 days in each case). The observed cell voltage was unaffected by the agitation of the electrode components.

Using the above-determined value of the mercury–mercurous cobalticyanide standard oxidation potential, the standard oxidation potential of the silver–silver cobalticyanide electrode is computed to be

$$3Ag(s) + Co(CN)_6^{3-}(aq,\ a = 1) = Ag_3Co(CN)_6(s) + 3e^- \quad E° = -0.298 \pm 0.001 \text{ v.}$$

Discussion

Taking the standard oxidation potential at 25° of the Ag–Ag^+ electrode as -0.799 v. and that of the Hg–Hg_2^{2+} electrode as -0.789 v.,[8] one computes

$$3Ag^+ + Co(CN)_6^{3-} = Ag_3Co(CN)_6(s) \quad \Delta G° = -34.66 \text{ kcal.}$$

$$3Hg_2^{2+} + 2Co(CN)_6^{3-} = (Hg_2)_3[Co(CN)_6]_2(s) \quad \Delta G° = -50.09 \text{ kcal.}$$

From these $\Delta G°$ values the solubility products of $Ag_3Co(CN)_6$ and $(Hg_2)_3[Co(CN)_6]_2(s)$ are computed to be 3.9×10^{-26} and 1.9×10^{-37}, respectively.

The previously reported value[1] for K_{sp} of $Ag_3Co(CN)_6$ is 8.6×10^{-21}. This value was obtained from potentiometric titration data in cells using salt bridges, a method which can introduce large uncertainties in the data. The K_{sp} values differ, however, by more than can be accounted for by a liquid junction potential of even 0.05 v., and the K_{sp} obtained in the potentiometric investigation may have been adversely affected by failure to attain equilibrium as well, since it was found in this investigation that the silver–silver cobalticyanide electrode is slow to come to equilibrium.

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CONTRIBUTION FROM THE JET PROPULSION LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA

Chloride Alkoxides of Pentavalent Tungsten[1]

BY OLGIERD J. KLEJNOT[2]

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Studies aimed at syntheses of the unknown tungsten hexa- and pentaalkoxides have led to the first isolation of tungsten(V) chloride alkoxides (I–III). The reported green $W_2Cl_4(OC_2H_5)_6$[3] obtained by reducing pentavalent solutions seems to be tetravalent with two ethanol ligands in place of two ethoxo ligands.

Dissolution of tungsten hexachloride in alcohols gave long-known yellow solutions,[3] but the evolution of chlorine in methanol or ethanol has only been noted now

$$WCl_6 + 2C_2H_5OH \longrightarrow {}^1/_2Cl_2 + WCl_3(OC_2H_5)_2 + 2HCl \tag{1}$$

$$Cl_2 + C_2H_5OH \longrightarrow CH_3CHO + 2HCl \tag{2}$$

A violent reaction, which probably involves the aldehyde, occurs at high concentration of products. On evaporation the reaction solutions render paramagnetic, ink-blue trichloride dialkoxides, $WCl_3(OCH_3)_2$ (I) and $WCl_3(OC_2H_5)_2$ (II), whose blue solutions in alcohol give with hydrogen chloride a pale yellow color, reverting to blue on partial evaporation *in vacuo*. The trichloride dialkoxides react with moisture and oxygen. In alcohol they form soluble complexes with NaF, NaCl, and the methoxides of Li, Na, and K. Pure alcohol solutions, however, show at room temperature a slow limited solvolysis, up to a low concentration of HCl, with blue (methanol) or red (ethanol) color. From a solution of II, di-μ-chloro-dichlorohexaethoxoditungsten(V) (III) is slowly precipitated in 4–15% yield

$$2WCl_3(OC_2H_5)_2 + 2C_2H_5OH \longrightarrow W_2Cl_4(OC_2H_5)_6 + 2HCl \tag{3}$$

Diamagnetic, red dimer III is inert to water, acids, and oxidizing agents, but is reactive toward bases. The dimeric formula and chemical evidence suggest a bioctahedral structure with two bridging chloro ligands and pentavalent tungsten atoms. The compound is

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(1) Results of one phase of research supported by the National Aeronautics and Space Administration under Contract No. NAS7-100.

