off-diagonal elements contribute as well.[23,24] Furthermore, at some point in the stepwise series, addition of a further Br^- would cause bond covalency to decrease preventing the metal ion from becoming too negatively charged. This decrease would in turn decrease the Raman intensity.[25] In any case it seems significant that the molar intensities of the various stepwise complexes formed from the same elements roughly obey the rule and do not vary by orders of magnitude. This is important since it means that if Raman studies fail to observe one or more of the stepwise complexes, these species do not occur in significant concentrations.

From the molar intensities, molar concentrations were determined. These are as displayed in Figures 2 and 3. If the molar concentrations are used to find equilibrium quotients as a function of temperature, apparent thermodynamic parameters may be derived. Values are listed in Table VII. All values refer to stepwise association equilibria $MBr_{n-1}^{(3-n)+} + Br^- = MBr_n^{(2-n)+}$ at 20° and a total concentration of $M + Br^- = 4\ M$. Within the range of 12 solutions there are no significant trends in the variation of Q with the ratio of Br^- to M^{2+}. Individual values of Q show a mean deviation of ±40%. These deviations along with uncertainties in determination of molar intensities should mean that thermodynamic values have reliabilities corresponding to ±1 kcal/mol. Because the standard states involved are those of concentrated solutions, the magnitude of the values should not be compared to that of the values obtained for the usual standard states. However, trends within the present values should be meaningful.

The enthalpy and entropy changes found for the zinc complexes are interesting in that both show special values for the first step of complex formation. These values are consistent with the indication from the Raman spectra that on formation of even the first bromide complex, hydration of the zinc ion is noticeably weakened. After the first step, the values follow a trend to be expected for addition of a Br^- to a progressively less positive, weakly hydrated zinc ion. For the cadmium complexes, a similar but somewhat smaller effect is observed for the first and last steps. Values for the two intermediate steps are not comparable since they involve the polymeric species characteristic of this system.

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The Preparation and Far-Infrared and Proton Magnetic Resonance Spectra of Some Tungsten(IV) and Tungsten(V) Chloride Alkoxide Dimers

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Received October 27, 1969

Solutions of WCl_5 in several alcohols that were basic with alkoxide ions were investigated and the diamagnetic alkoxide compounds $W(OC_2H_5)_5$ and $W_2Cl_4(OC_3H_7)_6$ and the yellow, paramagnetic solid $NaW(OC_2H_5)_6$ were isolated. The reaction of WCl_4 with alcohols was also studied. Green, diamagnetic dimers $W_2Cl_4(OR)_4(ROH)_2$ (R = CH_3, C_2H_5, 1-C_3H_7, 2-C_3H_7) were obtained. The far-ir, optical, and pmr spectra of these compounds are presented.

In previous studies[1,2] of tungsten(V) alkoxide compounds, both monomers and dimers have been reported. We have now prepared and characterized several new W(V) and W(IV) dimers. The far-ir, optical, and pmr spectra of these compounds have been measured.

Experimental Section

Materials.—Solvents and other starting materials were purified as described in previous work.[1,2] All operations were carried out under dry N_2.

Tungsten tetrachloride was prepared by the red phosphorus reduction of WCl_6.[3] Some preparations were contaminated with small amounts of unreacted phosphorus. *Anal.* Calcd for WCl_4: W, 56.54; Cl, 43.54. Found: W, 55.70; Cl, 43.10.

$W_2Cl_4(OC_2H_5)_6$ and $W_2Cl_2(OC_2H_5)_8$.—These compounds were prepared as previously reported.[1]

$W_2Cl_4(OC_3H_7)_6$ (I).—A 4.9-g portion of WCl_5 (0.014 mol) was added to 15 ml of 1-propanol cooled to −78°. The temperature of the solution was gradually increased to 0°. A sodium propoxide solution (prepared by treating 0.66 g of Na, 0.028 g-atom, with 35 ml of 1-propanol) was added to the dark green solution. The solution became green-brown and sodium chloride separated. The sodium chloride was removed by centrifuging and decanting the supernatant liquid. The resulting solution was allowed to reflux for 1.5 hr and was then stored overnight at −10°. The dark red crystals were filtered, washed with a small amount of 1-propanol, and dried *in vacuo*. *Anal.* Calcd for $WCl_2C_9H_{21}O_3$: W, 42.58; Cl, 16.42; C, 25.01; H, 4.86. Found: W, 42.67; Cl, 16.49; C, 25.16; H, 4.88. The theoretical molecular weight of the dimer is 864. The mass spectrum gave a series of peaks in the region of 862–868 mass units.

