

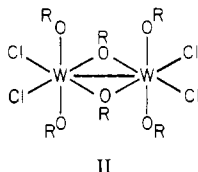
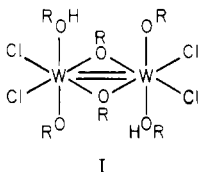
Alcohol Exchange and Oxidation Reactions of Doubly Bonded Ditungsten(IV) Complexes of the Type $W_2Cl_4(OR)_4(ROH)_2$: The Structural Identification of Novel Hydrogen-Bonded Bridging Systems

F. Albert Cotton,*^{1a} Larry R. Falvello,^{1a} Michael F. Fredrich,^{1a} David DeMarco,^{1b} and Richard A. Walton*^{1b}

Contribution from the Departments of Chemistry, Texas A&M University, College Station, Texas 77843, and Purdue University, West Lafayette, Indiana 47907.
Received August 27, 1982

Abstract: The alcohol/alkoxide exchange reactions of $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$ with $R'OH$ have been studied. When $R = C_2H_5$ and R' is a primary alkyl group, complete exchange occurs to give $W_2Cl_4(\mu-OR')_2(OR')_2(R'OH)_2$ with $R' = n-C_3H_7$, $n-C_4H_9$, $i-C_4H_9$, $n-C_5H_{11}$, and $n-C_8H_{17}$. When R' is a secondary alkyl group, only partial exchange occurs to give $W_2Cl_4(\mu-OC_2H_5)_2(OR')_2(R'OH)_2$ with $R' = 2-C_3H_7$, $2-C_4H_9$, and $3-C_5H_{11}$. The compound $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$ can be prepared by reaction of WCl_6 with $i-C_3H_7OH$. The proton NMR spectra of all of these compounds plus several others previously reported show that when the R groups in the nonbridging OR and ROH ligands are primary, OH proton exchange with free ROH is rapid, whereas when R is secondary, such exchange is slow on the NMR time scale. Three compounds with secondary R groups have been studied by X-ray crystallography: **1**, $W_2Cl_4(\mu-OC_2H_5)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$; **2**, $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$; **3**, $W_2Cl_4(\mu-OC_2H_5)_2(O-3-C_5H_{11})_2(3-C_5H_{11}OH)_2$. **1** crystallizes in space group $Cmmm$ with $a = 11.882$ (2) Å, $b = 16.919$ (3) Å, $c = 14.406$ (5) Å, and $Z = 4$. There are two independent molecules resident on positions of mmm (D_{2h}) symmetry, and some disorder in the $\mu-OC_2H_5$ group occurs. **2** crystallizes in space group $P2_1/c$ with $a = 14.190$ (5) Å, $b = 13.715$ (6) Å, $c = 15.509$ (7) Å, $\beta = 99.71$ (3)°, and $Z = 4$. There are two independent molecules, each residing on an inversion center. **3** crystallizes in space group $P\bar{1}$ with $a = 10.459$ (3) Å, $b = 11.205$ (3) Å, $c = 17.280$ (4) Å, $\alpha = 92.76$ (3)°, $\beta = 111.96$ (2)°, $\gamma = 105.62$ (2)°, and $Z = 2$. There are two crystallographically independent molecules residing on inversion centers. In **1** the $W-O_T$ bond lengths within each molecule appear to be equal, which would imply that the $ROHOR$ hydrogen bonds are symmetrical. In **2** and **3** there are small inequalities. The possible influence of crystalline environment on the symmetry of the $ROHOR$ bridging units is discussed.

Our recent elucidation of the electronic and molecular structures of the ditungsten(IV) alkoxides $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$, where $R = CH_3$ or C_2H_5 ,² and the related ditungsten(V) compounds $W_2Cl_4(\mu-OR)_2(OR)_4$,³ has demonstrated that the former group of molecules constitutes a new class of doubly bonded $[W=W]^{8+}$ species (structure I) that possess a $\sigma^2\pi^2$ ground-state



electronic configuration. The ditungsten(V) complexes bear a very close structural relationship to them (structure II); the most important differences are the presence of a $W-W$ bond of order 1, the presence of four terminal alkoxide ligands (as opposed to two alkoxide and two alcohol ligands in I), and the absence of a hydrogen bond between the adjacent sets of alkoxide and alcohol ligands. In these previous studies^{2,3} we found that the best method of preparing the ditungsten(V) species II was by the oxidation of I using O_2 or $Ag(I)$.

Since the methoxide and ethoxide derivatives of I possess a remarkable air stability compared to most other lower valent ditungsten complexes, we have taken the opportunity to explore the chemistry of this class of complexes by investigating the dependence of their structure and stability upon the nature of the alkyl substituents. We have accomplished this through the alcohol exchange reactions of the ethoxide $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ and have demonstrated that these molecules constitute the most extensive series of doubly bonded dimetal complexes yet discov-

ered.⁴ During the course of this work we have found that the extent of exchange is dependent upon the steric demands of the alkyl group and have used X-ray crystallography and 1H NMR spectroscopy to probe the structures of the resulting molecules in both the solid and solution states. An interesting and highly significant aspect of this work has been the discovery that the hydrogen bonds (symmetric vs. unsymmetric?) in molecules of structure type I are very sensitive to the nature of the alkyl group (secondary vs. primary). Oxidation of the ditungsten(IV) complexes to the analogous ditungsten(V) derivatives can be accomplished without change in the basic ligand geometry. The most recent results of our work are now described.

Experimental Section

Materials. Alcohols were readily available from commercial sources and were dried over molecular sieves. Nitric oxide and nitrogen dioxide were purchased from Matheson. Anhydrous ethanol- d_6 and isopropyl- d_7 alcohol- d_1 were purchased from Stohler Isotope Chemicals and ethanol- d_1 was purchased from Aldrich Chemical Co. Tungsten metal (0.5 μm) was purchased from Alfa Inorganics. WCl_6 was prepared by direct chlorination of the metal and sublimed prior to use. WCl_4 was prepared by the stoichiometric reduction of WCl_6 with $W(CO)_6$ in refluxing chlorobenzene for 24 h.⁵ The ditungsten(IV) ethoxy derivative $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OH)_2$ was prepared by using a procedure similar to that described by Reagan and Brubaker.⁶

Reaction Procedures. Unless otherwise stated all reactions were carried out under an atmosphere of nitrogen.

(4) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(5) Schaefer King, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972; see footnote 15 in this paper.

(6) (a) Reagan, W. J.; Brubaker, C. H., Jr., *Inorg. Chem.* **1970**, *9*, 827.

(b) This procedure was used with the following modification: prior to the reaction of WCl_4 with ethanol, the flask containing the WCl_4 was cooled to 0 °C by using an ice bath, and the appropriate amount of ethanol was added after it had been cooled to -78 °C. Following the isolation of green $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$, a quantity of the red ditungsten(V) complex $W_2Cl_4(\mu-OEt)_2(OEt)_4$ could be isolated from the reaction filtrate by bubbling molecular oxygen through it until its color changed from green to red. Upon reducing its volume, red crystals of $W_2Cl_4(\mu-OEt)_2(OEt)_4$ separated.

(1) (a) Texas A&M University. (b) Purdue University.

(2) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilsley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

(3) Cotton, F. A.; DeMarco, D.; Kolthammer, B. W. S.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 3048.

Alcohol Exchange Reactions Involving $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OH)_2$. Complexes of the type $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$, where $R = CH_3$, $n-C_3H_7$, $n-C_4H_9$, $n-C_5H_{11}$, $n-C_6H_{13}$, or $i-C_4H_9$, were made by the following general procedure.⁷ In a typical reaction, freshly recrystallized $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OH)_2$ (0.50 g, 0.64 mmol) was placed in a 50-ml three-neck round-bottom flask and approximately 5–8 mL of alcohol was added. The resulting suspension was heated at 50–60 °C for 5–10 min, by which time all of the starting ethoxide had dissolved. The green solution was filtered hot (in air) and then cooled to 0 °C. The green crystalline product that separated was filtered off, washed with hexane that had been chilled to –78 °C, and dried under vacuum. Yields using this method were good, ranging from 50 to 75%. Since the ¹H NMR and electronic absorption spectra adequately characterized each derivative and confirmed their purity, microanalytical data were obtained for one representative example, namely, the *n*-propyl derivative. Anal. Calcd for $C_{18}H_{44}Cl_4O_6W_2$: C, 24.95; H, 5.08. Found: C, 25.10; H, 5.04.

The mixed alkoxy complexes $W_2Cl_4(\mu-OR)_2(OR)_2(R'OH)_2$, where $R = C_2H_5$ and $R' = i-C_3H_7$, *sec*-C₄H₉, or *sec*-C₅H₁₁ (*sec*-C₅H₁₁ or *sec*-Pent or *sec*-pentyl are used to designate $(C_2H_5)_2CH-$ throughout this paper), were prepared by using a procedure similar to that described above.⁸ Yields again were very good, ranging from 60 to 90%. Anal. Calcd for $C_{16}H_{40}Cl_4O_6W_2$ ($R' = i-C_3H_7$): C, 22.92; H, 4.78. Found: C, 23.16; H, 4.64. Calcd for $C_{20}H_{48}Cl_4O_6W_2$ ($R' = sec-C_4H_9$): C, 26.85; H, 5.37. Found: C, 26.95; H, 5.15. Calcd for $C_{24}H_{56}Cl_4O_6W_2$ ($R' = sec-C_5H_{11}$): C, 30.32; H, 5.89. Found: C, 29.93; H, 5.89.

The Preparation of $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$. We found that this complex could not be prepared by the reaction of $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OH)_2$ with isopropyl alcohol. However, the desired product can be prepared by using a procedure similar to that first described by Reagan and Brubaker.^{6a} Tungsten(IV) chloride (2.0 g, 6.14 mmol) was added to a 50-ml three-neck round-bottom flask which was then cooled in an ice bath. A quantity of isopropyl alcohol (17 mL, 222 mmol) that had been chilled to –78 °C was added. The reaction mixture was stirred and allowed to warm to room temperature. After reaction had been allowed to proceed for a 5-h period, the resultant gold crystalline product was filtered off and dried. The filtrate was allowed to stand for 48 h, thereby permitting the isolation of a second batch of crystals. The product was recrystallized by dissolving it in a minimum volume of dichloromethane, adding an excess of hexanes, and slowly evaporating the solvent. This yielded the pure product in 27% yield.