(2) Unified Science Associates, Inc., Pasadena, Calif. 91105.

(3) A. Fischer and L. Michiels, *Z. anorg. Chem.*, **81**, 102 (1913); A. Fischer, *ibid.*, **81**, 170 (1913).

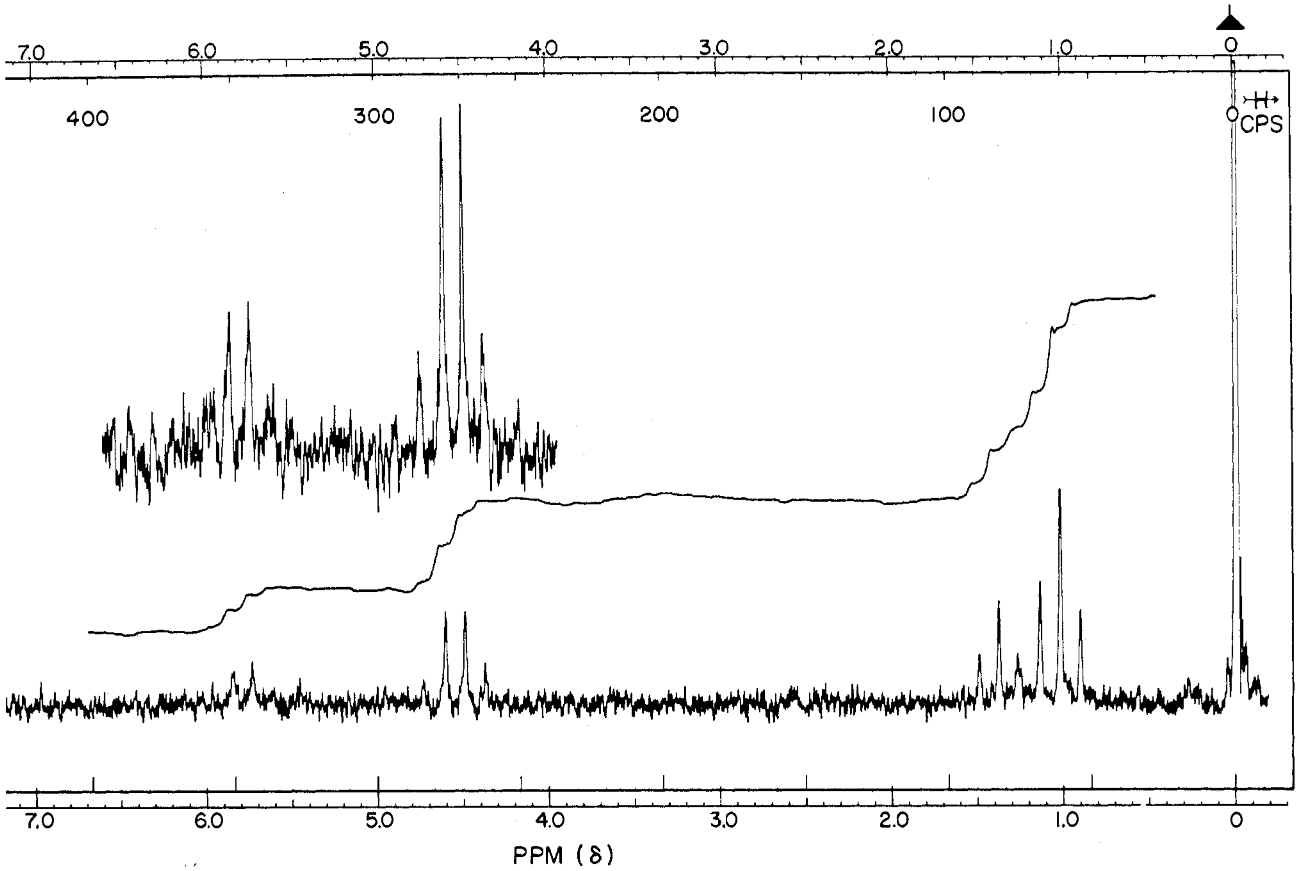

Figure 1.—N.m.r. spectra of $W_2Cl_4(OC_2H_5)_6$.

