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Complexes of Tungsten(V) Which Contain Alkoxide as a Ligand

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Solutions of WCl_5 in alcohols have been investigated. The solutions were acidic with HCl, neutral, or basic with alkoxide ion. A number of tetrachlorodialkoxo- and pentachloroalkoxotungstates(V) were prepared and characterized and spectra and magnetic properties were determined. A yellow compound $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$ was isolated from ethanol solutions which had been saturated with HCl. The pentachloroalkoxotungstate(V) species decomposed by the elimination of alkyl chloride to give a mixture of solid materials which probably contain tetrachlorooxotungstate(V).

In this laboratory, investigations of the preparation of paramagnetic chloroalkoxo or chloro alcohol complexes have been reported.[1-4] Tungsten(V) became of interest for comparison with molybdenum(V). Diagonal similarities to niobium(IV) could also be anticipated.

Funk and Naumann[5] prepared several tungsten(V) chloromethoxo dimers, a monomeric tungsten(V) chloromethoxoalcoholate, and the pyridinium and triethylammonium salt of the tetrachlorodimethoxotungstate(V) anion.

Klejnot[6] examined the behavior of WCl_6 in methanol and ethanol. He obtained a dimeric chloroethoxotungsten(V) species, a monomeric chloroethoxo compound of tungsten(V), and the analogous methoxo derivative.

Other tungsten(V) work has centered on a number of oxyhalide complexes,[7,8] amine derivatives,[9,10] and the hexahalo anion.[7,11-14]

Experimental Section

Materials.—Absolute ethanol was dried by distillation in the presence of sodium ethoxide and diethyl phthalate. Methanol was dried by distillation in the presence of magnesium; 1-propanol was dried by distillation in the presence of sodium. Tetraalkylammonium salts were reagent grade and dried in an oven. Anhydrous HCl was used directly from the cylinder.

Anhydrous WCl_5 was prepared from WCl_6 by reduction with phosphorus.[15] The WCl_6 was obtained from Climax Molybdenum Co., sublimed under a vacuum, and sealed in ampoules.

Thionyl chloride was reagent grade. Ethyl ether was dried over sodium. Nitromethane[16] was dried by distillation in the presence of Drierite. The distillate was then passed over a Dowex 50W-X8 resin to remove basic impurities. All solutions and compounds were stored under dry nitrogen.

Preparations. **$(C_2H_5)_4N(WCl_6)$.**—A 10.8-g sample of WCl_5 (0.03 mol) was added to a solution (−78°) which was prepared by saturating 25 ml of ethanol with HCl at 0°. The temperature of the suspension was increased to 0°. A solution of 4.98 g of tetraethylammonium chloride dissolved in 35 ml of ethanol was rapidly added to the yellow-brown solution. A dark green precipitate formed. It was washed with a 5:1 mixture of ethyl ether–ethanol and finally with ethyl ether. The compound was dried under vacuum. The resulting compound was approximately $(C_2H_5)_4N(WCl_6)$ but also contained a small amount of what was probably $(C_2H_5)_4N[W(OC_2H_5)Cl_5]$. The compound was purified by recrystallization from thionyl chloride; yield ~25%. *Anal.* Calcd for $WCl_6C_8H_{20}N$: W, 34.90; Cl, 40.38; C, 18.24; H, 3.83; N, 2.66. Found: W, 34.78; Cl, 39.94; C, 18.49; H, 4.02; N, 2.72.

$(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$.—A 10.8-g sample of WCl_5 (0.03 mol) was added to 25 ml of ethanol at −78°. After the temperature was increased to 0°, a yellow-green solution was obtained. A solution which was prepared by dissolving 4.98 g of $(C_2H_5)_4NCl$ (0.03 mol) in 35 ml of ethanol was rapidly added to it. A yellow-green precipitate formed immediately. The compound was filtered, washed with 5:1 ethyl ether–ethanol and finally with ethyl ether, and dried under vacuum. The resulting compound was a mixture of $(C_2H_5)_4N[W(OC_2H_5)Cl_5]$ and $(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$ as indicated by analysis, loss of ethyl chloride, and magnetic data (see below). A 50-ml portion of ethanol was added, the solution was stirred for 18 hr, and the mixture was converted to $(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$. The green compound was filtered, washed with ethyl ether–ethanol and finally with ethyl ether, and dried under vacuum. *Anal.* Calcd for $WCl_4C_{12}H_{30}O_2N$: W, 3.10; Cl, 25.97; C, 26.40; H, 5.54; N, 2.57. Found: W, 33.73; Cl, 26.25; C, 26.46; H, 5.68; N, 2.57.

