THE PREPARATION AND CHARACTERIZATION OF SOME TUNGSTEN (IV) AND TUNGSTEN (V) COMPLEXES

Thesis for the Degree of Ph. D.
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WILLIAM JOSEPH REAGAN
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THESIS

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THE PREPARATION AND CHARACTERIZATION OF SOME TUNGSTEN(IV) AND TUNGSTEN(V) COMPLEXES

presented by

William Joseph Reagan

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chem.

Carl H. Brubaker, Jr.
Major professor

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ABSTRACT

THE PREPARATION AND CHARACTERIZATION OF SOME TUNGSTEN(IV) AND TUNGSTEN(V) COMPLEXES

By

William Joseph Reagan

The reaction of WCl_5 with alcohols was investigated. The alcohol solutions were neutral, acidic (with HCl) and basic (with alkoxide ion). Light green tetrachlorodialkoxotungstate(V) and yellow pentachloroalkoxotungstate(V) complexes were prepared and characterized. The alkoxide group was methoxo and ethoxo and the cation was pyridinium and triethylammonium. Several new W(V) thiocyanate complexes, including $(C_2H_5)_4NW(NCS)Cl_5$ and $(C_2H_5)_4NW(NCS)(OC_2H_5)Cl_4$, were also isolated in this study.

The compounds exhibited normal field independent paramagnetism. The effective magnetic moments of the W(V) complexes varied as the spacing of the e and b_2 orbitals changed.

The esr and far ir spectra of these W(V) monomers indicated that the compounds possessed axial symmetry. The electronic transitions for these compounds were assigned on the basis of D_{4h} symmetry (<u>trans</u> configuration) for dialkoxide complexes and C_{4v} symmetry for the thiocyanate complexes.

William Joseph Reagan

The diamagnetic compounds, $W_2Cl_4(OR)_6$ and $W_2Cl_2(OR)_8$, R = C_2H_5, 1-C_3H_7, were isolated from basic alcohol solutions of WCl_5. A red black liquid, $W(OC_2H_5)_5$ and a yellow, paramagnetic solid, $NaW(OC_2H_5)_6$ were also prepared from basic ethanol solutions of WCl_5.

The reaction of WCl_4 with alcohols was also studied. Green, diamagnetic complexes, $W_2Cl_4(OR)_4(ROH)_2$, R = CH_3, C_2H_5, 1-C_3H_7, 2-C_3H_7, were obtained. These compounds were the only thermally stable W(IV) compounds prepared in this work. The black compound, $W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$ decomposed slowly and $W(OC_2H_5)_4$ could not be isolated.

The formulation of these W(V) and W(IV) compounds as dimers is supported by mass spectra and molecular weight determinations. A chloride bridged bioctahedral structure for the chloride alkoxide compounds is suggested by their diamagnetism and far ir and pmr spectra. The diamagnetism of $W(OC_2H_5)_5$ may indicate a dimeric or polymeric structure. Low temperature pmr studies of this compound could not distinguish between these possibilities.

Attempts to prepare molybdenum(V) thiocyanate and molybdenum(IV) chloride alkoxide complexes were unsuccessful.

THE PREPARATION AND CHARACTERIZATION OF SOME TUNGSTEN(IV) AND TUNGSTEN(V) COMPLEXES

By

William Joseph Reagan

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To Claudette

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INTRODUCTION

Interest in the coordination chemistry of tungsten has increased significantly in the last ten years. This activity is related to the importance of industrial tungsten chemicals and the renewed study of the heavy transition metals.

A recent review of the inorganic chemistry of tungsten[1] has emphasized its wide diversity. Examples of tungsten compounds range from the simple, octahedral $W(CO)_6$ to complex heteropolytungstates. The oxidation states of tungsten range from -2 to +6. Compounds containing the element in the higher oxidation states (+5,+6) are more numerous and more stable.

The properties of the various chlorides of tungsten are related to their molecular structures. Tungsten hexachloride, a blue black hygroscopic solid, is a monomer in the solid state[2] and in solution. A single crystal X-ray analysis[3] of tungsten pentachloride (a black, paramagnetic solid) has shown it to be isomorphous with molybdenum pentachloride. The molybdenum compound is a chloride-bridged dimer in the solid state[4] and a monomer in the vapor phase.[5] Black, diamagnetic tungsten tetrachloride is isomorphous with the corresponding tetrahalides of niobium

and tantalum.[6] NbI_4[7] has a structure of infinite chains of NbI_6 octahedra joined by chloride bridges and short metal-metal distances. The diamagnetism of WCl_4 is probably the result of similar metal-metal interactions.

The relative unreactivity of WCl_4 is a measure of the strength of its three dimensional ionic lattice structure. Most W(IV) compounds are prepared by reduction of the higher halides rather than by direct reaction with WCl_4. In contrast to this behavior, WCl_5 and WCl_6 have been used as starting reagents in a wide variety of chemical reactions.