Oxidation of Dinuclear Ditungsten(IV) Complexes to Their Ditungsten(V) Analogues. We have previously shown that facile oxidation of the doubly bonded complexes $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$ to the singly bonded analogues $W_2Cl_4(\mu-OR)_2(OR)_4$ can be accomplished by using either molecular oxygen or silver nitrate.³ In this work we expand the list of reagents that will perform this oxidation to include nitrogen dioxide and hydrogen peroxide.⁹ However, the new complexes of ditungsten(IV) described herein are best oxidized by using either silver nitrate or nitrogen dioxide. A general procedure for each will be described although either method can be used. The method of choice for recrystallization will be given for each complex so prepared.

Method A. In a typical reaction, approximately 0.5 g of a given dinuclear ditungsten(IV) complex was placed in a 100-ml three-neck round bottom flask. Chloroform (10–20 mL) was added, and a stream of gaseous nitrogen dioxide admixed with nitrogen¹⁰ was bubbled through the solution for 10–20 min. The reaction was judged to be complete when the solution turned from green to red. The reaction solution was flushed

with pure gaseous nitrogen for several minutes and then stripped to dryness under reduced pressure. The crude material was then recrystallized.

Method B. In a typical reaction, 0.5 g of a given dinuclear tungsten(IV) complex was placed in a 125-ml Erlenmeyer flask along with a stoichiometric amount of freshly ground silver nitrate. The flask was flushed with nitrogen, and 20 mL of deoxygenated acetone was added. The resulting mixture was stirred for 15–30 min by which time the color of solution had turned from green to red and silver metal had precipitated. The reaction mixture was filtered, and the filtrate was stripped to dryness under reduced pressure. The crude material was recrystallized.

Complexes of the type $W_2Cl_4(\mu-OR)_2(OR)_4$, where $R = CH_3$, $n-C_3H_7$, $n-C_4H_9$, $n-C_5H_{11}$, $n-C_6H_{13}$, or $i-C_4H_9$, were prepared by using method B.

$R = CH_3$: yield 75%; recrystallized from benzene–hexane mixtures upon cooling to –78 °C for 6 h.

$R = n-C_3H_7$: yield 20%. The impure complex was initially prepared as a red oil. The oil was loaded onto a 21 × 1 cm silica column (60–200 mesh) and the column eluted with petroleum ether. The red band was collected and evaporated to dryness. The pure compound was crystallized from hexanes at –78 °C.

$R = n-C_5H_{11}$: yield 25%. This complex was purified by chromatography as described for the *n*-butyl derivative.

$R = n-C_6H_{13}$: This complex was isolated as a red oil, and all attempts to crystallize it failed.

$R = i-C_4H_9$: yield 65%. Purification of this complex was achieved by dissolving the crude product in dichloromethane, filtering, and evaporating the solvent from the filtrate.

Complexes of the type $W_2Cl_4(\mu-OR)_2(OR)_4$, where $R = C_2H_5$ and $R' = i-C_3H_7$, *sec*-C₄H₉, or *sec*-C₅H₁₁, and the isopropoxide $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_4$ were prepared by using method A.

$R' = i-C_3H_7$: yield 48%; recrystallized from dichloromethane–hexane mixtures at –78 °C. Anal. Calcd for $C_{16}H_{38}Cl_4O_6W_2$: C, 22.97; H, 4.55. Found: C, 23.22; H, 4.75.

$R' = sec-C_4H_9$: yield 58%; recrystallized from chloroform–methanol mixtures at –78 °C. Anal. Calcd for $C_{20}H_{46}Cl_4O_6W_2$: C, 26.92; H, 5.16. Found: C, 27.09; H, 5.10.

$R' = sec-C_5H_{11}$: yield 48%; recrystallized from petroleum ether.

$R = R' = i-C_3H_7$: yield 63%. In this case, the oxidation was done in a 2:1 chloroform–isopropyl alcohol solvent mixture. When the oxidation was complete, the solvent was evaporated to about 2 mL under reduced pressure. The resulting red complex was filtered off, washed with cold (–78 °C) isopropyl alcohol and dried under vacuum. Anal. Calcd for $C_{18}H_{42}Cl_4O_6W_2$: C, 25.01; H, 4.86. Found: C, 25.07; H, 4.73.

Preparation of Single Crystals for Structure Determinations. Three of the ditungsten(IV) compounds were chosen for X-ray study: 1, $W_2Cl_4(\mu-OC_2H_5)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$; 2, $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_2(O-i-C_3H_7OH)_2$; 3, $W_2Cl_4(\mu-OC_2H_5)_2(O-sec-C_5H_{11})_2(sec-C_5H_{11}OH)_2$. To prepare crystals of 1 and 2, the compound was dissolved in chloroform and a layer of isopropyl alcohol placed over the solution; X-ray quality crystals grew near the interface. Crystals of 3 were obtained by allowing a warm 3-pentanol solution of the complex to cool to room temperature.

X-ray Structure Determinations. The fundamental crystallographic data and information concerning the collection and processing of data are given in Table I for all three compounds. In each case crystal quality was good and the crystals were stable during the period of data collection. In each case an empirical absorption correction, based on a series of ψ scans near $\chi = 90^\circ$, was made.¹¹ Details concerning the solution and refinement of each structure will now be summarized.

Compound 1. The systematic absences were consistent with each of the following C-centered orthorhombic space groups: $C222$, $Cmmm$, $Cmm2$, $C2mm$, and $Cm2m$, the latter two of which are rendered as $Amm2$ in *International Tables for X-ray Crystallography*. For each of the three polar settings, the structure was developed through location and refinement of the tungsten atoms and their first coordination shells (R ca. 10%). In each case, a difference map was then calculated to locate the carbon atoms. Disorder of the ethyl groups, of the type that would be required by either of the space groups $C222$ and $Cmmm$, was found in all of the polar settings. For example, in $Cmm2$, a difference peak corresponding to atom C(1A) was found at (0.055, 0.0, 0.312) and a peak of roughly equal density was found at (0.055, 0.0, –0.293); similar results were obtained with $C2mm$ and $Cm2m$. This type of equivalence is not required by the symmetry of these space groups; therefore, further consideration was given only to space groups $C222$ and $Cmmm$.

Detailed consideration of the geometry of the compound and the disorder involved in the crystal shows that identical patterns must exist

(7) The only modifications to this procedure were as follows: in the case of the methoxy derivative, the product is insoluble in hot methanol and can be filtered directly from the reaction mixture. In the workup of the octyl alcohol derivative, the product was washed with methanol that had first been chilled to –78 °C.

(8) In the case of the isopropyl derivative, the product is insoluble in hot isopropyl alcohol. For the *sec*-butyl derivative, the filtered reaction solution had to be chilled to –78 °C in order to induce crystallization.

(9) For example, oxidation of $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ to $W_2Cl_4(\mu-OEt)_2(OEt)_4$ in a yield of 50% was accomplished in acetone by using a tenfold excess of 30% hydrogen peroxide.

(10) (a) A dilute stream of nitrogen dioxide admixed with nitrogen was prepared by regulating the flow of each gas stream utilizing 8 mm teflon vacuum stopcocks. The resultant mixture was bubbled through the reaction solution at atmospheric pressure. (b) The use of nitrogen dioxide as an oxidant was discovered during studies of the reactions between the ditungsten(IV) complexes and nitric oxide. When pure nitric oxide (obtained by passing the gas stream through a cold trap at –78 °C prior to reaction) was bubbled through solutions of $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$, no reaction occurred. When the cold trap was omitted and the gas stream was taken directly from the tank, the green solutions slowly turned red, indicating that oxidation had occurred. It was apparent that nitrogen dioxide impurities in the nitric oxide had been responsible for the oxidations.

(11) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* 1968, A24, 351.

Table I. Crystallographic Data and Data Collection Parameters for Compounds 1-3

	1	2	3
formula	$W_2Cl_4C_{16}H_{40}O_6$	$W_2Cl_4C_{18}H_{44}O_6$	$W_2Cl_4C_{22}H_{54}O_6$
fw	838.02	866.05	880.13
space group	<i>Cmmm</i>	$P2_1/c$	$P\bar{1}$
<i>a</i> , Å	11.882 (2)	14.190 (5)	10.459 (3)
<i>b</i> , Å	16.919 (3)	13.715 (6)	11.205 (3)
<i>c</i> , Å	14.406 (5)	15.509 (7)	17.280 (4)
α , deg			92.76 (2)
β , deg		99.71 (3)	111.96 (2)
γ , deg			105.62 (2)
<i>V</i> , Å ³	2896 (2)	2975 (1)	1787.3 (8)
<i>Z</i>	4	4	2
<i>d</i> _{calcd} , g/cm ³	1.92	1.93	1.76
cryst size, mm	0.35 × 0.35 × 0.35	0.45 × 0.25 × 0.15	0.30 × 0.30 × 0.30
μ (Mo K α), cm ⁻¹	87.9	85.6	71.3
data collection instrument	Enraf-Nonius CAD-4	Syntex P $\bar{T}$	Nicolet R3m/E
radiation		Mo K α , graphite monochromated	
scan method		$2\theta-\omega$	
data collection range, 2θ	2°-50°; $+h, +k, +l$	4°-51°; $+h, +k, \pm l$	2.5°-55°; $+h, \pm k, \pm l$
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	1436, 1096	4285, 3018	8206, 6434
no. of parameters refined	89	271	353
<i>R</i> ^a	0.0419	0.0295	0.0507
<i>R</i> _w ^b	0.0512	0.0424	0.0539
quality-of-fit indicator ^c	1.58	0.968	1.41
largest shift/esd, final cycle	0.01	0.12	0.61

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

in both space groups *C222* and *Cmmm*. Refinement was therefore completed in the centrosymmetric group, which incorporates the full symmetry of the pattern at hand. It was encouraging that statistical indicators such as the Wilson plot¹² and the *N*(*Z*) test¹³ gave a preference for centrosymmetry; but these are, strictly speaking, not rigorously valid for structures of this type.

Refinement of positional and thermal parameters for the tungsten atoms, the isopropoxy groups, and the oxygen atoms of the ethoxy groups proceeded in a routine manner. The ethyl groups were refined with methods appropriate to their disorder.

The arrangement of the ethyl group in the two molecules is different. In molecule A, the α -carbon atom C(1A) is located 0.71 (3) Å away from the mirror plane perpendicular to *x*, while the β -carbon atom C(2A) is 0.22 (9) Å away from the same plane. In molecule B, it is the α -carbon atom C(1B), which is near the pertinent mirror plane (0.21 (11) Å), while C(2B) is 0.85 (7) Å away from that same plane. It was found possible to carry out a convergent refinement with both atoms C(2A) and C(1B) on the proximate special positions of symmetry *mm*2; the present refinement, however, leads to more chemically reasonable derived parameters.