$W_2Cl_2(OC_3H_7)_8$ (II).—This impure substance was prepared by the same procedure as I except that a sodium propoxide solution

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with a propoxide to tungsten ratio of 4:1 was used. *Anal.* Calcd for $WClC_{12}H_{28}O_4$: Cl, 7.78. Found: Cl, 8.63.

$W(OC_2H_5)_5$ (III).—A 6.49-g sample of WCl_5 (0.018 mol) was added to 10 ml of ethanol cooled to −78°. The temperature of the solution was increased to 0°. A sodium ethoxide solution (prepared by adding 2.11 g of Na, 0.090 g-atom, to 60 ml of ethanol) was added to the solution. The volume of the dark brown mixture was reduced by vacuum evaporation. The sodium chloride was then removed by centrifugation and filtration. The filtrate was then evaporated to dryness at 25° and 0.1 Torr. The brown liquid residue was sublimed at 120° and 0.1 Torr and a red-black liquid, which gelled upon cooling, was obtained. Because this compound was extremely sensitive to moisture, no commercial C–H analyses were obtained. *Anal.* Calcd for $WC_{10}H_{25}O_5$: W, 44.97; OC_2H_5, 55.03. Found: W, 44.40; OC_2H_5, 54.97.

$NaW(OC_2H_5)_6$ (IV).—A 5.27-g sample of WCl_5 (0.015 mol) was added to 10 ml of ethanol which had been cooled to −78°. The temperature of the solution was gradually increased to 0°. A sodium ethoxide solution (prepared by adding 2.01 g of Na, 0.087 g-atom, to 50 ml of ethanol) was added to the green solution. Sodium chloride separated from the dark blue solution. The volume of the solution was reduced by vacuum evaporation. The sodium chloride was then removed by centrifuging and filtering. The dark blue filtrate was evaporated to dryness and 20 ml of benzene was added. The dark blue solution was cooled to −10° for 12 hr. The yellow solid was filtered, washed with a small amount of benzene, and dried *in vacuo*. The W and $OC_2H_5^-$ analyses were low compared to those calculated for IV, but the ethoxide to tungsten ratio was 6:1. Chloride was *not* an impurity. The compound was paramagnetic and decomposed after standing in a sealed, evacuated tube for several days. *Anal.* Calcd for $WNaC_{12}H_{30}O_6$: W, 38.60; OC_2H_5, 56.60. Found: W, 36.05; OC_2H_5, 53.28.

Potassium ethoxide was also used in the preparation above. A yellow solid, most likely $KW(OC_2H_5)_6$, was isolated. This compound was less stable than the sodium salt. Ethanol was identified as a decomposition product.

$W_2Cl_4(OCH_3)_4(CH_3OH)_2$ (V).—A 5.9-g sample of WCl_4 was added to 20 ml of methanol that had been cooled to 0°. The temperature of the solution was increased to 25°. The gray-black solid gradually became yellow-green and the solution became green. After the mixture had been stirred for 3 hr, the yellow-green compound was filtered, washed with methanol, and dried under vacuum. The product was then added to 20 ml of methanol and stirred at 25° for 12 hr. Further reaction did not occur. The compound was filtered, washed with methanol, and dried under vacuum. *Anal.* Calcd for $WCl_2C_3H_{10}O_3$: W, 52.72; Cl, 20.33; C, 10.32; H, 2.87. Found: W, 52.14; Cl, 20.23; C, 10.17; H, 2.71. The oxidation state determination required 2.02 equiv of cerium/g-atom of W.

$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ (VI).—This compound was prepared by the same procedure as V except that ethanol was used in place of methanol. The dark green compound was recrystallized from a $CHCl_3$ and ethanol mixture; yield, 45%. *Anal.* Calcd for $WCl_2C_6H_{16}O_3$: W, 47.05; Cl, 18.14; C, 18.42; H, 4.09; OC_2H_5, 34.80. Found: W, 47.40; Cl, 17.95; C, 18.28; H, 4.02; OC_2H_5, 34.65. The theoretical molecular weight of the dimer is 782. The mass spectrum gave a series of peaks in the region of 778–784 mass units. The oxidation state determination required 2.23 equiv of Ce(IV)/g-atom of W.