Most of the experimental and theoretical work in the field has centered on the oxyhalide complexes, $MOX_5^=$, M = Mo, W; X = Cl^-, Br^-, I^-, SCN^-. Electron spin resonance, optical and infrared spectroscopic studies have been reported. (See Part II, Historical). Metal alkoxides, $M(OR)_xCl_{5-x}$, should provide a means of studying compounds without the M=O group being present. Since oxothiocyanato tungsten compounds have been prepared, mixed alkoxo-thiocyanato complexes would also be of interest. A comparison of the physical and chemical properties of oxo, alkoxo and alkoxo-thiocyanato compounds would provide information about metal-ligand interactions. Analogies to other systems could then be made. For this reason, an intensive study of the WCl_5-alcohol and WCl_5-thiocyanate reactions was considered worthwhile.

The effects of a change in oxidation state upon these alkoxide complexes could be investigated. WCl_4 is readily

prepared by a modification of the synthesis of WCl_5. The direct reaction of WCl_4 with alcohols has not been reported. Alkoxide complexes of W(IV) should be stable to disproportionation by analogy to other W(IV) compounds.

Monomeric complexes of the type, $W(OR)_nCl^-_{6-n}$ with $n > 2$ are unknown. A possible source of these anions could be the dimers, $[W(OR)_xCl_{5-x}]_2$, which are formed in basic (with alkoxide ion) alcohol solutions. The study of the reactions and properties of these dimers has been neglected. Since these compounds are diamagnetic, pmr spectroscopy can be used to study the orientation and reactivity of the alkoxide ligands. A far infrared analysis may clarify the nature of the bridging groups in these dimers. Recent ir studies[8] have shown that in $CoCl_2(Y)_2$ polymers, the Co-Cl bridging frequency is about 50 cm^{-1} below the terminal Co-Cl vibration.

HISTORICAL

Tungsten has been studied since the characterization of tungstic acid by Woulffe (1779) and Scheele (1781). The early workers of the twentieth century extended the solution chemistry of tungsten by the preparation of anionic halide and cyanide complexes. Compounds of the lower oxidation states were unknown until the discovery of the hexacarbonyl (1928) and cyclopentadienyl (1954) complexes. Most of the modern (post 1930) tungsten chemistry was concerned almost entirely with the lower oxidation states. With the more extensive use of non-aqueous solvents some interest is now being shown in anhydrous complexes of the higher halides. This latter area will be reviewed in this section.

One of the most important reactions of the tungsten halides is the abstraction of oxygen from solvents which contain oxygen or O-H groups. Oxo compounds, containing a metal oxygen double bond, are generally formed in this process. Oxygen abstraction occurred in the reaction of WCl_5 with acetone, tetrahydrofuran and dioxane.[9] Similar behavior has been observed for $MoCl_5$.[10-12]

Tungsten(V) and molybdenum(V) oxo compounds, $MOX_5^{=}$, $X = Cl^-$, Br^-, I^-, SCN^-, have been well characterized.[11-12] The metal halides are generally dissolved in concentrated

aqueous HX solutions. The addition of cations such as, Na^+, K^+, Cs^+ or NH_4^+ cause precipitation of solid $M_2'MOX_5$ complexes.[13-14] The electronic and magnetic properties of these compounds have been studied extensively.

There are few examples of analogous quadrivalent complexes. A compound originally formulated[15] as $K_2W(OH)Cl_5$ was prepared by the reduction of tungsten trioxide in concentrated HCl. More recently, this compound has been shown to be an oxygen bridged dimer, $K_4W_2OCl_{10}$.[16-17]

The magnetic properties of the $MOX_5^=$, M = Mo, W, complexes[11] are consistent with the presence of one d electron. Magnetic moments of the molybdenum complexes are close to the spin-only value. However, the tungsten compounds have lower moments (1.30-1.55 B.M.) which indicate some contribution from spin-orbit coupling. The magnetic moment and esr data for $K_4W_2OCl_{10}$[16] have been explained in terms of two unpaired electrons on each tungsten atom. König[17] has postulated that this compound is a W(III)-W(V) mixed valence compound.

Electron spin resonance studies of these oxo compounds have been reported.[18-29] The characteristic metal or ligand hyperfine structure has been observed in several cases.[25-29]

The electronic and charge transfer spectra of $MoOCl_5^=$ was first studied by Gray and Hare.[30] These workers based their assignments on the molecular orbital scheme of Ballhausen and Gray,[31] which successfully explained the long wavelength transitions of $[VO(H_2O)_5]^{2+}$. The two ligand

field bands of $MoOCl_5^=$ at ~14,000 cm^{-1} and ~22,000 cm^{-1} were assigned to the transitions, $B_2 \longrightarrow E$ and $B_2 \longrightarrow B_1$. The charge transfer bands were assigned as follows: 28.0 x 10^3 cm^{-1}, $B_2 \longrightarrow E(II)$; 32.3 x 10^3 cm^{-1}, $B_2 \longrightarrow B_2(I)$; and 40.0 x 10^3 cm^{-1}, $B_2 \longrightarrow E(III)$. These assignments were based on the assumption that charge transfer occurred primarily between the bonding metal-oxygen π-orbital and the metal nonbonding or antibonding orbitals. This work did not adequately explain certain experimental facts. For $MOX_5^=$ complexes, a change from Cl to Br ligands caused a large shift (6000-7000 cm^{-1}) in the low energy charge transfer band. Other workers[11,19] have pointed out that metal-halogen π-bonding must be considered to explain these data. Recent esr studies of the complexes[27,28] have confirmed the presence of significant metal-halogen π-bonding.