$(CH_3)_4N[W(OC_2H_5)_2Cl_4]$.—Tetramethylammonium chloride was added in place of tetraethylammonium chloride in the above preparation. The compound was obtained in better purity by the following procedure. A 7.2-g sample of WCl_5 (0.02 mol) was added to 35 ml of a cold (−78°) ethanol solution, which contained 0.04 mol of $Li(OC_2H_5)$. The heterogeneous mixture at −78° became a solution at 25°. Addition of a solution which contained 2.2 g of $(CH_3)_4NCl$ (0.02 mol) in 20 ml of ethanol caused a green compound to precipitate. The product was washed with a 5:1 ethyl ether–ethanol solution and then with pure ethyl ether. It was dried under vacuum; yield 76.30%.

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Anal. Calcd for $WCl_4C_8H_{22}O_2N$: W, 37.53; Cl, 28.95; C, 19.61; H, 4.53; N, 2.86. Found: W, 37.38; Cl, 29.41; C, 19.45; H, 4.48; N, 3.00.

$(CH_3)_4N[W(OCH_3)_2Cl_4]$.—The procedure was similar to the final preparation of the previous compound except methanol was used in the place of ethanol; yield 74.11%. *Anal.* Calcd for $WCl_4C_6H_{18}O_2N$: W, 39.80; Cl, 30.70; C, 15.60; H, 3.93; N, 3.03. Found: W, 40.02; Cl, 30.74; C, 15.70; H, 4.09; N, 3.24.

$[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$.—A 10.8-g sample of WCl_5 (0.03 mol) was added to 25 ml of ethanol (−78°) which had been saturated with HCl at 0°. The temperature was increased to 0°. After 15 min, a solution which contained 3.3 g of $[(CH_3)_4N]Cl$ (0.03 mol) in 35 ml of ethanol was rapidly added. Two hours later, a yellow precipitate was filtered, washed twice with a 5:2 ethyl ether–ethanol solution and finally with ethyl ether, and then dried under vacuum; yield 40.78%. *Anal.* Calcd for $WCl_6C_{10}H_{29}ON_2$: W, 31.17; Cl, 36.06; OC_2H_5, 7.63; C, 20.36; H, 4.96; N, 4.75. Found: W, 31.01; Cl, 36.30; OC_2H_5, 8.16; C, 20.21; H, 4.95; N, 4.88.

$(C_2H_5)_4N[W(OC_2H_5)Cl_5]$.—The procedure was the same as in the preparation of $(C_2H_5)_4NWCl_6$, except that before the isolation of the dark green compound, HCl was bubbled through the suspension and it was converted into a yellow compound. Considerable heat was evolved when the HCl was introduced; yield 76.36%. *Anal.* Calcd for $WCl_5C_{10}H_{25}ON$: W, 34.27; Cl, 33.06; OC_2H_5, 8.40; C, 22.39; H, 4.70; N, 2.61. Found: W, 33.99; Cl, 32.93; OC_2H_5, 8.04; C, 22.15; H, 4.84; N, 2.67.

$(CH_3(CH_2)_3)_4N[W(OC_2H_5)Cl_5]$.—The procedure was analogous to that used in the preparation of $(C_2H_5)_4N[W(OC_2H_5)Cl_5]$ except tetrabutylammonium chloride was substituted for tetraethylammonium chloride; yield 47.54%. *Anal.* Calcd for $WCl_5C_{18}H_{41}ON$: W, 28.34; Cl, 27.33; C, 33.33; H, 6.37; N, 2.16. Found: W, 28.17; Cl, 27.76; C, 33.30; H, 6.45; N, 2.13.

$(CH_4CH_2CH_2)_4N[W(OC_2H_5)Cl_5]$.—The procedure was the same as in the preparation of $(C_2H_5)_4N[W(OC_2H_5)Cl_5]$ except tetrapropylammonium chloride was substituted for tetraethylammonium chloride; yield 46.50%. *Anal.* Calcd for $WCl_5C_{14}H_{33}ON$: W, 31.03; Cl, 29.92; C, 28.38; H, 5.61; N, 2.36. Found: W, 30.72; Cl, 29.92; C, 28.15; H, 5.71; N, 2.36.