$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$ (VII).—This dark green compound was prepared by the same procedure as the previous complex except for the use of propanol. The compound was recrystallized from a mixture of diethyl ether and 1-propanol. *Anal.* Calcd for $WCl_2C_9H_{22}O_3$: W, 42.48; Cl, 16.38; C, 24.95; H, 5.08. Found: W, 42.57; Cl, 16.35; C, 25.10; H, 5.04.

$W_2Cl_4(2\text{-}OC_3H_7)_4(C_3H_7OH\text{-}2)_2$ (VIII).—An orange-brown solid was prepared by the same procedure as the previous complex. The compound was also recrystallized from a mixture of diethyl ether and 2-propanol. *Anal.* Calcd for $WCl_2C_9H_{22}O_3$: W, 42.48; Cl, 16.38; C, 24.95; H, 5.08. Found: W, 42.50; Cl, 16.28; C, 24.67; H, 4.92.

$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$ (IX).—A 2.26-g sample of VI was dissolved in 20 ml of $CHCl_3$. A solution of 1 ml of pyridine in 10 ml of $CHCl_3$ was added to the dark yellow-green solution. The volume of the dark red solution, which resulted, was reduced by evaporation. An orange precipitate formed when the mixture was cooled to −78°. The compound was separated by rapid filtration, washed with a small amount of $CHCl_3$, and dried under vacuum. *Anal.* Calcd for $WCl_2C_9H_{15}N$: W, 43.38; Cl, 16.73; C, 25.48; H, 3.54; N, 3.30. Found: W, 43.40; Cl, 16.50; C, 25.24; H, 3.43; N, 3.26. The theoretical molecular weight of the dimer is 848. The mass spectrum gave a series of peaks in the region of 846–852 mass units.

$W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$ (X).—A 4.38-g (0.011-mol) portion of VI was suspended in 20 ml of ethanol. A potassium ethoxide solution (prepared by adding 0.438 g of K, 0.011 g-atom, to 15 ml of ethanol) was added to the green mixture. The color became dark green and KCl separated from the solution. The mixture was stirred for 2 hr and the KCl was removed by filtration. The resulting solution was stored at −10° for 12 hr. The black crystalline product was filtered, washed with a small amount of ethanol, and dried under vacuum. *Anal.* Calcd for $WClC_8H_{21}O_4$: W, 45.93; Cl, 8.85; OC_2H_5, 45.02. Found: W, 46.00; Cl, 9.15; OC_2H_5, 41.10; 1.96 reduction equiv/g-atom of W. This compound decomposed, with evolution of ethanol vapor. Commercial C–H analysis were not obtained.

Attempts to Prepare $W(OC_2H_5)_4$.—A 4.46-g sample (0.012 mol) of VI was suspended in 10 ml of ethanol. A potassium ethoxide solution (prepared by treating 0.892 g of K, 0.023 g-atom, with 30 ml of ethanol) was added to the mixture. The solution became black and KCl separated. The mixture was stirred for 1 hr and the KCl was removed by filtration. The blue-black filtrate was then evaporated to dryness. A black liquid residue was obtained. This residue was sublimed at 110° and 0.1 Torr. A very dark red liquid resulted from this treatment. Elemental analyses and ir and pmr spectra indicated that this compound was III with a small amount of an unidentified impurity. *Anal.* Calcd for $W(OC_2H_5)_5$: W, 44.97; OC_2H_5, 55.03. Found: W, 45.17; OC_2H_5, 51.22.

Reactions of $W(OC_2H_5)_5$.—About 1.2 g of $W(OC_2H_5)_5$ was added to a solution of 3 ml of pyridine in 10 ml of ethanol saturated with HCl. The solution changed from dark red to orange. No precipitate was observed after the solution was allowed to cool to −10°. No precipitate or color change was observed when a small sample of $W(OC_2H_5)_5$ was added to a solution of tetraethylammonium chloride in ethanol.