The far infrared spectra of a number of these oxo complexes have been measured. Sabatini and Bertini[32] assigned the vibrations of $MOX_5^=$ species on the basis of C_{4v} symmetry. $4A_1$ and 4E modes are infrared active. The A_1 modes are two M-X vibrations, one M-O stretch and O-M-X and X-M-X deformations. The E modes include pairs of M-X stretching, X-M-X and O-M-X bending vibrations.

Under strictly anhydrous conditions, many hydrolytically unstable, nonoxo complexes of the tungsten halides have been prepared.

Solutions of WCl_6 or $MoCl_5$ in acetone or similar solvents react with the thiocyanate ion to give substituted products, $W(NCS)_6$ and $Mo(NCS)_5$.[33] These compounds were only isolated with at least two solvent molecules attached, as in $W(NCS)_6 \cdot 2(CH_3)_2CO$. Anionic complexes of niobium(V) and tantalum(V), $M(NCS)_6^-$ have been isolated recently.[34-37] Infrared spectra of these complexes indicate the presence of N-bonded thiocyanates. The corresponding molybdenum or tungsten derivatives are unknown.

Certain solvents, such as pyridine and acetonitrile, cause reduction of W(V) or W(VI) chlorides and bromides. Either WCl_6 or WCl_5 reacts with refluxing pyridine to form complexes of the type $WCl_4(py)_2$ (py = pyridine).[6] The reaction proceeds with the formation of the 1-(4-pyridyl)-pyridinium ion. Prolonged contact of these reagents leads to the formation of $WCl_3(py)_2$.[38] The compounds, $WCl_4(RCN)_2$;[39] R = CH_3, C_2H_5, C_3H_7, have been prepared by the reaction of the higher tungsten halides with anhydrous nitriles.

The magnetic moments of the compounds, WCl_4L_2 are lower than predicted for W(IV) (d^2) complexes: $WCl_4(py)_2$,[5] 1.60 B.M., $WCl_4(CH_3CN)_2$,[39] 1.78 B.M.. A molecular weight measurement was obtained only for the propyl cyanide derivative. It was monomeric in benzene. The observation[39] of two C ≡ N and two M-Cl stretching frequencies for $MoCl_4(CH_3CN)_2$ may be an indication of a <u>cis</u> octahedral configuration.

Under mild conditions, reduction of WCl_6 by nitrogen containing ligands proceeds only to the +5 state. Greenwood et al.[40,41] have isolated the complexes, WCl_5L_2, L = pyridine, 2,2'-bipyridine and 1,2-bis(diphenylphosphinoethane) from the reaction of WCl_6 and the ligand in carbon tetrachloride. Brown and Ruble[42] prepared similar products by the reaction of WCl_6, WCl_5 and WBr_5 with 2,4,6-trimethylpyridine and benzonitrile in methylene chloride. Conductivity data indicated that these compounds should be formulated as $[WX_4L_2]^+X^-$.

The magnetic moments of the WX_5L_2 complexes are in the range of other W(V) compounds. The absorption bands of these species in the visible region, usually assigned as d-d transitions, have abnormally high molar absorptivities (200 $M^{-1}cm^{-1}$). No esr data have been reported.

The preparation of several complexes of W(III) and W(IV) by the reaction of $WCl_4(CH_3CN)_2$ and 1,2-bis(diphenylphosphinoethane)(diphos) has been reported.[43] The compounds were formulated as $[WCl_3(diphos)]_2$, $[WCl_3(diphos)_2]$, and $[WCl_2(diphos)_2]^+Cl^-$. Strong bands at 244 and 258 cm^{-1} in the far infrared spectrum of the dimer were assigned to bridging chlorine vibrations.

A variety of complexes were prepared by the reaction of the tungsten halides with aliphatic amines. The reaction of secondary and tertiary amines with WCl_6 formed complexes of the type, $(NH_2R_2)_2WCl_6$ and $(NHR_3)_2WCl_6$.[44] The W(V) complexes $WCl_2(NHR)_3$ were obtained when WCl_5 was allowed to react with primary amines.