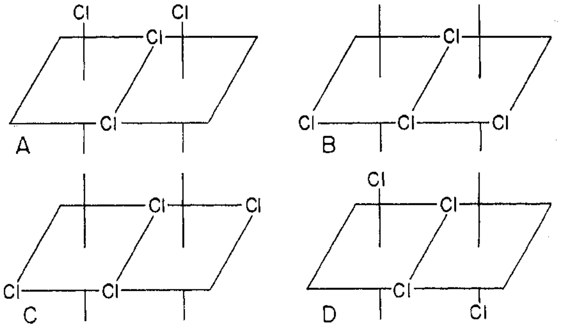

Figure 2.—Chloro-bridged isomers of $W_2Cl_4(OC_2H_5)_6$ with 4:2 ratio of two kinds of ethoxyl.

inert to KI in methanol, as is also reported for $Nb_2Cl_2(OC_2H_5)_6py_2$.[4] However, sodium iodide in acetone exchanges all chloro ligands, as in chloro-bridged platinum complexes.[5] With sodium ethoxide in ethanol two soluble complexes are formed, formally composed $NaCl \cdot W(OC_2H_5)_5$ and $NaOC_2H_5 \cdot W(OC_2H_5)_5$.

N.m.r. spectra of the single isomer III (Figure 1) show two groups of proton signals with an intensity ratio of 2:1, indicating four and two ethoxyls in two different environments. This agrees with the complexity[4] of the infrared spectra. The dipole moment suggests an unsymmetrical ligand distribution. Assumed chloro bridging (eight isomers) leads to four isomers with a 4:2 ethoxyl ratio, two of which are unsymmetrical (Figure 2, A and B). The large relative chemical shift fits B (two ethoxyls *trans* to Cl) rather than A (all *trans*). Estimation of the dipole moment using partial moments of 4.5 (W–Cl) and 2.9 ($W-OC_2H_5$) gives 3.2 D. (twice 1.6, parallel) for isomer A and 2.26 D. for isomer B. Ethoxo bridging (sixteen isomers) provides two symmetrical isomers with a 4:2 ethoxyl ratio and is unlikely as III is inert to water. Therefore configuration B is assumed as the correct one, pending the results of structure determination by single-crystal X-ray technique.[6] In accordance with predictions by Sheldon,[7] dimer III is expected to contain short metal–metal bonding between tungsten atoms displaced toward each other from the centers of coordination octahedra.

Experimental

Materials.—Tungsten hexachloride (Climax Molybdenum and Alfa Inorganics) was sublimed under vacuum and stored in dry nitrogen. *Anal.* Calcd. for WCl_6: W, 46.36; Cl, 53.63. Found: W, 46.70; Cl, 51.57. Methanol, ethanol, and potassium and sodium iodides were reagent grade.

Measurements.—Spectra in the ultraviolet and visible ranges were obtained using a Beckman Model DK-2 spectrophotometer and 1-cm. silica cells modified as ampoules. Infrared spectra between 4000 and 500 cm.$^{-1}$ were obtained using a Perkin-Elmer Model 421 spectrophotometer and KBr pellets. N.m.r. spectra were obtained using a Varian Associates Model A-60 and e.p.r.

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(4) R. A. D. Wentworth and C. H. Brubaker, Jr., *Inorg. Chem.*, **3**, 47 (1964).

(5) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

(6) Kindly undertaken by Dr. N. F. Yannoni, Air Force Cambridge Research Laboratories, Bedford, Mass. (to be published).

(7) J. C. Sheldon, *Australian J. Chem.*, **17**, 1191 (1964).

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 mμ. 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 mμ. 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
AT NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

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,