Reaction of WCl_4 with Alcohols.—At 0°, WCl_4 formed a black suspension in alcohols. After the temperature was increased to 25°, green W(IV) complexes and dark green solutions were obtained. The addition of alcohol solutions of $(C_2H_5)_4NCl$ resulted in the precipitation of light green solids. Elemental analyses and magnetic susceptibility measurements confirmed the identity of these compounds as tetraethylammonium salts of the tetrachlorodialkoxotungstate(V) anion. *Anal.* Calcd for $(C_2H_5)_4NW(OC_2H_5)_2Cl_4$: W, 33.69; Cl, 25.97. Found: W, 34.00; Cl, 25.98; $\mu(297°K) = 1.47$ BM. Calcd for $(C_2H_5)_4NW(OCH_3)_2Cl_4$: W, 35.51; Cl, 27.39. Found: W, 35.66; Cl, 27.39; $\mu(297°K) = 1.51$ BM.

In acidic (with HCl) ethanol or propanol some evidence for oxygen abstraction was found. Impure complexes were isolated from these solutions, and spectra showed the presence of both W=O and W—O—C groups.

Physical Properties of W(IV) Compounds.—The tungsten(IV) methoxide complex was insoluble in methanol and other common organic solvents. The corresponding ethoxide and propoxide compounds were slightly soluble in the parent alcohol and very soluble in chloroform and benzene. All of these W(IV) compounds were insoluble in water and dilute acids but were readily decomposed by aqueous base.

Analyses.—W, Cl, and ethoxide analyses were performed as described earlier.[1] C–H–N analyses were performed by Spang

Table I

Pmr Spectra of W(V) and W(IV) Dimers[a]

Compound	Solvent	τ(CH_3), ppm	τ(CH_2), ppm
$W_2Cl_4(OC_2H_5)_6$[b]	CCl_4	1.03 (2)	4.57 (2)
		1.38 (1)	5.83 (1)
$W_2Cl_2(OC_2H_5)_8$	CCl_4	0.98	5.22 (1)
		1.38	5.23 (1)
$W(OC_2H_5)_5$	CCl_4	1.22	4.75
$W_2Cl_4(OC_3H_7)_6$	CCl_4	Complex	4.47 (2)
			5.58 (1)
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$	$CHCl_3$	1.25 (2)	4.56 (2)
		1.38 (1)	5.47 (1)
$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$[c]	$CHCl_3$	1.42	5.88
$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$	$CHCl_3$	Complex	4.35 (2)
			5.17 (1)
$W_2Cl_4(2\text{-}OC_3H_7)_4(C_3H_7OH\text{-}2)_2$	$CHCl_3$	1.22	
		1.75	

[a] TMS used as internal standard; all spectra were run at 35°. Relative intensities are in parentheses. [b] Results agree with ref 4. [c] Treated with TMS; resonance measured against $CHCl_3$ (7.27 ppm).

Microanalytical Laboratory, Ann Arbor, Mich., and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Oxidation-State Determinations. Cerimetric.—Samples were hydrolyzed in dilute ammonia and then acidified with sulfuric acid. Excess cerium(IV) sulfate solution was added and the mixture was stirred for 12 hr. Cerium(III) tungstate was removed by filtration and the excess Ce(IV) was determined with standard ferrous ammonium sulfate solution. Ferroin served as the indicator. Some oxidation of the alcohol ligands was observed. For compounds containing ethanol or ethoxide as ligands, the ethanol analysis served as an indirect oxidation-state determination, since simultaneous oxidation of W and ethanol occurred.

Ir, Optical, Pmr, and Mass Spectra and Magnetic Susceptibility Measurements.—Ir and optical spectra were determined as before.[1,2] Pmr spectra were recorded in a Varian A 56/60 spectrometer, equipped with a variable-temperature controller. TMS was used as an internal standard. The mass spectra of the dimers were obtained by Dr. L. Shadoff, Dow Chemical Co., Midland, Mich. Samples were sealed in melting-point capillaries which were broken in the direct-probe pumping chamber of a CEC21-110B mass spectrometer. The magnetic susceptibilities of solid compounds were determined by the Gouy method. The diamagnetism of some samples, including $W(OC_2H_5)_5$, was confirmed by the sharp pmr spectra and the absence of an epr signal.

Results and Discussion

All of the compounds prepared in this study, except $NaW(OC_2H_5)_6$, were found to be diamagnetic. Mass spectroscopic data for $W_2Cl_4(OC_3H_7)_6$, $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$, and $W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$ have confirmed the dimeric nature of these compounds. A chloride-bridged bioctahedral structure was proposed for $W_2Cl_4(OC_2H_5)_6$ by Klejnot.[4] Although the identity of the bridging groups is still uncertain, all of these W(IV) and W(V) compounds probably have similar structures.