The hexahalo derivatives are known for both W(V) and W(IV). As indicated above, $WCl_6^=$ salts were formed by the reaction of WCl_6 with secondary and tertiary amines. The interaction of WCl_6 with alkali-metal halides under dry conditions at 130^0 yielded the complex chlorides, M_2WCl_6, M = K, Rb, Cs, Tl.[46] Various procedures have been used to prepare the hexachlorotungstate(V) complexes. The reaction of WCl_5 with alkali metal chlorides in chlorobenzene formed $MWCl_6$.[47] Thionyl chloride reduced WCl_6 to WCl_6^-. The addition of tetraalkylammonium chloride to this solution precipitated the complex, R_4NWCl_6.[48]

The magnetic moments of these hexachloro complexes are lower than the predicted spin-only values. The compound $(C_2H_5)_4NWCl_6$ has a room temperature magnetic moment of 0.66 B.M.[49] Anti-ferromagnetism is indicated by a Neèl temperature of 140^0K. The magnetic moment of K_2WCl_6 is reported[46] as 1.43 B.M. A high θ value (190^0K) also suggests anti-ferromagnetic behavior.

The metal-chloride stretching frequency of these compounds has been measured. In $(C_2H_5)_4NWCl_6$, the W-Cl stretch is at 329 cm^{-1}.[48] Cs_2WCl_6 has a similar absorption at 308 cm^{-1}.[49] The M-Cl stretching frequency is lowered by about 25 cm^{-1} upon changing the metal oxidation state from +5 to +4. The same trend was observed for Nb and Ta hexahalo complexes.[50]

An unusual W(IV) compound with 8-Hydroxyquinoline as a ligand has recently been prepared. Tetrakis(8-quinolinolato)tungsten(IV)[51] was isolated from the products of a

sealed-tube reaction between $(NH_4)_3W_2Cl_9$ and 8-quinolinol. This compound is believed to be the first completely chelated eight-coordinate complex of tungsten.

The metal halide alcohol systems are also of interest. Under moderate conditions, metal alkoxides, $M(OR)_x$, free of oxo impurities, can be isolated. Bradley[52] and his co-workers have investigated the alkoxide chemistry of many transition metals. These complexes are generally polymers. $Ti(OC_2H_5)_4$ is trimeric in the solid state.[53] Heavy transition metal alkoxides are usually dimers. An edge-shared bioctahedral structure has been proposed[54] for $[M(OR)_5]_2$, M = Nb, Ta; R = CH_3, C_2H_5.

Yellow solutions of WCl_6 in alcohols have been known for many years. A green product, $W_2Cl_4(OC_2H_5)_6$[55,56] was reportedly formed by the reduction of W(VI) ethanol solutions. Klejnot[57] reexamined this system and found that reduction took place. He isolated two blue, paramagnetic chloride alkoxides, $W(OR)_2Cl_3$, R = CH_3, C_2H_5. A red, diamagnetic dimer, $[W(OC_2H_5)_3Cl_2]_2$ was isolated after prolonged treatment of $W(OC_2H_5)_2Cl_3$ with ethanol. A chloride-bridged, bioctahedral structure for the dimer was postulated on the basis of pmr spectra and dipole moment data.

Compounds of the type $WO(OR)_4$[58] have been prepared by the reaction of $WOCl_4$ with ammonia in alcohol. The reaction of WBr_5 with phenol and methanol was studied.[59] The compounds, $W(OPh)_2Br_3$ and $W(OPh)_3Br_2 \cdot PhOH$, Ph = C_6H_5, were prepared but no methoxide complexes were isolated.

The reaction of $MoCl_5$ and WCl_5 with methanol has been investigated. Funk and co-workers[60-62] isolated similar products in each case. At temperatures below -10^0, a green solvate, $M(OCH_3)_2Cl_3 \cdot 3CH_3OH$, was isolated. The addition of pyridine or pyridinium chloride to the reaction solution of the pentahalides in methanol precipitated the yellow-green $(py)M(OCH_3)_2Cl_4$. The compound $[M(OCH_3)_3Cl_2]_2$ was obtained when a methanol solution of $(py)M(OCH_3)_2Cl_4$ was made basic with pyridine. Another dimer, $[M(OCH_3)_4Cl]_2$ was isolated when pyridine was added to the reaction solution of MCl_5 and methanol. In excess pyridine, the W(V) chloride alkoxides were reduced to a W(IV) compound, $W(OCH_3)_2Cl_2 \cdot 2C_5H_5N$.

Under certain conditions, both $MoCl_5$ and WCl_5 formed oxo compounds in methanol. The complex, $(py)_2WOCl_5$ was obtained by the addition of pyridinium chloride to a hot solution of WCl_5 in methanol. An attempt[61] to prepare $Mo(OCH_3)_5$ resulted in the formation of an oxo-alkoxo complex, $MoO(OCH_3)_3 \cdot \frac{1}{2}CH_3OH$. In alcohol solution, this decomposition proceeds with the formation of dimethylether:

$$Mo(OCH_3)_5 \longrightarrow MoO(OCH_3)_3 + (CH_3)_2O.$$

In most cases, only the preparations and elemental analyses of these compounds were reported. The magnetic moments of $(py)W(OCH_3)_2Cl_4$ and $(py)_2WOCl_5$ were reported[62] as 1.48 and 1.52 B.M., respectively.