$(C_2H_5)_4N[W(OCH_3)Cl_5]$.—The compound was obtained by the substitution of methanol for ethanol in the procedure for the preparation of $(C_2H_5)_4N[W(OC_2H_5)Cl_5]$; yield 72.57%. *Anal.* Calcd for $WCl_5C_9H_{13}ON$: W, 35.19; Cl, 33.93. Found: W, 35.35; Cl, 33.49. The compound decomposed too rapidly to allow us to obtain commercial C, H, and N analyses.

$(C_2H_5)_4N[W(1\text{-}OC_3H_7)Cl_5]$.—A 5.4-g sample of WCl_5 (0.015 mol) was added to 20 ml of 1-propanol (−78°) which had been saturated with HCl at 0°. The solution was allowed to warm to room temperature. Immediately after the solution changed from yellow-brown to light green (10–20 min), a solution of 2.5 g of $[(C_2H_5)_4N]Cl$ (0.015 mol) in 20 ml of 1-propanol was added to it. A yellow compound was obtained in 53.60% yield. The complex was washed with a 5:1 ethyl ether–1-propanol solution and finally with pure ethyl ether. It was dried under vacuum. *Anal.* Calcd for $WCl_5C_{11}H_{27}ON$: W, 33.45; Cl, 32.18. Found: W, 33.21; Cl, 32.11.

$(C_2H_5)_4N(WOCl_4)$.—$(C_2H_5)_4N[W(OC_2H_5)Cl_5]$ decomposed by spontaneous evolution of C_2H_5Cl to give a blue compound, $(C_2H_5)_4N(WOCl_4)$. *Anal.* Calcd for $WCl_4C_8H_{20}ON$: W, 38.96; Cl, 30.05; C, 20.36; H, 4.27; N, 2.97. Found: W, 38.39; Cl, 29.84; C, 20.39; H, 4.50; N, 2.84.

$[C_5H_6N][W(OCH_3)_2Cl_4]$.—A 13.5-g sample of WCl_5 (0.037 mol) was added carefully to 23 ml of methanol cooled to −40° in a Dry Ice–chloroform slush bath. The dark green solution was treated with either a methanol–pyridine mixture or pyridinium chloride (0.037 mol), and a green solid separated. The crystals were filtered, washed with ether and methanol, and dried *in vacuo;* yield 50–60%. *Anal.* Calcd for $C_7H_{12}O_2NCl_4W$: C, 17.96; H, 2.57; N, 2.99; Cl, 30.32; W, 39.31. Found: C, 17.94; H, 2.55; N, 2.90; Cl, 30.30; W, 39.32.

$[C_5H_6N][W(OC_2H_5)_2Cl_4]$.—A 10-g sample of WCl_5 (0.027 mol) was added to 20 ml of ethanol cooled to −78° with a Dry Ice–propanol bath. The solution was gradually warmed to 0° and stirred for 1 hr. Then pyridinium chloride or a pyridine–ethanol mixture (0.027 mol) was added, and the product was filtered, washed with ether and ethanol, and dried *in vacuo*. *Anal.* Calcd for $C_9H_{16}O_2NCl_4W$: C, 21.79; H, 3.23; N, 2.82; Cl, 28.60; W, 37.09. Found: C, 21.86; H, 3.36; N, 2.86; Cl, 28.49; W, 36.90.

$W_2Cl_4(OC_2H_5)_6$.—A 5-g sample of WCl_5 (0.014 mol) was added to ethanol at −78°. The solution was gradually warmed to 0°. A sodium ethoxide solution (prepared by treating 0.64 g of Na (0.028 g-atom) with 20 ml of ethanol) was added dropwise to the green solution. The color became red-brown and sodium chloride separated from the solution. The sodium chloride was removed by centrifuging and decanting the mixture. The resulting solution was allowed to reflux for 2 hr and was then stored at −15° overnight. Red crystals[6] formed slowly; yield 25%. *Anal.* Calcd for $W_2Cl_4(OC_2H_5)_6$: Cl, 18.18; W, 47.15. Found: Cl, 18.12; W, 47.21.