For the final refinement, the anisotropic thermal parameters of the atoms in the ethyl group of molecule A were averaged across the mirror plane perpendicular to *x* (i.e., only the principal components were allowed to be nonzero. In addition, the parameter β_{11} for atom C(2A) was held fixed at a value found in a previous refinement with the *x* coordinate of this atom fixed. Similar restraints were applied to molecule B. This gave a final refinement that was convergent and otherwise well behaved. A difference Fourier map at the end of refinement showed no peak greater than 1.0 e/Å³ which was not a ghost of a tungsten atom. The atomic positional parameters are listed in Table II.

Compound 2. The crystal of this compound was established to be monoclinic by the diffractometer autoindexing procedure, and this was verified by photographs which revealed a single mirror plane. Systematic absences indicated unambiguously space group $P2_1/c$, and the cell volume implied the presence of four molecules.

The positions of the two independent tungsten atoms in the asymmetric unit were given by the MULTAN series of direct-methods programs. Successive least-squares refinements and difference Fourier maps yielded the locations of the chlorine and oxygen atoms and then of the carbon atoms. The positional and anisotropic thermal parameters of all 30 atoms, as well as an overall scale factor—271 parameters in all—were refined in the final least-squares cycle. A final difference map had no peak with density greater than 0.68 e/Å³. The positional parameters are listed in Table III.

Table II. Atomic Positional Parameters for Compound 1, $W_2Cl_4(\mu\text{-OC}_2\text{H}_5)_2(\text{O}-i\text{-C}_3\text{H}_7)_2(i\text{-C}_3\text{H}_7\text{OH})_2$ ^a

atom	<i>x</i>	<i>y</i>	<i>z</i>
W(1A)	0.0000 (0)	0.07354 (4)	0.50000 (0)
W(1B)	0.0000 (0)	0.50000 (0)	0.08673 (5)
Cl(1A)	0.0000 (0)	0.1758 (2)	0.3850 (3)
Cl(1B)	0.1391 (4)	0.5000 (0)	0.2050 (3)
O(1A)	0.0000 (0)	0.0000 (0)	0.3892 (8)
O(1B)	0.1350 (11)	0.5000 (0)	0.0000 (0)
O(2A)	0.1673 (6)	0.0731 (4)	0.5000 (0)
O(2B)	0.0000 (0)	0.3821 (6)	0.0876 (6)
C(1A)	0.060 (2)	0.0000 (0)	0.3010 (16)
C(1B)	0.251 (3)	0.4875 (62)	0.0000 (0)
C(2A)	-0.018 (9)	0.0000 (0)	0.2271 (21)
C(2B)	0.310 (3)	0.5501 (38)	0.0000 (0)
C(3A)	0.251 (1)	0.1379 (7)	0.5000 (0)
C(3B)	0.000 (0)	0.3246 (9)	0.1652 (10)
C(4A)	0.318 (1)	0.1310 (8)	0.4103 (9)
C(4B)	0.108 (1)	0.2776 (9)	0.1566 (10)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Compound 3. The autoindexing procedure led to a triclinic cell, whose volume was consistent with the presence of two molecules. Assuming space group $P\bar{1}$, the structure solution was commenced by locating two independent tungsten atoms using the SHELXTL software package.¹⁴ Successive refinements and Fourier maps led to finding and refining 39 atoms using anisotropic thermal parameters. A final difference map showed no significant features. The final positional parameters are listed in Table IV.

Thermal parameters and structure factors for all three structures are available as supplementary material.

Spectroscopic Characterizations and Electrochemical Measurements. The ¹H NMR spectra of CDCl₃ solutions were recorded on a Perkin-Elmer R-32 90MHz instrument using Me₄Si as an internal standard. Electronic absorption spectra were measured on CHCl₃ solutions (unless otherwise stated) by using a Varian series 634 spectrophotometer.

Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. *E*_{1/2} values (taken as (*E*_{pa} + *E*_{pc})/2) were referenced to the saturated potassium chloride calomel electrode

(12) Wilson, A. J. C. *Acta Crystallogr.* **1949**, *2*, 318.

(13) Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.

(14) For structures **1** and **2** all crystallographic computing was done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX. Software was from the Enraf-Nonius Structure Determination Package. For structure **3**, G. M. Sheldrick's "Nicolet SHELXTL Operations Manual", Nicolet XRD Corp., Cupertino, CA, 1981, was followed.

Table III. Atomic Positional Parameters for Compound 2, $W_2Cl_4(\mu-O-i-C_3H_7)_2(O-i-C_3H_7)_2(i-C_3H_7OH)_2$ ^a

atom	x	y	z
W(1A)	-0.00624 (3)	0.06547 (3)	0.05547 (3)
W(1B)	0.56543 (3)	0.04468 (3)	0.46994 (3)
Cl(1A)	-0.1295 (2)	0.1535 (2)	0.1109 (2)
Cl(2A)	0.1022 (2)	0.1646 (2)	0.1536 (2)
Cl(1B)	0.5778 (2)	0.1735 (2)	0.3683 (2)
Cl(2B)	0.7366 (2)	0.0478 (2)	0.4973 (2)
O(1A)	0.1129 (4)	0.0068 (5)	0.0217 (4)
O(2A)	-0.0054 (5)	-0.0334 (4)	0.1475 (4)
O(3A)	-0.0101 (5)	0.1659 (4)	-0.0385 (4)
O(1B)	0.5791 (5)	-0.0591 (5)	0.5631 (4)
O(2B)	0.5648 (5)	-0.0527 (5)	0.3795 (4)
O(3B)	0.5655 (5)	0.1462 (4)	0.5629 (4)
C(1A)	0.2169 (8)	0.0161 (8)	0.0508 (8)
C(2A)	0.2601 (10)	0.0515 (10)	-0.0293 (10)
C(3A)	0.2564 (11)	-0.0825 (10)	0.0899 (8)
C(4A)	-0.0087 (9)	-0.0233 (8)	0.2421 (6)
C(5A)	-0.0998 (11)	-0.0709 (10)	0.2597 (8)
C(6A)	0.0852 (11)	-0.0715 (11)	0.2894 (8)
C(7A)	-0.0143 (10)	0.2748 (7)	-0.0408 (8)
C(8A)	0.0853 (11)	0.3110 (11)	-0.0544 (11)
C(9A)	-0.0981 (11)	0.3042 (9)	-0.1080 (10)
C(1B)	0.6582 (9)	-0.1026 (9)	0.6224 (8)
C(2B)	0.6615 (10)	-0.2100 (9)	0.6045 (9)
C(3B)	0.6441 (11)	-0.0791 (11)	0.7184 (8)
C(4B)	0.6298 (9)	-0.0671 (8)	0.3159 (7)
C(5B)	0.5669 (11)	-0.0652 (10)	0.2256 (8)
C(6B)	0.6813 (10)	-0.1639 (9)	0.3370 (9)
C(7B)	0.6245 (8)	0.2330 (8)	0.5902 (7)
C(8B)	0.6741 (10)	0.2200 (11)	0.6807 (8)
C(9B)	0.5548 (12)	0.3222 (9)	0.5761 (11)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

(SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Potential control of coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. All voltammetric measurements were made at a platinum bead electrode in solutions deaerated with a stream of dry nitrogen gas.

Results and Discussion

(A) Alcohol Exchange Reactions. In 1969 Clark and Wentworth¹⁵ reported that the reaction of $(Bu_4N)_3W_2Cl_9$ with alcohols leads to the ditungsten(III) complexes $W_2Cl_4(OR)_2(ROH)_4$, where $R = Me, Et, \text{ or } n\text{-Pr}$. These three complexes were found to be readily interconverted via conventional alcohol exchange reactions. Recently, we have demonstrated² that these molecules are in reality the ditungsten(IV) species $W_2Cl_4(OR)_4(ROH)_2$ and that they contain both bridging and terminal alkoxide ligands in addition to two coordinated alcohols (structure I). Accordingly, they are best represented as $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$. We have confirmed that alcohol exchange reactions occur smoothly and in high yield. Thus, upon warming the ethoxide derivative with an excess of a neat primary alcohol, a range of molecules of the type $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$ can be formed. By this means we have isolated, in addition to the methoxide and ethoxide, derivatives where $R = n\text{-Pr}, n\text{-Bu}, n\text{-Pent}, n\text{-Oct}$, and $i\text{-Bu}$, thereby expanding considerably the range of such complexes that are known. The striking similarity of their electronic absorption spectra (λ_{max} at 742–730 and 433–420 nm) and their electrochemical properties (Table V) to those of the structurally characterized methoxide and ethoxide² attests to their structural identity.

In contrast to the preceding results, when exchange of the ethoxide and ethanol ligands of $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ was carried out by using secondary alcohols $R'OH$, where $R' = i\text{-Pr}, sec\text{-Bu}$, or $sec\text{-Pent}$, mixed alkoxy species of the type $W_2Cl_4(\mu-OEt)_2(OR')_2(R'OH)_2$ were obtained whose properties

Table IV. Atomic Positional Parameters ($\times 10^4$) for Compound 3, $W_2Cl_4(\mu-OC_2H_5)_2(O-sec-C_5H_{11})_2(sec-C_5H_{11}OH)_2$ ^a

atom	x	y	z
WA	34 (1)	-926 (1)	368 (1)
Cl(A1)	767 (3)	-2744 (2)	265 (2)
Cl(A2)	-547 (3)	-1630 (2)	1512 (1)
O(A1)	-649 (6)	536 (5)	594 (3)
O(A2)	2066 (6)	23 (5)	1186 (3)
O(A3)	-1975 (5)	-1857 (5)	-437 (3)
C(A1)	-630 (18)	1281 (13)	1330 (9)
C(A1)*	-1696 (25)	706 (22)	892 (15)
C(A2)	-2044 (23)	1098 (20)	1312 (18)
C(A2)*	-980 (58)	1459 (42)	1745 (27)
C(A3)	3119 (10)	-374 (10)	1880 (6)
C(A4)	4361 (12)	-403 (13)	1606 (8)
C(A5)	5388 (14)	-960 (14)	2188 (9)
C(A6)	3870 (21)	811 (22)	2639 (11)
C(A6)*	3033 (26)	88 (26)	2771 (14)
C(A7)	3191 (20)	1313 (18)	2948 (9)
C(A8)	-2877 (10)	-3127 (8)	-509 (6)
C(A9)	-2972 (14)	-3918 (10)	-1296 (7)
C(A10)	-3715 (17)	-5352 (11)	-1324 (8)
C(A11)	-4390 (15)	-3048 (12)	-627 (12)
C(A12)	-4547 (16)	-2322 (14)	-10 (12)
WB	246 (1)	5949 (1)	5504 (1)
Cl(B1)	2308 (3)	7295 (2)	6673 (1)
Cl(B2)	-1140 (3)	7171 (3)	5765 (2)
O(B1)	-1659 (6)	4956 (5)	4556 (3)
O(B2)	722 (6)	7049 (5)	4729 (3)
O(B3)	-237 (6)	4821 (5)	6291 (3)
C(B1)	-3164 (13)	4578 (16)	4451 (9)
C(B2)	-4045 (18)	5017 (19)	3834 (13)
C(B3)	1093 (12)	8426 (9)	4797 (7)
C(B4)	2758 (13)	8924 (9)	4978 (7)
C(B5)	3350 (14)	10402 (11)	5210 (9)
C(B6)	261 (15)	8706 (12)	3895 (9)
C(B7)	-1250 (19)	8174 (19)	3638 (10)
C(B8)	-124 (11)	5155 (10)	7160 (5)
C(B9)	1097 (13)	4757 (9)	7751 (6)
C(B10)	1452 (15)	5175 (12)	8681 (7)
C(B11)	-1661 (19)	4771 (17)	7151 (10)
C(B12)	-2434 (20)	3535 (14)	6904 (11)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Table V. Cyclic Voltammetric Data for Ditungsten(IV) and Ditungsten(V) Alkoxides^a