McClung et al.[63] reexamined the $MoCl_5$-alcohol system. The compounds, $(py)Mo(OCH_3)_2Cl_4$, $C_9H_8NMo(OCH_3)_2Cl_4$,

$[(CH_3)_4N]Mo(OCH_3)_2Cl_4$ and $(py)Mo(OC_2H_5)_2Cl_4$, were prepared and characterized. The methoxide complexes were prepared by a variation of Funk's original procedure.[61] Methanol was slowly added to $MoCl_5$, which was cooled to -78^0. A methanol solution of the appropriate cation was added and the yellow-green tetrachlorodialkoxomolybdate(V) salts were formed. The ethoxide derivative was prepared by alkoxide exchange of $(py)Mo(OCH_3)_2Cl_4$ in ethanol. Several attempts to prepare a chloropentamethoxomolybdate(V) salt or other ethoxo complexes were unsuccessful.

The magnetic properties and visible, uv, ir and esr spectra of these complexes were measured. The room temperature magnetic moments were close to the spin-only value. The visible and uv spectra were measured and the transitions were qualitatively assigned by analogy to the results for the $MoOCl_5^=$ ion. The d-d transitions were the $B_2 \longrightarrow E$ at 14,000 cm^{-1} and the $B_2 \longrightarrow B_1$ at 23,000 cm^{-1}. The third ligand field band required by D_{4h} or C_{4v} symmetry, $B_2 \longrightarrow A_1$, was apparently masked by the intense charge transfer bands. The esr spectra of the solid compounds or of the frozen solutions of these complexes were resolved into $g_{||}$ and $g_{\perp}$ values. On this basis, the <u>trans</u> isomer (axial symmetry) was required.

Clark and Wentworth[64] reported that yellow-green, diamagnetic complexes, $W_2Cl_4(OR)_2(ROH)_4$, R = CH_3, C_2H_5, 1-C_3H_7, were formed by the reaction of $[(\underline{n}\text{-}C_4H_9)_4N]_3W_2Cl_9$ with refluxing alcohol. The ir and pmr spectra of the ethoxoethanol

complex were similar to the data for Klejnot's dimer, $W_2Cl_4(OC_2H_5)_6$.[57] No conclusion as to the nature of the bridging group in these W(III) dimers was made.

EXPERIMENTAL

A. Preparation and Standardization of Analytical Reagents

Silver Nitrate:- A 16.98 g sample of reagent grade silver nitrate was dissolved in 1 liter of distilled water. The concentration (0.1N) of this solution was determined by titration with a standard sodium chloride solution.

Potassium Dichromate:- To prepare a solution of about 1.0N potassium dichromate, 49.03 g of dried reagent grade potassium dichromate was dissolved in water and diluted to one liter. The concentration of this solution was determined by an indirect method. An aliquot of the dichromate solution was added to an aqueous solution of excess potassium iodide. The iodine that was generated was then titrated with standard sodium thiosulfate solution. Starch solution served as the indicator.

Sodium Thiosulfate:- A 0.1N sodium thiosulfate solution was prepared by diluting Fisher Scientific Co.'s analytical grade "concentrated" sodium thiosulfate solution.

Cerium Sulfate:- A 0.1N cerium(IV) sulfate solution was prepared from Fisher Scientific Co.'s reagent grade cerium(IV) sulfate solution. The concentration of this

solution was checked by titration with standard ferrous ammonium sulfate solution. Ferroin was used as the indicator.

Ferrous Ammonium Sulfate:- A 0.1N ferrous ammonium sulfate solution was prepared by diluting a Fisher Scientific Co.'s analytical grade "concentrated" ferrous ammonium sulfate solution.

B. Materials

Tungsten Hexachloride:- A commercial grade (Climax Molybdenum Co.) of WCl_6 was purified by repeated sublimation under vacuum.

Analysis Calculated for WCl_6: W, 46.36; Cl, 53.64.
Found: W, 46.47; Cl, 53.74.

Tungsten Pentachloride:- Tungsten pentachloride was prepared by the red phosphorus reduction of WCl_6.[65] The product was purified by vacuum sublimation.

Analysis Calculated for WCl_5: W, 50.91; Cl, 49.09.
Found: W, 50.70.

Tungsten Tetrachloride:- Tungsten tetrachloride was also prepared by the red phosphorus reduction of WCl_6.[65] Slightly less than the stoichiometric amount of phosphorus was used to prevent the formation of lower tungsten halides. WCl_4 was obtained as a grey-black solid. The compound was not volatile and could not be purified. Some preparations were contaminated with small amounts of unreacted phosphorus.

Analysis Calculated for WCl_4: W, 56.45; Cl, 43.54.

Found: W, 55.70; Cl, 43.10.

Molybdenum Pentachloride:- Molybdenum pentachloride was obtained from Climax Molybdenum Co. It was purified by fractional sublimation.

Molybdenum Tetrachloride:- Molybdenum tetrachloride was prepared according to the procedure of Larsen and Moore.[66]

Solvents:- Pyridine and triethylamine were dried by distillation in the presence of barium oxide. Ethyl ether was stored over sodium metal. Chloroform, methylene chloride and carbon tetrachloride were dried by distillation in the presence of phosphorus pentoxide.