$W_2Cl_4(OCH_3)_6$.—A 10.8-g sample of WCl_3 (0.03 mol) was cooled to −78° before addition to 25 ml of CH_3OH also at −78°. The purple solution became green at room temperature. A red-brown solid remained upon vacuum evaporation of the solution. The product was purified by addition of 30 ml of CH_3OH to the solid. The small amount of precipitate which remained was filtered and discarded. The red-brown solution was concentrated to 10 ml by vacuum evaporation, cooled at −10° for 2 hr, filtered, washed with a small amount of ethyl ether, and dried under vacuum. *Anal.* Calcd for $WCl_2C_3H_9O_3$: W, 52.85; Cl, 20.39. Found: W, 52.83; Cl, 20.43.

$W_2Cl_2(OC_2H_5)_3$.—This compound was prepared by the same method as the previous chloride alkoxide. A sodium ethoxide solution with an ethoxide to tungsten ratio of 4:1 was used. *Anal.* Calcd for $W_2Cl_2(OC_2H_5)_8$: Cl, 8.87; OC_2H_5, 45.08; W, 46.04. Found: Cl, 9.87; OC_2H_5, 44.34; W, 46.23.

Analyses.—All compounds were dissolved in an ammonium hydroxide–hydrogen peroxide solution. Tungsten was determined by precipitation with 8-hydroxyquinoline.[17] Chloride was determined by potentiometric titration with silver nitrate. Ethoxide was determined by oxidation with excess dichromate; then the excess dichromate was treated with KI and the iodine liberated was determined with thiosulfate.[18] Difficulties arose in the treatment of all tetraalkylammonium salts except those with the tetramethylammonium ion. The other cations precipitated some dichromate and all precipitated iodide. C, H, and N were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Magnetic Moments.—Magnetic susceptibilities were determined at 70, 195, and 297°K. $CuSO_4 \cdot 5H_2O$ served for calibration. Corrections[19] for diamagnetism of the ligands were made. All samples were measured at several field strengths to check for ferromagnetism.

Optical Spectra.—Infrared spectra were determined in Nujol mulls. A Unicam SP-200 spectrophotometer was used. Visible and ultraviolet spectra were determined with a Cary Model 14 spectrophotometer, a Unicam SP-800 spectrophotometer, and/or a Bausch and Lomb Spectronic-600 to which is connected an integrating-sphere reflectance attachment.

Solution spectra of monoalkoxo and $WOCl_4^-$ species were obtained by use of nitromethane as the solvent, because compounds which are dissolved in an alcohol are converted to a dialkoxide and then undergo further decomposition (within 24 hr)

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and change from a green to a yellow solution. Spectra of dialkoxo species could be determined in alcohol or nitromethane.

Experimental Techniques.—All reactions were carried out under dry N_2 because the compounds are air and moisture sensitive. Filtrations were effected by use of suction. Compounds were dried *in vacuo* and stored under dry N_2.

Reactions of Solutions of WCl_5.—As saturated HCl solutions of WCl_5 were warmed from −78 to 25°, the color changed from black-green to yellow-brown to light green. Dark green solutions were obtained at room temperatures if the alcohol was not saturated with HCl. The dark green solution persisted through a lithium alkoxide:WCl_5 ratio of 2:1. Dimers formed as the alkoxide concentration increased.[5] The solution became red-brown at 2–4 mol of LiOR/mol of WCl_5, red at 4–6 mol of LiOR/mol of WCl_5, and black at 6 mol of LiOR/mol of WCl_5.

Results and Discussion

Scheme I summarizes the reactions of WCl_5 in the alcohols which were studied.