R	R'	$W_2Cl_4(\mu-OR)_2(OR')_2(R'OH)_2$ ^b	$W_2Cl_4(\mu-OR)_2(OR')_4$	
		$E_{p,a}$	$E_{1/2}(\text{red.})^c$	$E_{p,c}$
Et	Et	+0.80	-0.76 (100)	-1.32
<i>n</i> -Pr	<i>n</i> -Pr	+0.84	-0.78 (150)	-1.40
<i>n</i> -Bu	<i>n</i> -Bu	+0.87	-0.80 (300)	-1.62
<i>n</i> -Pent	<i>n</i> -Pent	+0.90	-0.76 (160)	
<i>n</i> -Oct	<i>n</i> -Oct	+0.96	-0.79 (240)	
<i>i</i> -Pr	<i>i</i> -Pr	+0.80	-0.89 (140)	-1.30
<i>i</i> -Bu	<i>i</i> -Bu	+1.02	-0.74 (130)	-1.60
Et	<i>i</i> -Pr	+0.89	-0.81 (100)	-1.52
Et	<i>sec</i> -Bu	+0.96	-0.81 (100)	-1.60
Et	<i>sec</i> -Pent	+0.98	-0.80 (120)	

^a In V vs. SCE with a Pt-bead electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All data were recorded at $\nu = 200$ mV/s. ^b These complexes also show an irreversible reduction at potentials $\lesssim -0.8$ V. Since this process is much less well-defined than the irreversible oxidation at $E_{p,a} \gtrsim +0.8$ V, we have not considered it further at this time. ^c $E_{p,a} - E_{p,c}$ value in mV.

were nonetheless very similar to those exhibited by the unmixed compounds $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$, with λ_{max} values of 742–730 and 424–421 nm in the electronic absorption spectra of chloroform solutions and electrochemical properties as listed in Table V. ¹H NMR spectroscopy showed that the bridging ethoxide ligands had not been replaced, a result that was confirmed

Table VI. ^1H NMR Spectra of Ditungsten(IV) and Ditungsten(V) Alkoxides

compd	^1H chem shifts, ^a δ				
	hydroxyl	$\alpha\text{-CH}_2$ (bridge)	$\alpha\text{-CH}_2$ (terminal)	$\alpha\text{-CH}$ (bridge)	$\alpha\text{-CH}$ (terminal)
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_2(\text{EtOH})_2$	10.7 (s, br)	5.44 (c)	4.53 (q)		
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_4$		5.83 (q)	4.57 (q)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Pr})_2(\text{O-}n\text{-Pr})_2(n\text{-PrOH})_2$	10.88 (s, br)	5.20 (t)	4.41 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Pr})_2(\text{O-}n\text{-Pr})_4$		5.59 (t)	4.50 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Bu})_2(\text{O-}n\text{-Bu})_2(n\text{-BuOH})_2$	11.05 (s, br)	5.30 (t)	4.52 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Bu})_2(\text{O-}n\text{-Bu})_4$		5.71 (t)	4.54 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Pent})_2(\text{O-}n\text{-Pent})_2(n\text{-PentOH})_2$	11.01 (s, br)	5.24 (t)	4.47 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Pent})_2(\text{O-}n\text{-Pent})_4$		5.68 (t)	4.53 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Oct})_2(\text{O-}n\text{-Oct})_2(n\text{-OctOH})_2$	11.09 (s, br)	5.29 (t)	4.50 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Oct})_2(\text{O-}n\text{-Oct})_4$		5.73 (t)	4.59 (t)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Pr})_2(\text{O-}i\text{-Pr})_2(i\text{-PrOH})_2$	11.32 (t)			7.10 (h)	5.27 (o)
$\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Pr})_2(\text{O-}i\text{-Pr})_4$				7.42 (h)	5.46 (h)
$\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Bu})_2(\text{O-}i\text{-Bu})_2(i\text{-BuOH})_2$	11.24 (s, br)	4.95 (d)	4.31 (d)		
$\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Bu})_2(\text{O-}i\text{-Bu})_4$		5.45 (d)	4.42 (d)		
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}i\text{-Pr})_2(i\text{-PrOH})_2$	11.41 (t)	5.30 (m) ^b			5.30 (m) ^b
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}i\text{-Pr})_4$		5.76 (q)			5.31 (h)
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}sec\text{-Bu})_2(sec\text{-BuOH})_2$	11.24 (t)	5.34 (q)			5.03 (h)
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}sec\text{-Bu})_4$		5.77 (q)			5.14 (s')
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}sec\text{-Pent})_2(sec\text{-PentOH})_2$	10.87 (t)	5.32 (q)			4.89 (s')
$\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}sec\text{-Pent})_4$		5.80 (q)			5.06 (q')

^a All spectra were recorded at 35 °C in CDCl_3 with Me_4Si as an internal reference. Abbreviations are as follows: singlet, (s); doublet, (d); triplet, (t); quartet, (q); quintet, (q'); sextet, (s'); heptet, (h); octet, (o); multiplet, (m). The magnitudes of the coupling constants are as follows: hydroxyl ($J \approx 5$ Hz); methylene ($J \approx 7\text{--}8$ Hz); methine ($J \approx 5\text{--}7$ Hz). ^b The expected quartet from the α -methylene protons of the $\mu\text{-OEt}$ ligands and the octet from the α -methine protons of the terminal $\text{O-}i\text{-Pr}$ and $i\text{-PrOH}$ ligands overlap to give a multiplet centered at ca. 5.30 δ .

by crystal structure determinations on the mixed ethoxide-isopropoxide and ethoxide-*sec*-pentoxide derivatives (vide infra).

Since the bridging ethoxide ligands were not replaced upon reaction with secondary alcohols, the question arose as to whether this behavior reflected in some way an unfavorable steric interaction when secondary alkoxide ligands occupied these bridging positions. The answer to this question was provided upon consideration of an earlier report by Reagan and Brubaker.^{6a} As these workers first described, one of the methods available for the synthesis of ditungsten(IV) complexes of the type $\text{W}_2\text{Cl}_4(\mu\text{-OR})_2(\text{OR})_2(\text{ROH})_2$ is through the direct reaction of the appropriate alcohol with tungsten(IV) chloride. In the case of isopropyl alcohol, such a procedure was described^{6a} as yielding an orange-brown complex formulated as $\text{W}_2\text{Cl}_4(\text{O-}i\text{-Pr})_4(i\text{-PrOH})_2$. The reported color struck us as peculiar because the other ditungsten(IV) alkoxides are bright green. Nonetheless, we have confirmed the synthesis of this complex and, furthermore, find that it possesses a very similar electronic absorption spectrum (λ_{max} values of 750 and 442 nm) and electrochemical properties (Table V) to all other complexes of this type.¹⁶ Its structural formulation as $\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Pr})_2(\text{O-}i\text{-Pr})_2(i\text{-PrOH})_2$ has been confirmed by a single-crystal X-ray structure analysis, thereby establishing that bridging secondary alkoxide ligands do not lead to any unusual instability in this class of compounds.

(B) Oxidation of Ditungsten(IV) Alkoxides to Their Ditungsten(V) Analogues. We have demonstrated previously^{2,3} that the ethoxide complex of ditungsten(IV), $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_2(\text{EtOH})_2$, can be oxidized to $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_4$ by oxygen or silver nitrate. This reaction proceeds in high yield and constitutes the best method of preparing the latter complex. Since the electrochemical properties of all the ditungsten(IV) complexes are so similar (Table V), each showing an irreversible oxidation in the range +0.80 to +1.02 V, it was anticipated that each could be oxidized chemically in a manner similar to that found^{2,3} for the ethoxide. This we have now shown is the case, since all the green ditungsten(IV) complexes are oxidized to the analogous $\text{W}_2\text{Cl}_4(\mu\text{-OR})_2(\text{OR})_4$. In the present work we have found that nitrogen dioxide and silver nitrate are the most convenient oxidants. The electrochemical and spectroscopic properties of the resulting

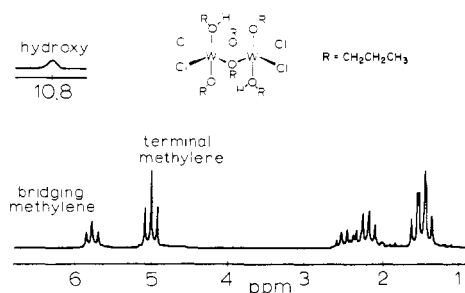


Figure 1. The ^1H NMR spectrum of a CDCl_3 solution of $\text{W}_2\text{Cl}_4(\mu\text{-O-}n\text{-Pr})_2(\text{O-}n\text{-Pr})_2(n\text{-PrOH})_2$.

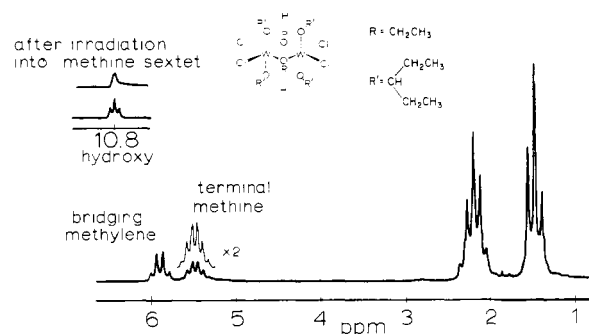


Figure 2. The ^1H NMR spectrum of a CDCl_3 solution of $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}sec\text{-Pent})_2(sec\text{-PentOH})_2$.

ditungsten(V) complexes are in accord with those found for the structurally characterized ethoxide derivative,³ thereby confirming their identity. The cyclic voltammograms of dichloromethane solutions (containing tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte) are characterized by a reduction at $E_{1/2} \approx -0.8$ V, which approaches reversibility ($i_{p,c}/i_{p,a} \approx 1$), and an irreversible reduction close to the solvent limit (at a potential more negative than -1.30 V). We have demonstrated previously² that in the case of $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_4$ the reduction at ca. -0.8 V corresponds to a one-electron process.