Methanol was dried by distillation in the presence of magnesium turnings.[67] Ethanol was dried by distillation in the presence of sodium ethoxide and diethylphthalate.[68] 1-Propanol and 2-propanol were dried by distillation in the presence of sodium.

Tetraethylammonium Chloride:- This material was Eastman Organic Chemicals white label grade. It was dried at 110° for 8 hours.

Nitrogen and Hydrogen Chloride:- Prepurified nitrogen (Liquid Carbonic Co.) was used after being passed through a system to remove residual oxygen and water. Copper turnings heated to 600° and B.T.S. catalyst (Badische Anilin und

Soda-Fabrik AG) served to remove oxygen. Drying towers containing Drierite and calcium chloride served for removal of water. Gaseous HCl was the Matheson Co.'s anhydrous material.

C. Analytical Methods

Ethoxide Determination:- Ethanol or ethoxide was determined by the potassium dichromate oxidation method.[69] A weighed sample of the compound was added to a known excess of acidic ($\sim 15\%$ H_2SO_4) dichromate solution. The mixture was allowed to boil until the tungsten was converted to yellow tungstic acid. Tungsten was oxidized from W(V) or W(IV) to W(VI) at the same time the alcohol was oxidized. An aliquot of the excess dichromate was then treated with an aqueous potassium iodide solution. The iodine that was formed was then titrated with standard sodium thiosulfate solution. A starch indicator was used.

Oxidation State Determination:- Samples were hydrolyzed in dilute ammonia and then acidified with sulfuric acid. Excess Ce(IV) sulfate solution was added and the mixture was stirred for 12 hours. 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 the ethanol content was also known from elemental analysis, the

reducing equivalents of the tungsten present could be determined by subtracting the equivalents of ethanol from the total number of equivalents found in the dichromate analysis.

Tungsten and Chloride Analyses:- A weighed sample of the compound was hydrolyzed in dilute ammonia and then oxidized with hydrogen peroxide. The solution was digested on a steam bath for one hour. The clear solution was then cooled and diluted in a volumetric flask. Separate portions were used for the tungsten and chloride analyses.

An aliquot of the tungstate solution was added to a 400 ml beaker. A large excess (10 ml) of a solution of 4 g of 8-hydroxyquinoline in 100 ml of absolute ethanol was added. The solution was allowed to boil and tungsten was precipitated by the addition of acetic acid. The yellow precipitate was collected on a pre-weighed extra-fine porcelain filter crucible, washed with hot water and dried at 110^0. The amount of tungsten present was calculated from the weight of the oxinate complex, $WO_2(C_9H_6OH)_2$.[70]

The chloride concentration of an acidified portion of the solution was determined by a potentiometric titration with standard silver nitrate solution. A Beckman model G pH meter and silver-silver chloride electrodes were used for the titration.

Molybdenum Analysis:- Molybdenum was determined by the same procedure as tungsten.

Carbon, Nitrogen, Hydrogen and Sulfur Analyses:- These analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Molecular Weight Determinations:- The cryoscopic technique was used to determine the molecular weights of compounds in benzene solutions. These analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

D. Apparatus and Experimental Techniques

A dry-box was used for opening sealed reaction tubes and for weighing and storing starting materials and compounds.

All the other operations were carried out under a dry nitrogen atmosphere or under vacuum. The "Schlenk tube" technique, recently outlined by Herzog,[71] was used in this work.

Reaction vessels were 100 and 250 ml round bottom Pyrex flasks. Glass tubes fitted with fritted glass discs were used for filtrations. Both types of apparatus were equipped with ground glass joints and sidearm stopcocks. Nitrogen was forced through the sidearm when the flask was opened to provide an inert atmosphere. Clean glassware, which was dried at 110^0, was cooled under vacuum and then filled with nitrogen.

Solvents were allowed to reflux under nitrogen until needed. The collection vessel was designed by D. P. Rillema.[72] Liquids were transferred with a dry pipet under a strong nitrogen flow.

E. Preparation of Compounds

Pyridinium Pentachlorooxotungstate(V):- A 5.0 g sample of WCl_5 (0.0138 mol) was added to 15 ml of 2-propanol which was cooled to -15^0. The solution became blue. The suspension was saturated with HCl at 0^0. After one hour, an isopropanol solution of pyridinium chloride (0.014 mol) was added to the mixture. A light blue solid separated from the solution. The compound was filtered, washed with ether and a small amount of thionyl chloride and dried under vacuum.

Analysis Calculated for $(C_5H_6N)_2WOCl_5$: W, 34.23; Cl, 33.00; C, 22.35; H, 2.25; N, 5.21.

Found: W, 34.06; Cl, 33.00; C, 22.27; H, 2.18; N, 5.17.