For each of the monomeric compounds described in the Experimental Section, visible–ultraviolet and infrared spectra were obtained. Table I gives the important infrared absorption bands. All of the compounds have an absorption between 1020 and 1100 cm^{-1} which can be attributed to a C–O stretching of a coordinated alkoxide group.[3,20]

TABLE I

INFRARED FEATURES OF TUNGSTEN(V) COMPOUNDS

Compound	ν(C–O), cm^{-1}	ν(others), cm^{-1}
$(CH_3)_4N[W(OCH_3)_2Cl_4]$	1080, 1160	
$(CH_3)_4N[W(OC_2H_5)_2Cl_4]$	1052, 1093	Plus all $(CH_3)_4N^+$ bands
$[(CH_3)_4N]_2[W(OC_2H_5Cl_6]$	1060	3500 (O–H?)
$(C_2H_5)_4N(WCl_6)$	. . .	
$(C_2H_5)_4N[W(OCH_3)Cl_5]$	1080	
$(C_2H_5)_4N[W(OC_2H_5)Cl_5]$	1029	Plus all $(C_2H_5)_4N^+$ bands
$(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$	1060, 1095	
$(C_2H_5)_4N[W(n\text{-}OC_3H_7)Cl_5]$	1060	
$(C_2H_5)_4N(WOCl_4)$	. . .	W=O at 990
$(CH_3CH_2CH_2)_4N[W(OC_2H_5)Cl_5]$	1050, 1088	Plus all $(CH_3CH_2CH_2)_4N^+$ bands
$(CH_3(CH_2)_3)_4N[W(OC_2H_5)Cl_5]$	1063, 1099	Plus all $(CH_3(CH_2)_3)_4N^+$ bands
$(C_5H_6N)[W(OCH_3)Cl_4]$	1060	Plus all $C_5H_6N^+$ bands
$(C_5H_6N)[W(OC_2H_5)Cl_4]$	1060, 1090	
$W_2Cl_4(OC_2H_5)_2$	1060, 1090	
$W_2Cl_2(OC_2H_5)_8$	1060, 1090	

Table II contains the important near-infrared–visible–ultraviolet features for these compounds. The electronic spectra suggest octahedral or tetragonal symmetry. The low-energy band at 5800 cm^{-1} is probably an infrared overtone or multiple vibration.

Five absorption maxima were found in the solid-state spectrum of $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$. The compound was only slightly soluble in nitromethane and ethanol so that solution spectra could not be obtained. An O–H stretch at 3600 cm^{-1} in the infrared spectrum indicates an impurity may have been present. The electronic spectrum tends to rule out a double salt, such as $[(CH_3)_4N][W(OC_2H_5)Cl_5]\cdot[(CH_3)_4N]Cl$. The magnetic susceptibilities (Table III) differ in magnitude and temperature dependence from both the monalkoxopentachlorotungstate(V) salt and the hexachlorotungstate(V) compounds. The compound is probably seven-coordinate.

$(C_2H_5)_4N(WCl)_6$ was previously prepared by the reduction of WCl_6 in thionyl chloride.[21] The preparation of $(C_2H_5)_4N(WCl_6)$ in ethanol is unreported. Although a one-step process for the preparation was desired, none was found satisfactory. The compound had to be purified by reprecipitation (and possible alkoxide replacement by chloride ion) in thionyl chloride. Spectroscopic and magnetic results were in accord with the data reported previously.[7,11–13] The dimers are diamagnetic.

Calculations outlined by Figgis[22] were attempted for the dialkoxo complexes, which are assumed to be tetragonal (*trans*) on the basis of their electronic spectra and the analogy with the corresponding molybdenum(V) compounds.[3] The measured magnetic susceptibilities at 77, 195, and 297°K are given in Table III. The weak temperature dependence of the magnetic susceptibilities is reflected in the small negative values of the Weiss constant ($\theta \sim -2°K$) and nearly constant values of the magnetic moments. Thus, the conclusions which can be drawn from the method are qualitative. Figgis' ν is defined as Δ/λ, where Δ is the separation of the t_{2g} orbitals created by the tetragonal distortion of the ligand field and λ is the spin–orbit coupling constant. The data indicate ν is greater than 10, Δ probably ranges from 8000 to 11,000 cm^{-1}, and thus λ is approximately 500 cm^{-1}. This value agrees with that found for λ in the tungsten(V) oxyhalide compounds.[7]

The magnetic moments increase as the number of alkoxide groups increases and suggest the formation of a strong tungsten–oxygen multiple bond which increases the spacing between the e and b_2 orbitals. As a result, the spin–orbit contribution to the magnetic moment is lowered.