(C) ^1H NMR Spectra of Ditungsten Complexes. The appropriate data for all ditungsten(IV) species and their ditungsten(V) analogues are given in Table VI, and the ^1H NMR spectra of

(16) The difference in color between the isopropoxide and the other ditungsten(IV) alkoxides is reflected by the small bathochromic shift of the electronic absorption bands of the former complex.

representative examples are shown in Figures 1 and 2. To simplify the presentation of the spectroscopic data, Table VI contains resonances due to the hydroxyl protons, the α -methylene protons of the primary alcohols, and the secondary alcohol methine protons only. The remaining proton resonances provide little helpful information; these data are available elsewhere.¹⁷ For both classes of complexes the integration of the spectra is in accord with formulation of the complexes as given in Table VI. In all instances, resonances due to bridging alkoxides occur downfield of those which characterize the terminal ligands. In our subsequent discussion we will focus on the 1H NMR spectroscopic properties of the ditungsten(IV) complexes of the types $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$ and $W_2Cl_4(\mu-OEt)_2(OR')_2(R'OH)_2$.

(a) $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$. The absence of methylene quartets at 5.44 and 4.53 ppm is evidence that upon reacting $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ with *n*-PrOH, *n*-BuOH, *n*-PentOH, *n*-OctOH, and *i*-BuOH, complete substitution of the ethoxide and ethanol ligands takes place. This is signaled by the appearance of triplets at 5.30–5.20 and 4.55–4.40 ppm (in the ratio 1:2) as well as the retention of a broad resonance close to 11 ppm due to the hydroxyl protons (Table VI). Since the terminal alkoxide and alcohol ligands are equivalent on the NMR time scale, it is apparent that an exchange process is occurring. However, because the methyl and methylene resonances in the 1H NMR spectra of $CDCl_3$ solutions of these complexes were unaffected by the addition of free alcohol, we can rule out dissociative terminal ligand exchange under these mild conditions. Accordingly, a process involving the hydroxyl proton of the bound alcohol ligands is the most likely possibility. In this event, three exchange mechanisms for the hydroxyl proton can be envisioned. (1) An intramolecular exchange of the hydroxyl proton between the oxygens of syn axial OR and ROH ligands. (2) An intermolecular exchange of the hydroxyl protons between terminal oxygen atoms of different dinuclear moieties. (3) An exchange between the hydroxyl proton of the bound alcohol ligands and the protons associated with trace amounts of free alcohol in solution. The absence of coupling of the hydroxyl proton to the α -methylene protons of the terminal ligands, along with the observation that the only change in the spectrum of the ethoxide derivative in $CDCl_3$ solution between +80 and –55 °C is a slight broadening of the resonance at 11 ppm, rules out the occurrence solely of an intramolecular exchange process. It is conceivable that an intermolecular exchange is operative, possibly assisted by a trace amount of free alcohol. In this context, the following observation is noteworthy. In preparing the primary alcohol derivatives from the ethoxide complex by alcohol exchange, the chemical shift of the hydroxyl proton resonance varied by up to 1 ppm, depending upon how thoroughly the reactant alcohol had been pumped off. We have found that in the presence of an observable quantity of free alcohol, the hydroxyl protons of $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ and those of free EtOH enter into a rapid exchange process. Thus when 0.2 μ L of ethanol was added to 500 μ L of a 0.38 M solution of the ethoxide derivative $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ (i.e., an approximately 100-fold excess of bound alcohol to free alcohol), the chemical shift of the hydroxyl protons of the bound alcohol ligands changed from 10.76 to 10.63 ppm; with the hydroxyl protons of free ethanol occurring at 2.41 ppm, the observed resonance for the two exchanging species (at 10.63 ppm) can be compared to a calculated value of 10.68 ppm. When a more concentrated solution was prepared (comprising 600 μ L of a 0.32 M solution of the complex and 11.2 μ L of ethanol- d_1 , i.e. a 2:1 excess of bound protons to free alcohol deuterium atoms), the resonance shifted to 7.88 ppm, as expected.¹⁸ When the solution temperature was lowered from 35 °C, the hydroxyl signal broadened considerably and was indistinguishable from the base line at –50 °C. Upon further cooling, a very weak broad signal emerged around 11 ppm. The lower temperature limit could not be ascertained because of

the low solubility of the complex below –50 °C. The frequency difference between the exchanging protons ($W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ plus ethanol) and the bound hydroxyl protons of the pure ethoxide complex at 35 °C is 258 Hz, which corresponds to an approximate exchange rate of $1.5 (\pm 0.1) \times 10^3 s^{-1}$.

(b) $W_2Cl_4(\mu-OEt)_2(OR')_2(R'OH)_2$. The 1H NMR spectrum of the *sec*-pentyl derivative $W_2Cl_4(\mu-OEt)_2(O-sec-Pent)_2(sec-PentOH)_2$, which is representative of those of the mixed alkoxides of the type $W_2Cl_4(\mu-OEt)_2(OR')_2(R'OH)_2$ (Table VI), is presented in Figure 2. The quartet at 5.32 ppm is evidence that during the reaction of $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ with *sec*-pentyl alcohol, the terminal ligands have been replaced leaving the bridging ethoxide ligands intact. The α -methine protons of the terminal ligands appear as an apparent first-order sextet at 4.89 ppm,¹⁹ and the hydroxyl protons of the bound alcohols appear as a triplet at 10.87 ppm. Decoupling experiments confirm that the hydroxyl protons are coupled to the two α -methine protons of the terminal ligands as witnessed by the collapse of the triplet at 10.87 ppm to a singlet when irradiating into the α -methine sextet at 4.89 ppm (see Figure 2). We propose that for the secondary derivatives of the type $W_2Cl_4(\mu-OEt)_2(OR')_2(R'OH)_2$, $R' = i$ -Pr, *sec*-Bu, and *sec*-Pent, both intermolecular proton exchange and proton exchange with free alcohol are inhibited. This contrasts with the situation pertaining to the $W_2Cl_4(\mu-OR)_2(OR)_2(ROH)_2$ derivatives (vide supra). The spectrum of the *sec*-pentyl derivative is virtually unchanged between +55 and –55 °C. Addition of an equal molar volume of ethanol- d_1 produces no change in the spectrum; the hydroxyl proton resonance remains unshifted and sharp for several hours at room temperature. These observations are consistent with a fast intramolecular exchange of the hydroxyl protons between the oxygens of the terminal ligands and hence their observed coupling to the α -methine protons of the terminal ligands. The absence of exchange with free alcohol may reflect an increase in the hydrophobic environment about the hydrogen bond when the more highly branched secondary alkyl substituents are present.

(D) A Consideration of the Mechanism of the Alcohol Exchange Reactions of $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$. Ethanol- d_6 and isopropyl- d_7 alcohol- d_1 were chosen to model the exchange of the ethoxide derivative with primary and secondary alcohols, respectively. Alkoxide exchange occurring in chloroform solutions of the ethoxide complex with either ethanol or isopropyl alcohol (present in at least a 10-fold excess per bound terminal alkoxide-alcohol ligand) proceeds in two discrete steps. At fairly low temperatures, 45–65 °C, terminal ligand substitution occurs. At higher temperatures, 80–100 °C, substitution of the bridging alkoxides occurs. In the case of terminal substitution by ethanol- d_6 under pseudo-first-order conditions,²⁰ $\ln c$ vs. t plots were linear;

(19) For the terminal *sec*-pentoxide ligands of the complex $W_2Cl_4(\mu-OEt)_2(O-sec-Pent)_2(sec-PentOH)_2$ that are bridged by the symmetrical hydrogen bond, the β -methylene protons (A), the α -methine protons (B), and the hydroxyl proton (X) form an $A_4A'_2BB'X$ spin system. All coupling constants are close to 5 Hz, thereby leading to an apparent first-order sextet for the α -methine protons and a triplet for the hydroxyl protons.

(20) Kinetic measurements of the alcohol exchange reactions involving the ethoxy derivative $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OH)_2$ were carried out by the following procedure. The C_2H_5OD derivative $W_2Cl_4(\mu-OC_2H_5)_2(OC_2H_5)_2(C_2H_5OD)_2$ (0.05 g, 0.064 mmol) was dissolved in $CDCl_3$ (0.4 mL), and the solution was transferred to an NMR tube that could be attached to a 9-mm vacuum O-ring joint. A 40-fold excess (2.6 mmol) of either ethanol- d_6 or isopropyl- d_7 alcohol- d_1 was added. The assembly was then attached to a vacuum line, the liquid contents were frozen by using liquid nitrogen, and the NMR tube was then evacuated and sealed. The sample was allowed to warm to 0 °C and maintained at that temperature until measurements (at various temperatures) were taken. The rate of exchange of the terminal alcohol and alkoxy ligands by free alcohol was measured by monitoring the disappearance of the methylene protons of the terminal ethanol and ethoxy ligands of the complex.

(21) To prepare this complex, freshly recrystallized $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$ (0.5 g) was suspended in 10 mL of ethanol- d_1 and heated to 55 °C. Sufficient $CDCl_3$ was then slowly added until all of the starting material had dissolved. The resulting solution was warmed at 55 °C for five more minutes and filtered while hot. An additional 15 mL of ethanol- d_1 was added to the filtrate which was then cooled to 0 °C. The green crystalline product was filtered and dried under vacuum. Replacement of the hydroxy protons with deuterium was confirmed by 1H NMR spectroscopy.

(17) DeMarco, D. Ph.D. Thesis, Purdue University, 1982.

(18) Ethanol- d_1 was used so that the signal associated with the exchanging protons could be kept at a reasonably low intensity compared to the other signals in the spectrum. Again the observed value of 7.88 ppm is in good agreement with the calculated one of 7.87 ppm.