Triethylammonium Pentachloromethoxotungstate(V):- A 5.0 g sample of WCl_5 was added to a solution of 10 ml methanol which was saturated with HCl and cooled to -78^0. The temperature of the solution was increased to 0^0. The color changed from black to yellow brown. A solution of 3 ml triethylamine in 10 ml methanol which was saturated with HCl was added to the brown solution. The mixture was cooled to -78^0 and was saturated with HCl. After 10 minutes, a yellow precipitate formed. The compound dissolved when the temperature of the solution was raised above -20^0. Therefore, the product was separated rapidly by filtration, washed with an ether-methanol mixture, then pure ether and it was then dried under vacuum.

Analysis Calculated for $(C_2H_5)_3NHW(OCH_3)Cl_5$: W, 37.20; Cl, 35.87.

Found: W, 37.29; Cl, 35.74.

Triethylammonium Pentachloroethoxotungstate(V):- This compound was prepared by the same procedures as the previous complex except that ethanol was used in place of methanol.

Analysis calculated for $(C_2H_5)_3NHW(OC_2H_5)Cl_5$: W, 36.18; Cl, 34.88.

Found: W, 36.01; Cl, 34.79.

No commercial C, H analyses were obtained for these monoalkoxo compounds.

Pyridinium Tetrachlorodimethoxotungstate(V):- A 13.5 g sample of WCl_5 (0.037 mol) was added carefully to 23 ml methanol which was cooled to -40^0 in a Dry-ice-chloroform slush bath. The dark green solution was treated with either a methanol-pyridine mixture or pyridinium chloride (0.037 mol) and a green solid separated. The crystals were filtered, washed with ether and methanol, pure ether, and dried under vacuum.

Analysis calculated for $C_5H_6NW(OCH_3)_2Cl_4$: W, 39.31; Cl, 30.32; C, 17.96; H, 2.57; N, 2.99.

Found: W, 39.32; Cl, 30.30; C, 17.94; H, 2.55; N, 2.90.

Pyridinium Tetrachlorodiethoxotungstate(V):- A 10.0 g sample of WCl_5 (0.027 mol) was added to 20 ml ethanol which was cooled to -78^0 in a Dry Ice-propanol bath. The solution

was gradually warmed to 0^0 and stirred for one hour. Then pyridinium chloride or a pyridine-ethanol mixture (0.027 mol) was added. The light green product was separated by filtration, washed with ether and ethanol, then pure ether, and was dried under vacuum.

Analysis calculated for $C_5H_6NW(OC_2H_5)_2Cl_4$: W, 37.09; Cl, 28.60; C, 21.79; H, 3.23; N, 2.82.

Found: W, 36.90; Cl, 28.49; C, 21.86; H, 3.36; N, 2.86.

Tetraethylammonium Pentachloroisothiocyanatotungstate(V):- A 6.13 g sample of WCl_5 (0.0169 mol) was suspended in 20 ml $CHCl_3$. A $CHCl_3$ solution of tetraethylammonium thiocyanate (0.017 mol) was added to the mixture. After 1 hour of vigorous stirring, the solution changed from orange to dark brown. The reaction mixture was stirred for about 15 hours then the dark brown product was removed by filtration, washed with a mixture of $CHCl_3$ and ether, then pure ether and was dried under vacuum. The tetraethylammonium thiocyanate solution was prepared by treating an ethanol solution of tetraethylammonium chloride (2.88 g, 0.0173 mol) with an ethanol solution of 1.33 g ammonium thiocyanate. The ammonium chloride that formed was filtered off and the filtrate containing the $(C_2H_5)_4NSCN$ was evaporated to dryness. A technique of repeated ether washing and vacuum evaporation was used to remove residual alcohol from the product. Finally, 20 ml $CHCl_3$ was added and the solution was filtered to remove a small residue of NH_4Cl.

Analysis calculated for $(C_2H_5)_4NW(NCS)Cl_5$: W, 33.48; Cl, 32.28; C, 19.67; H, 3.64; N, 5.10; S, 5.83.

Found: W. 33.98; Cl, 32.03; C, 19.47; H, 3.47; N, 4.98; S, 5.76.

Tetraethylammonium Tetrachloroethoxoisothiocyanato-tungstate(V):- A 7.45 g portion of WCl_5 (0.0206 mol) was added to 10 ml ethanol which was cooled to -78^0. The temperature was increased to 0^0 and a solution of 3.14 g ammonium thiocyanate (0.041 mol) in 20 ml ethanol was added. Ammonium chloride separated from the dark green solution. The mixture was stored at -10^0 for three hours. The ammonium chloride was then removed by filtration and a solution of tetraethylammonium thiocyanate (0.021 mol) in 15 ml ethanol was added. The yellow-green compound was separated by filtration, washed with a 1:1 mixture of ethanol and ether, followed by pure ether and was dried under vacuum. The tetraethylammonium thiocyanate solution was prepared by treating an ethanol solution of tetraethylammonium chloride (3.42 g, 0.021 mol) with 1.62 g (0.02 mol) ammonium thiocyanate in 25 ml ethanol. The volume of the solution was reduced by vacuum evaporation and the ammonium chloride was removed by filtration.