The pentachloralkoxotungstate(V) salts are perhaps the most interesting species isolated. They decompose in the solid state by elimination of an alkyl chloride to give mainly the tetrachlorooxotungstate(V) derivative, but there is some other product that we have been unable to identify. Both an infrared spectrum of the gas above the compound and analyses of initial and final product indicate loss of alkyl chloride according to the equation

$$R_4N[W(OR)Cl_5] \xrightarrow{-RCl} R_4N[WOCl_4] + \text{other solid products}$$

The same alkyl chloride was evolved regardless of the cation. When R was ethyl, C_2H_5Cl was produced, and methyl gave CH_3Cl. The complex changed color from yellow to blue when the alkyl halide was evolved. The C–O stretch diminished in intensity as the alkyl halide evolved and a W–O stretch appeared. The electron absorptions of the product were shifted to higher energies and had different molar absorptivities. Spectra of the tetrachlorooxotungstate(V) complexes were similiar to those already reported.

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SCHEME I

REACTIONS OF WCl_5 IN ALCOHOLS

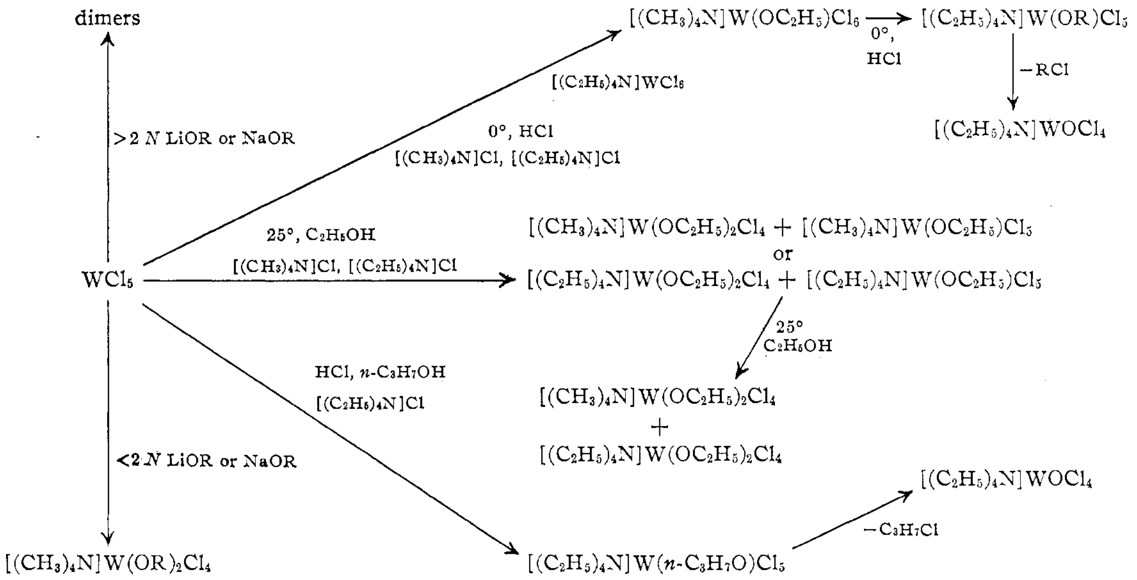

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF COMPOUNDS

Compound	Medium	$10^3\nu$, cm^{-1} (ϵ_{max})
$(CH_3)_4N[W(OCH_3)_2Cl_4]$	Solid	10.9, 13.5, 21.7 sh, 25.3
	Nitromethane	10.6 (10.9), 13.7 (12.6), 25.0 (26.1)
	Methanol	10.6 (10.9), 13.7 (12.6), 21.1 (~13.5) sh, 25.0 (~26) sh, 30.8 (~775) sh, 34.6 (~4670) sh
$(CH_3)_4N[W(OC_2H_5)_2Cl_4]$	Solid	11.1, 14.1, 24.7 sh
	Nitromethane	10.8 (12.5), 14.0 (13.6), 24.7 (25.1)
	Ethanol	10.8 (12.5), 14.0 (13.6), 24.7 (~26) sh, 30.8 (~750) sh, 35.5 (~5188) sh
$[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$	Solid	5.8, 7.5, 8.2, 15.4, 24.7 sh
$(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$	Solid	5.8, 11.6, 14.1, 24.5 sh
	Nitromethane	10.9 (12.7), 13.9 (13.4), 24.3 (22.7)
	Ethanol	10.9 (12.7), 13.9 (13.4), 24.3 (~20) sh, 30.8 (~750) sh, 35.5 (~5188) sh
$(C_2H_5)_4N[W(OC_2H_5)Cl_5]$	Solid	5.8, 8.6, 13.7, 23.3 sh
	Nitromethane	5.8 (4.6), 8.7 (7.2), 23.3 (7.2)
$(C_2H_5)_4N[W(OCH_3)Cl_5]$	Solid	5.8, 8.4, 15.1, 22.6 sh
	Nitromethane	5.7 (4.8), 8.4 (6.8), 22.5 (7.6)