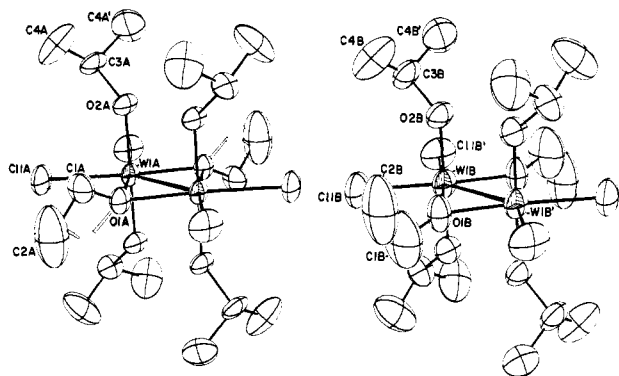


Figure 3. ORTEP drawings of the two crystallographically independent molecules of compound 1. The two disordered conformations of the μ -OC₂H₅ groups are shown in molecule A. 50% probability ellipsoids are used.

the rate constant at 55 °C was approximately $3.0 (\pm 0.5) \times 10^{-3} \text{ s}^{-1}$. When similar substitutions were performed by using isopropyl-*d*₇ alcohol-*d*₁ in *c* vs. *t* plots were nonlinear. We feel that in the case of isopropyl alcohol this reflects the widely different rate constants for substitution of the various species encountered between the limits of $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OEt})_2(\text{EtOH})_2$ and $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{O-}i\text{-Pr})_2(\text{O-}i\text{-PrOH})_2$. Although an exact determination of the substitution mechanisms is beyond the scope of this investigation, the data for terminal substitution are consistent with an *I_d* mechanism. This is supported by the observation that for alcohol-free chloroform solutions of the ethoxide complex, dissociation of bound ethanol does not occur between +35 and +85 °C.

As stated previously, only at elevated temperatures (>80 °C) does bridge substitution begin to occur. It may appear tempting to invoke a terminal alkoxide-bridge alkoxide exchange mechanism, but for several reasons we feel that this is not the case. First, and perhaps most important, alcohol-free solutions of the ethoxide complex give no hint of fluxionality; the ¹H NMR spectra remain unaffected between +85 and -55 °C. There appears to be no low-energy pathway for exchange of terminal and bridging ligands. Support for this notion is found upon considering the ¹H NMR spectra of other multiply bonded dinuclear complexes that adopt the same type of edge-sharing bioctahedra geometry such as $\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4$ ²² and $\text{W}_2\text{Cl}_6\text{L}_4$ ²³ (L = PR₃ or THF), which indicate that these molecules are also nonfluxional. Thus substitution of the bridging alkoxide ligands may occur by breaking of a W-OR(bridge) bond with subsequent capture of the vacant coordination site by an alcohol molecule in the outer coordination sphere.

This still leaves open the questions as to why under the *preparative reaction conditions* we employed (see Experimental Section), complete exchange occurs with the primary alcohols but only partial exchange with secondary alcohols. It is likely that the relatively low temperatures (50–60 °C) that are generally reached during the exchange experiments, the change in the solvent system (from neat alcohol in the preparative scale experiments to chloroform-alcohol solutions for the NMR measurements), along with the increased steric constraints encountered as the primary ethoxide-ethanol ligands are progressively replaced by the secondary ones (R'OH) account for the substitution terminating at the stage $\text{W}_2\text{Cl}_4(\mu\text{-OEt})_2(\text{OR}')_2(\text{R'OH})_2$. In the case of the alcoholysis of tungsten(IV) chloride by isopropyl alcohol, resulting in the formation of $\text{W}_2\text{Cl}_4(\mu\text{-O-}i\text{-Pr})_2(\text{O-}i\text{-PrOH})_2$, the same mechanistic constraints are no longer pertinent and the

Table VII. Bond Lengths (Å) in Compound 1^a

	molecule A	molecule B
W(1)-W(1')	2.488 (1)	2.499 (1)
-Cl(1)	2.395 (3)	2.374 (3)
-O(1)	2.023 (8)	2.034 (9)
-O(2)	1.987 (6)	1.995 (8)
O(1)-C(1)	1.46 (2)	1.39 (3)
O(2)-C(3)	1.48 (1)	1.48 (1)
C(1)-C(2)	1.41 (6)	1.27 (9)
C(3)-C(4)	1.52 (1)	1.51 (1)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Table VIII. Table of Bond Angles (deg) in Compound 1^a

	molecule A	molecule B
W(1')-W(1)-Cl(1)	136.22 (8)	135.9 (1)
-O(1)	52.1 (2)	52.1 (2)
-O(2)	89.8 (2)	90.4 (2)
Cl(1)-W(1)-Cl(1')	87.6 (2)	88.3 (2)
-O(1)	84.2 (2)	83.8 (2)
-O(1')	171.7 (2)	172.0 (2)
-O(2)	90.2 (1)	89.7 (2)
O(1)-W(1)-O(1')	104.1 (3)	104.2 (4)
-O(2)	89.9 (1)	90.2 (1)
O(2)-W(1)-O(2')	179.6 (3)	179.3 (4)
W(1)-O(1)-W(1')	75.9 (3)	75.8 (4)
-C(1)	133.5 (5)	141.2 (8)
W(1)-O(2)-C(3)	132.2 (6)	131.4 (7)
O(1)-C(1)-C(2)	110 (3)	115 (7)
O(2)-C(3)-C(4)	107.1 (6)	106.4 (7)
C(4)-C(3)-C(4')	117 (1)	116 (2)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

fully substituted isopropoxide derivative can be produced.

(E) Crystallographic Structural Results. Compound 1. As explained in the Experimental Section, the choice of the correct space group is not easy or, in the final analysis, absolutely unambiguous, for this compound. Fortunately, both the overall molecular structure and the details of greatest interest to us are not sensitive to the choice.

The numbering scheme was chosen to distinguish the two independent molecules occupying the asymmetric portion of the unit cell. Labels containing "A" refer to atoms of the molecule centered about the *mmm* (d) position while labels containing "B" refer to atoms of the molecule centered about the *mmm* (b) position. Each of these molecules is shown in Figure 3. Molecules A and B each reside about independent *mmm* centers and therefore possess rigorous crystallographic *D_{2h}* symmetry. There exists, however, a slight disorder involving C(X1) and C(X2) of the ethoxide chain O(X1)-C(X1)-C(X2) (X = A or B). This disorder results from the impossibility of all atoms of the ethoxide chain lying on the mirror plane-mirror plane intersection. Whereas O(X1) does occupy an *mm* position, C(X1) and C(X2) occupy only *m* positions and are reflected in the second nearby mirror plane to produce false, symmetry-related positions. While this disorder raised some concern as to the choice of space group, the noncentrosymmetric choice does not eliminate the disorder. Attempts to refine an isotropic model as *C222* indicated the original choice of *Cmmm* was correct.

Tables VII and VIII give the bond lengths and bond angles for molecules 1A and 1B, following the labeling scheme defined in Figure 3. It is clear from these numbers that the two molecules are essentially identical.

We emphasize at this point that because of the crystallographic *mmm* symmetry imposed on each molecule, the four W-O_T (T means terminal) distances in each molecule (as well as the four W-O_B distances) are required to refine to identical values. For the two molecules the W-O_T values are 1.987 (6) and 1.995 (8) Å; the difference between them is not statistically significant, and the mean value, 1.991 [3] Å,²⁷ could be used in general discussion.

(22) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392.

(23) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(24) Bacon, G. E. "Neutron Scattering in Chemistry"; Butterworths: London, 1977, Chapter 4.

(25) Williams, J. M.; Schneemeyer, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 5780.

(26) de la Vega, J. R. *Acc. Chem. Res.* **1982**, *15*, 185.

Table IX. Bond Lengths (Å) in Compound 2^a

	molecule A	molecule B
W(1)-W(1')	2.514 (1)	2.530 (1)
-Cl(1)	2.400 (3)	2.394 (3)
-Cl(2)	2.397 (3)	2.394 (3)
-O(1)	2.020 (7)	2.014 (7)
-O(1')	2.024 (7)	2.038 (7)
-O(2)	1.967 (7)	1.936 (7)
-O(3)	1.999 (7)	2.004 (7)
O(1)-C(1)	1.47 (1)	1.45 (1)
O(2)-C(4)	1.48 (1)	1.47 (1)
O(3)-C(7)	1.50 (1)	1.48 (1)
C(1)-C(2)	1.55 (2)	1.50 (2)
-C(3)	1.55 (2)	1.57 (2)
C(4)-C(5)	1.51 (2)	1.53 (2)
-C(6)	1.56 (2)	1.52 (2)
C(7)-C(8)	1.55 (2)	1.47 (2)
-C(9)	1.50 (2)	1.56 (2)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Table X. Table of Bond Angles (deg) in Compound 2^a

	molecule A	molecule B
W(1')-W(1)-Cl(1)	138.07 (8)	137.74 (9)
-Cl(2)	136.73 (8)	136.77 (9)
-O(1)	51.6 (2)	51.8 (2)
-O(1')	51.2 (2)	50.9 (2)
-O(2)	90.7 (2)	91.1 (2)
-O(3)	89.4 (2)	89.0 (2)
Cl(1)-W(1)-Cl(2)	85.2 (1)	85.3 (1)
-O(1)	170.3 (2)	170.1 (2)
-O(1')	86.6 (2)	86.9 (2)
-O(2)	90.2 (2)	91.4 (2)
-O(3)	89.0 (2)	88.3 (2)
Cl(2)-W(1)-O(1)	85.1 (2)	85.0 (2)
-O(1')	171.8 (2)	172.1 (2)
-O(2)	90.3 (2)	91.2 (2)
-O(3)	90.5 (2)	89.0 (2)
O(1)-W(1)-O(1')	103.1 (2)	102.7 (2)
-O(2)	90.6 (3)	91.2 (3)
-O(3)	90.4 (3)	89.2 (3)
O(1')-W(1)-O(2)	90.2 (3)	90.2 (3)
-O(3)	88.9 (3)	89.5 (3)
O(2)-W(1)-O(3)	178.8 (3)	179.6 (3)
W(1)-O(1)-W(1')	76.9 (2)	77.3 (2)
-C(1)	136.5 (7)	135.6 (7)
W(1)-O(1')-C(1)	146.5 (7)	146.7 (7)
W(1)-O(2)-C(4)	131.0 (6)	130.6 (7)
W(1)-O(3)-C(7)	134.5 (7)	134.3 (7)
O(1)-C(1)-C(2)	107 (1)	109 (1)
-C(3)	109 (1)	108 (1)
C(2)-C(1)-C(3)	115 (1)	113 (1)
O(2)-C(4)-C(5)	108 (1)	106 (1)
-C(6)	105 (1)	108 (1)
C(5)-C(4)-C(6)	115 (1)	113 (1)
O(3)-C(7)-C(8)	107 (1)	109 (1)
-C(9)	108 (1)	106 (1)
C(8)-C(7)-C(9)	117 (1)	115 (1)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Compound 2. Again, the structure contains two independent molecules, but now the only crystallographically imposed symmetry arises from the presence of an inversion center at the midpoint of each molecule. The two molecules are again labeled A and B and their structures are shown in Figure 4. The bond distances and angles are given in Tables IX and X, respectively. As in 1, the two independent molecules are similar, but in this case there are some statistically real differences, as comparison of the two columns in Table IX especially will indicate. Molecule A comes closer to having C_{2h} ($2/m$) symmetry than does B. Of particular

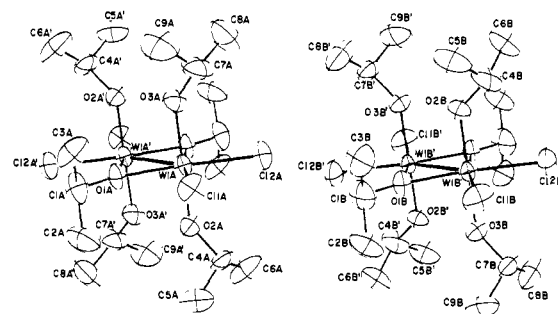


Figure 4. ORTEP drawings of the two independent molecules of compound 2, each of which has an inversion center. 50% probability ellipsoids are used.