The pmr absorptions of the dimers are listed in Table I. An interesting comparison can be made between $W_2Cl_4(OC_2H_5)_6$ and $W_2Cl_2(OC_2H_5)_8$. The relatively simple spectrum of $W_2Cl_2(OC_2H_5)_8$, consisting of two closely spaced quartets of equal intensity, would be compatible with a symmetrical structure and chloride bridging. A far-ir absorption at 218 cm^{-1} for $W_2Cl_4(OC_2H_5)_6$ and at 228 cm^{-1} for $W_2Cl_2(OC_2H_5)_8$ may be the W–Cl bridge vibration. A comparison of the propoxide derivatives was not possible because pure $W_2Cl_2(OC_3H_7)_8$ was not obtained.

Bradley and Holloway[5] have proposed an edge-shared bioctahedral structure for niobium and tantalum pentaalkoxides. The pmr spectrum of $[Ta(OCH_3)_5]_2$ above 40° gave one peak at 5.78 ppm. At −58°, the single methyl resonance split into three peaks (5.78, 5.68, 5.97 ppm) with intensity ratios of 2:2:1. These results were interpreted as evidence for the three types of alkoxide groups in the edge-shared bioctahedron. Uranium pentaethoxide[6] was similar. At 35°, $W(OC_2H_5)_5$ has a simple pmr spectrum, probably due to rapid intramolecular exchange between terminal and bridging ethoxide groups. Low-temperature studies (to −80°) in carbon disulfide or *n*-pentane failed to resolve the expected splitting of the methylene quartet. Until molecular weight or mass spectral data can be obtained, the structure of $W(OC_2H_5)_5$ will remain uncertain. The diamagnetism of the complex suggests a dimer or higher polymer. Attempts to convert this compound into a monomer were also unsuccessful. The breakdown of the dimer (or polymer) structure resulted in decomposition.

Solid tungsten(IV) chloride alkoxides and solutions containing W(V) species were obtained when WCl_4 was allowed to react with the alcohols studied. No evidence for W(III) or W(II) species was found. Therefore a normal disproportionation reaction is unlikely. The nature of the oxidizing agent is unknown.

The pmr spectra of the tungsten(IV) alkoxoalcohol complexes are very similar to those listed by Clark and Wentworth for the W(III) compounds $W_2Cl_4(OR)_2(ROH)_4$ (R = CH_3, C_2H_5, C_3H_7). However, products different from those reported by Clark and Wentworth were isolated from the reaction of the ethoxoethanol compounds with pyridine. A brown, air-sensitive material was reported[7] as the result of the reaction of the W(III) complex with pyridine. An orange compound, $W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$, was isolated from the

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TABLE II

ELECTRONIC ABSORPTION SPECTRA OF TUNGSTEN COMPOUNDS

Compound	Abs max × 10^{-3}, cm^{-1}
$W_2Cl_4(OC_3H_7)_6$	Benzene: 18.66 (228), 23.53 (685)
$W_2Cl_4(OCH_3)_4(CH_3OH)_2$	Solid: 13.0, 14.3, 15.4
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$	Solid: 13.9, 20.8 $CHCl_3$: 13.5 (211), 16.4, 15.6 sh, 23.4 (24,480)
$W_2Cl_4(OC_3H_7)_4(C_3H_7OH)_2$	Solid: 13.4, 15.6 sh, 19.6, 26.3 $CHCl_3$: 13.5 (232), 16.4, 15.6 sh, 23.45 (∼4000) C_6H_6: 13.4 (186), 16.4, 15.6 sh, 23.4 (3696)

TABLE III

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF DIMERIC TUNGSTEN SPECIES (WITH POSSIBLE ASSIGNMENT)