$(C_2H_5)_4N[W(n\text{-}OC_3H_7)Cl_5]$	Solid	5.8, 8.5
	Nitromethane	5.8 (5.2), 8.7 (8.2)
$(C_3H_7)_4N[W(OC_2H_5)Cl_5]$	Solid	5.8, 8.5, 22.9
	Nitromethane	5.8 (4.7), 8.6 (7.3)
$(C_4H_9)_4N[W(OC_2H_5)Cl_5]$	Solid	5.8, 8.40, 23.3
	Nitromethane	5.8 (5.1), 8.6 (7.1)
$(C_2H_5)_4N(WOCl_4)$	Solid	5.8, 9.6, 12.3, 17.5, 25.0
	Nitromethane	11.2 (11.6), 14.2 (18.4), 26.0 (14.4)
$(C_5H_6N)W(OCH_3)_2Cl_4$	Solid	11.1, 13.9, 24.1
	Methanol	11.2 (12), 14.3 (15), 25.0 (~15), 30.8 (>10^3), 35.0 (>10^3)
$(C_5H_6N)W(OC_2H_5)Cl_4$	Solid	14.5, 25.6
	Ethanol	11.4 (12), 13.9 (13) 25.0 (60), 30.8 (600), 34.5 (~10^3)

TABLE III

MEASURED MAGNETIC SUSCEPTIBILITIES AND MAGNETIC MOMENTS

Compound	Temp, °C	$10^6\chi_m'$, cgsu	μ, BM	θ, °K
$(CH_3)_4N[W(OCH_3)_2Cl_4]$	297	973	1.53	−2
	195	1465	1.52	
	77	3679	1.51	
$(CH_3)_4N[W(OC_2H_5)_2Cl_4]$	297	1002	1.55	−2
	195	1503	1.54	
	77	3769	1.53	
$(C_2H_5)_4N[W(OC_2H_5)_2Cl_4]$	297	977	1.53	−2
	195	1486	1.53	
	77	3743	1.52	
$(C_2H_5)_4N[W(OCH_3)Cl_5]$	297	745	1.34	−3
	195	1195	1.33	
	77	1117	1.33	
$(C_2H_5)_4N[W(OC_2H_5)Cl_5]$	297	777	1.36	−2
	195	1175	1.36	
	77	2969	1.36	
$(C_3H_7)_4N[W(OC_2H_5)Cl_5]$	297	831	1.41	−4
	195	1246	1.40	
	77	3127	1.39	
$(C_4H_9)_4N[W(OC_2H_5)Cl_5]$	297	803	1.39	−2
	195	1223	1.39	
	77	3012	1.39	
$(C_2H_5)_4N[W(OC_3H_7)Cl_5]$	297	797	1.38	−2
	195	1219	1.38	
	77	3075	1.38	
$[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$	297	873	1.45	−81
	195	1143	1.34	
	77	1986	1.11	
$(C_2H_5)_4N[WOCl_4]$	297	863	1.44	12
	195	1226	1.39	
	77	3204	1.41	
$(C_5H_6N)[W(OCH_3)Cl_4]$	297	913.9	1.48	
$(C_5H_6N)[W(OC_2H_5)Cl_4]$	297	947.1	1.51	

The relative heterogeneous rates of alkyl chloride evolution were determined qualitatively by use of a constant-volume Warburg appartus. With tetraethylammonium ion as the cation, the appearance rate of alkyl chloride was in the order $CH_3Cl > C_2H_5Cl > C_3H_7Cl$. The rate of ethyl chloride evolution was found to decrease as the cation increased in size in the order tetraethyl > tetrapropyl > tetrabutyl.

The reaction yields about 1 mol of RCl/mol of reactant, but the solid product is not pure and the impurities cannot be identified.

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