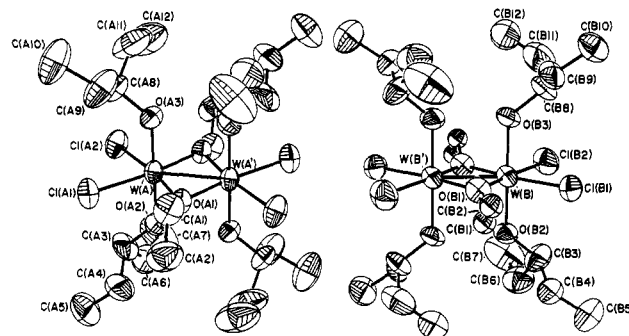


Figure 5. ORTEP drawings of the two independent molecules of compound 3, each of which has an inversion center. 50% probability ellipsoids are used.

Table XI. Bond Distances (Å) in Compound 3

atoms ^c	length ^a		
	X = A	X = B	average ^b
W(X)-W(X')	2.489 (1)	2.491 (1)	2.490 (1, 1, 1)
W(X)-Cl(X1)	2.383 (3)	2.388 (2)	2.385 (3, 2, 3)
W(X)-Cl(X2)	2.385 (3)	2.383 (4)	
W(X)-O(X1)	2.031 (6)	2.033 (7)	2.032 (7, 1, 1)
W(X)-O(X1')	2.022 (6)	2.020 (4)	2.021 (5, 1, 1)
W(X)-O(X2)	2.010 (4)	1.973 (6)	1.994 (5, 16, 21)
W(X)-O(X3)	1.983 (4)	2.008 (6)	
O(X1)-C(X1)	1.48 (2)	1.45 (2)	1.45 (2, 2, 3)
O(A1)-C(A1)*	1.42 (3)		
O(X2)-C(X3)	1.48 (1)	1.47 (1)	1.47 (1, 1, 2)
O(X3)-C(X8)	1.45 (1)	1.48 (1)	
C(X1)-C(X2)	1.43 (3)	1.34 (3)	1.41 (4, 5, 7)
C(A1)*-C(A2)*	1.47 (5)		
C(X3)-C(X4)	1.55 (2)	1.58 (2)	
C(X3)-C(X6)	1.61 (2)	1.57 (2)	
C(A3)-C(A6)*	1.64 (3)		
C(X4)-C(X5)	1.47 (2)	1.58 (2)	
C(X6)-C(X7)	1.26 (4)	1.41 (2)	1.50 (2, 8, 24)
C(A6)*-C(A7)	1.34 (4)		
C(X8)-C(X9)	1.54 (2)	1.50 (2)	
C(X8)-C(X11)	1.55 (2)	1.54 (2)	
C(X9)-C(X10)	1.58 (2)	1.53 (2)	
C(X11)-C(X12)	1.40 (3)	1.36 (2)	
C(A1)...C(A1)*	1.08 (2)		
C(A2)...C(A2)*	1.03 (5)		
C(A1)...C(A2)*	0.95 (7)		
C(A1)*...C(A2)	1.05 (4)		

^a The figure in parentheses following each value is the estimated standard deviation in the least significant digit.

^b The figures in parentheses following each average value are the root-mean-square value of the estimated standard deviation for an individual datum, the mean deviation, and the maximum deviation from the mean.

^c An asterisk indicates atoms of lower occupancy for the three disordered atoms.

interest are the two independent W-O_T distances in each molecule. In A the difference between the two is 0.032 (10) Å, which is at the threshold of being significant, while in B the difference is 0.068

(27) The estimated deviation in square brackets is calculated as $[] = [\sum \Delta_i / n(n-1)]^{1/2}$ in which Δ_i is the deviation of the i th (of n) value from the arithmetic mean of the n values.

Table XII. Bond Angles (deg) in Compound 3

atoms	angle ^a		
	X = A	X = B	average ^b
W(X')-W(X)-Cl(X1)	136.1 (1)	135.8 (1)	136.0 (1, 2, 2)
W(X')-W(X)-Cl(X2)	135.9 (1)	136.2 (1)	
W(X')-W(X)-O(X1)	51.9 (2)	52.3 (2)	52.1 (2, 3, 3)
W(X')-W(X)-O(X1')	52.3 (2)	51.8 (1)	
W(X')-W(X)-O(X2)	89.3 (2)	90.6 (2)	89.9 (2, 7, 8)
W(X')-W(X)-O(X3)	90.6 (2)	89.1 (2)	
Cl(X1)-W(X)-Cl(X2)	88.0 (1)	87.9 (1)	88.0 (1, 1, 1)
Cl(X1)-W(X)-O(X1)	172.0 (2)	171.8 (1)	171.8 (2, 1, 2)
Cl(X2)-W(X)-O(X1')	171.7 (2)	171.8 (1)	
Cl(X1)-W(X)-O(X1')	83.8 (2)	84.0 (1)	83.9 (2, 1, 1)
Cl(X2)-W(X)-O(X1)	84.0 (2)	83.9 (2)	
Cl(X1)-W(X)-O(X2)	89.5 (2)	90.1 (1)	
Cl(X1)-W(X)-O(X3)	90.8 (2)	90.0 (1)	90.1 (2, 5, 10)
Cl(X2)-W(X)-O(X2)	90.1 (2)	91.1 (2)	
Cl(X2)-W(X)-O(X3)	89.8 (2)	89.2 (2)	
O(X1)-W(X)-O(X1')	104.2 (2)	104.2 (2)	104.2 (2, 0, 0)
O(X1)-W(X)-O(X2)	90.3 (2)	90.3 (2)	
O(X1)-W(X)-O(X3)	89.4 (2)	89.5 (2)	89.9 (2, 6, 12)
O(X1')-W(X)-O(X2)	88.8 (2)	90.4 (3)	
O(X1')-W(X)-O(X3)	91.3 (2)	89.3 (3)	
O(X2)-W(X)-O(X3)	179.7 (2)	179.7 (3)	179.7 (3, 0, 0)
W(X)-O(X1)-W(X')	75.8 (2)	75.8 (2)	75.8 (2, 0, 0)
C(X1)-O(X1)-W(X)	135.7 (1)	135.6 (8)	
C(X1)-O(X1)-W(X')	137.8 (7)	134.7 (7)	136.4 (8, 14, 29)
C(A1)*-O(A1)-W(A)	135.7 (10)		
C(A1)*-O(A1)-W(A')	139.3 (11)		
O(X1)-C(X1)-C(X2)	112.6 (13)	115.4 (15)	112.9 (20, 17, 25)
O(A1)-C(A1)*-C(A2)*	110.6 (29)		
W(X)-O(X2)-C(X3)	130.7 (5)	129.9 (7)	130.2 (6, 6, 8)
W(X)-O(X3)-C(X8)	130.9 (5)	129.4 (5)	
O(X2)-C(X3)-C(X4)	106.4 (9)	106.0 (9)	
O(X2)-C(X3)-C(X6)	104.8 (11)	106.8 (7)	
O(X2)-C(A3)-C(A6)*	108.4 (13)		107.0 (9, 10, 22)
O(X3)-C(X8)-C(X9)	107.7 (9)	107.1 (10)	
O(X3)-C(X8)-C(X11)	106.8 (8)	108.8 (8)	
C(X4)-C(X3)-C(X6)	103.1 (11)	106.1 (10)	
C(A4)-C(X3)-C(X6)*	134.9 (11)		115.6 (10, 109, 19)
C(X9)-C(X8)-C(X11)	110.4 (9)	123.6 (11)	
C(X3)-C(X4)-C(X5)	112.0 (13)	110.9 (11)	
C(X3)-C(X6)-C(X7)	124.5 (16)	110.3 (13)	
C(X3)-C(A6)*-C(A7)	116.4 (20)		114.9 (14, 40, 9)
C(X8)-C(X9)-C(X10)	110.1 (11)	113.0 (11)	
C(X8)-C(X11)-C(X12)	120.2 (11)	116.7 (19)	

^a The figure in parentheses following each value is the estimated standard deviation in the least significant digit. ^b The figures in parentheses following each average value are the root-mean-square value of the estimated standard deviation for an individual datum, the mean deviation, and the maximum deviation from the mean.

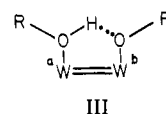
^c An asterisk indicates atoms of lower occupancy for the three disordered atoms.

(10) Å and this must be considered real.

Compound 3. Once again, the crystal is built of two crystallographically independent molecules. As in **2**, these reside on inversion centers and are very similar to each other. The two molecules are depicted in Figure 5 and the bond lengths and angles are listed in Tables XI and XII. In this case, the W-O_T distances in each molecule show small differences, 0.027 (6) Å in A and 0.035 (9) Å in B. These differences, about equal to 4σ, might be considered real, but there could be some reservation about this.

(F) Comparison and Interpretation of Structures. We have now a total of five compounds, spanning eight independent molecules and nine independent pairs of W-O_T distances, for which there are crystallographic data. This count includes the previously studied² W₂Cl₄(μ-OR)₂(OR)₂(ROH)₂, R = CH₃ and C₂H₅, compounds. In general the structures are very similar, as shown by the results assembled in Table XIII. The W-W bond lengths range from 2.481 (1) to 2.530 (1) Å, with an average value of 2.497 [6] Å.²⁷ Similarly, the W-Cl bond lengths range only from 2.374 (3) to 2.400 (3), with an average value of 2.389 [2] Å, and the W-O_B bond lengths range only from 2.014 (7) to 2.038 (7) Å with an average value of 2.026 [2] Å.

The important dissimilarities are in the W-O_T distances and how they vary within one molecule. This point can be discussed with reference to the moiety depicted in III. The distances marked a and b are given in Table XIII as items 4 and 3, respectively.