$W_2Cl_2(OC_2H_5)_8$		$W(OC_2H_5)_5$	
600 s	ν(W–O)	615 s	ν(W–O)
519 s	ν(W–O)	582 s	ν(W–O)
387 m	ν(O–W–O)	550 sh	
282 s	ν(W–Cl)		
228 m	ν(W–Cl)		
$W_2Cl_4(OC_3H_7)_6$		**$W_2(OCH_3)_4Cl_4(CH_3OH)_2$**	
652 m		575 m	ν(W–O)
619 s	ν(W–O)	532 s	ν(W–O)
575 s	ν(W–O)	476 s	
515 s		460 s	
449 m		412 w	
418 m		332 w	
377 m		306, 299 vs	ν(W–Cl)
297, 301 vs	ν(W–Cl)	245 m	ν(W–Cl)
266 sh		203 w	
229 m	ν(W–Cl)		
188 m			
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$		**$W_2Cl_4(1\text{-}OC_3H_7)_4(1\text{-}C_3H_7OH)_2$**	
586 s	ν(W–O)	615 s	ν(W–O)
526 s	ν(W–O)	561 s	ν(W–O)
478 m	ν(O–W–O)	455 m	ν(O–W–O)
379 m		412 m	
319 s	ν(W–Cl)	305 s	ν(W–Cl)
302 s	ν(W–Cl)	255 m	ν(W–Cl)
290 sh			
265 m			
245 m	ν(W–Cl)		
$W_2Cl_4(2\text{-}OC_3H_7)_4(2\text{-}C_3H_7OH)_2$		**$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$**	
617 s	ν(W–O)	648 s	
586 s	ν(W–O)	609 s	ν(W–O)
486 m	ν(O–W–O)	559 s	ν(W–O)
449 m		476 m	ν(O–W–O)
407 m 307 sh 294 s	ν(W–Cl)	449 w	
		397 w	
		315 sh 291, 296 vs 280 s	ν(W–Cl) ν(W–N)
250 m	ν(W–Cl)	230 m	ν(W–Cl)
194 w		205 w	
		185 w	

analogous reaction of the tungsten(IV) ethoxoethanol compound. The electronic spectra of the W(III) and W(IV) dimers are also quite similar. The W(IV) compounds have two well-defined shoulders on the high-energy side of the band at 13,500 cm^{-1} (Table II). The small effect of the oxidation state upon physical properties is evident from the close similarities of the pmr and ir spectra of the compounds $W_2Cl_4(OC_2H_5)_6$,[4] $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$, and $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$.[6]

The far-ir absorptions of the W(IV) and W(V) dimers are given in Table III. Tentative assignments were based on previous work.[2] In general, the W–O stretching frequency was observed between 600 and 500 cm^{-1}, the W–Cl and W–N stretches were observed about 300 cm^{-1}, and the W–Cl bridge vibration was observed about 250 cm^{-1}. As the alkoxide increased in size, the metal–oxygen stretch increased in frequency. This trend was noted previously for monomeric alkoxides. No apparent change in the W–Cl stretching frequency occurred when the oxidation state changed. These compounds have near-ir absorptions characteristic of bound alkoxide in the 1000–1100-cm^{-1} region (Table IV). A saturated $CHCl_3$ solution of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ showed bands assigned to bound ethoxide only. No O–H stretch at 3500 cm^{-1} was observed.

TABLE IV

FEATURES OF INFRARED SPECTRA OF W(V) AND W(IV) COMPOUNDS (1000–1100 CM^{-1})

$W_2Cl_4(OC_2H_5)_6$[a]	984 s, 1050 s, 1078 sh, 1100 m
$W_2Cl_2(OC_2H_5)_8$	1020 sh, 1060 s, 1075 s, 1100 m
$W(OC_2H_5)_5$	1040 sh, 1060 s, 1095 m
$W_2Cl_4(OC_3H_7)_6$	980 s, 1010 s, 1070 s, 1100 m
$W_2Cl_2(OC_3H_7)_8$	985 s, 1005 s, 1080 s, 1100 m
$W_2Cl_4(OCH_3)_4(CH_3OH)_2$	980 s, 1010 s, 1080 w
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$	1010 s, 1095 s 1020 s, 1060 sh, 1095 m ($CHCl_3$ soln)
$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$	1040 m, 1060 s
$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$	1000 m, 1045 s, 1095 m Pyridine bands: 1610 w, 690 s, 755 s
$W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$	1045 s, 1060 s, 1095 s
$NaW(OC_2H_5)_6$	1060 s, 1095 m

[a] Spectra agree with ref 4.

The dimers $W_2Cl_4(OR)_4(ROH)_2$ were the only stable W(IV) compounds prepared in this work. The black compound $W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$ decomposed slowly in a sealed tube, and $W(OC_2H_5)_4$ could not be isolated.

Acknowledgments.—This work has been supported by a grant from the National Science Foundation. The authors are grateful to Dr. L. Shadoff, Dow Chemical Co., Midland, Mich., for measuring the mass spectra.