In the two previously reported structures, there were, statistically speaking, highly significant (7-9σ) differences between these distances, the values of a-b being 0.086 (8) and 0.058 (8) Å. These differences appeared (and still appear) to justify the stated conclusion² that the syn-axial ligands are distinctly nonequivalent, being ROH and RO⁻, albeit connected by a rather strong (O...O = ca. 2.48 Å) hydrogen bond. In view of the nonequivalence of the two W-O bonds, the hydrogen bond would naturally be assumed to be unsymmetrical. In these two compounds, as in all others with primary R groups, the hydrogen atom gives only a broad singlet in the NMR spectrum; for reasons stated earlier, this can most satisfactorily be explained by assuming that this hydrogen atom undergoes rapid exchange with ROH molecules, deliberately added or adventitiously present, in solution.

In the compounds whose structures are reported here, and in other compounds where the R groups of the axial ligands are secondary alkyl groups, the bridging hydrogen atoms give rise to triplets in the NMR and clearly remain within a given RO-H...OR unit for periods that are long on the NMR time scale. Moreover, they appear to be coupled equally to both R groups. The latter observation could, of course, be explained by a rapid hopping or tunnelling of this proton in an unsymmetrical (double-minimum) hydrogen bond. It is also consistent with a symmetrical hydrogen bond, but for this to be true, we should also expect the two W-O bonds to be equivalent (and hence of equal lengths).

For compound **1** the two W-O_T bonds are equivalent crystallographically and thus they necessarily refine to equal values. This, of course, is only the appearance given by an ensemble of molecules, each of which might have unequal bond lengths but with a random scrambling of the molecular orientations. A disordered array of molecules containing unequal bonds cannot be conclusively ruled out, but the inequality of the bond lengths would have to be small. While it is difficult to put an exact limit on the permissible difference, it can probably not exceed three times the esd, which means 0.018 and 0.024 Å for the two independent molecules in compound **1**. A difference of the order of 0.02 Å is of uncertain physical meaning, since vibrational amplitudes are considerably greater than this. Moreover, as inspection of Figure 3 will show, the shapes of the thermal ellipsoids for the O_T atoms show no elongation in the direction expected for a model in which W-O_T bonds of different lengths are disordered. We feel that in compound **1** all the units of type III are, in fact, symmetrical because they find themselves in environments that do nothing to break the symmetry.

In compounds **2** and **3**, there are differences between the a and b bonds, but with one exception they are small (ca. 0.03 Å) and barely significant statistically (3σ-4σ). The question that arises, but cannot be objectively answered, is whether these differences represent distortions imposed by an unsymmetrical environment on a system that tends inherently to be symmetrical.

(G) Are the Hydrogen Bonds Symmetrical? The general question of what conditions cause, or are at least conducive to, the formation of symmetrical hydrogen bonds has been debated for several decades, at least. It is now clear that there is no simple cause and effect relationship with shortness alone. It is doubtless true that there is some upper limit on the X to X distance in an X-H...X bond beyond which a centering of the proton will not be favored in any environment. There does not, however, seem to be any distance below which centering becomes mandatory, although the shorter bonds are more likely to be centered, or nearly so, provided the general environment is favorable. Thus, while some O...H...O bonds with distances of ca. 2.40 Å are nearly or exactly centric,²⁴ there is the classic case of the H₂O...H...OH₂⁺

Table XIII. Comparison of Internuclear Distances (Å) in All Structurally Characterized $W_2Cl_4(OR)_4(ROH)_2$ Molecules

	R = CH ₃	R = C ₂ H ₅	1		2		3	
			A	B	A	B	A	B
1 W-W	2.481 (1)	2.483 (1)	2.488 (1)	2.499 (1)	2.514 (1)	2.530 (1)	2.489 (1)	2.491 (1)
2 W-OR _B	2.032 (6)	2.021 (5)	2.023 (8)	2.034 (9)	2.020 (7)	2.014 (7)	2.031 (6)	2.033 (7)
	2.036 (6)	2.023 (6)			2.024 (7)	2.038 (7)	2.022 (6)	2.020 (4)
		2.030 (6)						
		2.015 (6)						
3 W-OR _T	1.950 (5)	1.968 (6)	1.987 (6)	1.995 (8)	1.967 (7)	1.936 (7)	1.983 (4)	1.973 (6)
		1.955 (6)						
4 W-O(H)R	2.036 (6)	2.016 (6)	1.987 (6)	1.995 (8)	1.999 (7)	2.004 (7)	2.010 (4)	2.008 (6)
		2.023 (5)						
4-3 ^a	0.086 (8)	0.058 (8)	0	0	0.032 (10)	0.068 (10)	0.027 (6)	0.035 (9)
5 O _T ...O _T	2.483 (7)	2.488 (8)	2.473 (7)	2.524 (12)	2.516 (9)	2.533 (10)		
		2.489 (7)						
6 W-Cl	2.382 (2)	2.391 (2)	2.395 (3)	2.374 (3)	2.400 (3)	2.394 (3)	2.383 (3)	2.388 (2)
	2.389 (2)	2.389 (3)			2.397 (3)	2.394 (3)	2.385 (3)	2.383 (4)
		2.387 (3)						
		2.391 (3)						

^a The W-O(H)R bond length minus the W-OR_T bond length.

ion in sulfosalicylic acid trihydrate that has O...O = 2.436 Å but is very unsymmetric, with O-H distances of 1.095 and 1.341 Å.²⁴

The case of the HF₂⁻ ion is also instructive. Although this shortest of hydrogen bonds (F...F = 2.26 Å) probably has a great tendency to be symmetric and is so in a number of compounds, such as KHF₂, in the *p*-toluidinium compound, it is quite unsymmetrical, with F...H distances of 1.025 and 1.235 Å, evidently because it resides in a very unsymmetrical environment.²⁵ From this and similar results there emerges the Williams proposal²⁵ that "regardless of the 'shortness' of the X...X bond in the (X-H-X)⁺ moiety the molecular geometry of the hydrogen bond is strongly dependent on the near-neighbor environment."

In the compounds we are describing in this and our earlier paper we appear to be dealing with an even more complex situation, in which *the geometry of the hydrogen bond and that of its near-neighbor environment are interdependent, rather than the former being simply dictated by the latter*. We believe that when the two W-O bonds are the same length, the proton must reside at a position equidistant from both oxygen atoms, whereas, the more unequal are two W-O bonds, the more closely the proton will approach the oxygen atom making the longer bond to the metal atom, thus creating more of an RO-H...OR situation.

Since in no case have we been able to observe the position of the hydrogen atom, the foregoing statements remain in need of direct experimental proof. Without doubt, the best possible evidence as to their correctness would be provided by a neutron diffraction study. Efforts are therefore being made to grow suitably large crystals.

Even if, as we expect, our postulate of the interrelationship between the equality of the W-O bonds on the one hand and the symmetry of the hydrogen bond on the other is confirmed, there remains the interesting question of causality. Why does the whole ROHOR bridging system, including the W-O bonds change from symmetric, or nearly symmetric in some cases (those reported here) to distinctly unsymmetric in others (those previously reported)? Presumably the two arrangements have approximately equal stability, and only the slightest variations of the packing forces exerted by their surroundings can thus determine which arrangement would prevail.

Conclusions. While some uncertainties remain, the following statements summarize what we believe are the key features of the behavior of the syn-axial ligand pairs in the $W_2Cl_4(OR)_4(ROH)_2$ molecules.

(1) In all cases the hydrogen bonds are short and strong.

(2) The energy difference between a slightly unsymmetrical and truly symmetrical arrangement is in each case small enough that packing forces in the crystalline compounds might dictate which structure is adopted. In the case of compound 1, it seems that the symmetrical environment of the molecule has in fact stabilized a symmetrical hydrogen bond.

(3) In the absence of exchange with external hydrogen atoms, the bridging hydrogen atoms in an unsymmetrical hydrogen bond oscillate rapidly between the two minima, thus making this case indistinguishable by NMR from the case of a truly symmetrical hydrogen bond.

(4) The principal effect of changing from primary to secondary R groups on the solution behavior is that the latter provide so much steric encumbrance that proton exchange with external molecules becomes too slow to affect the appearance of the NMR spectra.

(5) We may finally note that systems formally similar to those examined here also occur, perhaps more widely, in organic compounds.²⁶ In these cases it is equally difficult to establish with certainty by experimental means the most stable configuration, but because of the greater feasibility of ab initio calculations in these light-atom systems, there is a greater opportunity for theoretical work.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE-79-09233) at Purdue University and the Robert A. Welch Foundation (No. A-494) at Texas A&M University is gratefully acknowledged.

Registry No. 1, 85202-62-6; 2, 85202-63-7; 3, 85202-64-8; $W_2Cl_4(\mu-OEt)_2(OEt)_2(EtOH)_2$, 78350-74-0; $W_2Cl_4(\mu-OEt)_2(OEt)_4$, 12389-29-6; $W_2Cl_4(\mu-O-n-Pr)_2(O-n-Pr)_2(n-PrOH)_2$, 83801-94-9; $W_2Cl_4(\mu-O-n-Pr)_2(O-n-Pr)_4$, 85202-65-9; $W_2Cl_4(\mu-O-n-Bu)_2(O-n-Bu)_2(n-BuOH)_2$, 85202-66-0; $W_2Cl_4(\mu-O-n-Bu)_2(O-n-Bu)_4$, 85202-67-1; $W_2Cl_4(\mu-O-n-Pent)_2(O-n-Pent)_2(n-PentOH)_2$, 85202-68-2; $W_2Cl_4(\mu-O-n-Pent)_2(O-n-Pent)_4$, 85202-69-3; $W_2Cl_4(\mu-O-n-Oct)_2(O-n-Oct)_2(n-OctOH)_2$, 85220-64-0; $W_2Cl_4(\mu-O-n-Oct)_2(O-n-Oct)_4$, 85220-65-1; $W_2Cl_4(\mu-O-i-Pr)_2(O-i-Pr)_4$, 85202-70-6; $W_2Cl_4(\mu-O-i-Bu)_2(O-i-Bu)_2(i-BuOH)_2$, 85220-66-2; $W_2Cl_4(\mu-O-i-Bu)_2(O-i-Bu)_4$, 85202-71-7; $W_2Cl_4(\mu-OEt)_2(O-i-Pr)_4$, 85202-72-8; $W_2Cl_4(\mu-OEt)_2(O-sec-Bu)_2(sec-BuOH)_2$, 85202-73-9; $W_2Cl_4(\mu-OEt)_2(O-sec-Bu)_4$, 85202-74-0; $W_2Cl_4(\mu-OEt)_2(O-sec-Pent)_4$, 85202-75-1; $W_2Cl_4(\mu-OMe)_2(OMe)_4$, 85202-76-2; W, 7440-33-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors for the three structures (63 pages). Ordering information is given on any current masthead page.