Analysis calculated for $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$: W, 32.91; Cl, 25.38.

Found: W, 32.37; Cl, 24.98.

No Commercial C, H, N, S analyses were obtained. The compound decomposed with evolution of ethyl chloride.

Analysis calculated for $(C_2H_5)_4NW(NCS)Cl_5$: W, 33.48; Cl, 32.28; C, 19.67; H, 3.64; N, 5.10; S, 5.83.

Found: W. 33.98; Cl, 32.03; C, 19.47; H, 3.47; N, 4.98; S, 5.76.

Tetraethylammonium Tetrachloroethoxoisothiocyanato-tungstate(V):- A 7.45 g portion of WCl_5 (0.0206 mol) was added to 10 ml ethanol which was cooled to -78^0. The temperature was increased to 0^0 and a solution of 3.14 g ammonium thiocyanate (0.041 mol) in 20 ml ethanol was added. Ammonium chloride separated from the dark green solution. The mixture was stored at -10^0 for three hours. The ammonium chloride was then removed by filtration and a solution of tetraethylammonium thiocyanate (0.021 mol) in 15 ml ethanol was added. The yellow-green compound was separated by filtration, washed with a 1:1 mixture of ethanol and ether, followed by pure ether and was dried under vacuum. The tetraethylammonium thiocyanate solution was prepared by treating an ethanol solution of tetraethylammonium chloride (3.42 g, 0.021 mol) with 1.62 g (0.02 mol) ammonium thiocyanate in 25 ml ethanol. The volume of the solution was reduced by vacuum evaporation and the ammonium chloride was removed by filtration.

Analysis calculated for $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$: W, 32.91; Cl, 25.38.

Found: W, 32.37; Cl, 24.98.

No Commercial C, H, N, S analyses were obtained. The compound decomposed with evolution of ethyl chloride.

Dimers of W(V): $W_2Cl_4(OC_2H_5)_6$, $W_2Cl_4(OC_3H_7)_6$:-

$W_2Cl_4(OC_2H_5)_6$: A 5.0 g sample of WCl_5 (0.014 mol) was added to ethanol at -78°. The solution was gradually warmed to 0°. A sodium ethoxide solution (prepared by treating 0.64 g of Na (0.028 g-atom) with 20 ml ethanol) was added to the green solution. The color became red-brown and sodium chloride separated from the solution. The sodium chloride was removed by centrifuging and decanting the mixture. The resulting solution was allowed to reflux for 2 hours and was then stored at -15° overnight. The dark red crystals were filtered, washed with a small amount of ethanol and dried in vacuo.

Analysis calculated for $W_2Cl_4(OC_2H_5)_6$: W, 47.15; Cl, 18.18; C, 18.48;, H, 3.88.

Found: W, 47.21, Cl, 18.12; C, 18.41; H, 3.79.

$W_2Cl_4(OC_3H_7)_6$: This dark red compound was prepared by the same procedure as $W_2Cl_4(OC_2H_5)_6$ except that 1-propanol was used in place of ethanol.

Analysis calculated for $W_2Cl_4(OC_3H_7)_6$: 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.

Dimers of W(V): $W_2Cl_2(OC_2H_5)_8$; $W_2Cl_2(OC_3H_7)_8$:-

$W_2Cl_2(OC_2H_5)_8$: This compound was prepared by the same method as $W_2Cl_4(OC_2H_5)_6$ except that a sodium ethoxide solution with an ethoxide to tungsten ratio of 4:1 was used.

Analysis calculated for $W_2Cl_2(OC_2H_5)_8$: W, 46.04, Cl, 8.87; C, 24.04; H, 5.00; OC_2H_5, 45.08.

Found: W, 46.35; Cl, 9.12; C, 23.45; H, 4.86; OC_2H_5, 44.34.

$W_2Cl_2(OC_3H_7)_8$: This compound was prepared by the same procedure as $W_2Cl_4(OC_3H_7)_6$ except that a sodium propoxide solution with a propoxide to tungsten ratio of 4:1 was used.

Analysis calculated for $W_2Cl_2(OC_3H_7)_8$: W, 40.38; Cl, 7.78.

Found: Cl, 8.63.

$W(OC_2H_5)_5$:- A 6.49 g sample of WCl_5 (0.018 mol) was added to 10 ml ethanol cooled to -78^0. The temperature of the solution was increased to 0^0. A sodium ethoxide solution [prepared by adding 2.11 g Na (0.090 g-atom) to 60 ml 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 25^0 and 0.1 torr. The brown liquid residue was allowed to distill at 120^0 and 0.1 torr and a red-black liquid, which gelled upon cooling, was obtained in the distillate. Because this compound was extremely sensitive to moisture, no commercial C, H analyses were obtained.

Analysis calculated for $W(OC_2H_5)_5$: W, 44.97; OC_2H_5, 55.03.

Found: W, 44.40; OC_2H_5, 54.97.

Sodium Hexaethoxotungstate(V):- A 5.27 g sample of WCl_5 (0.015 mol) was added to 10 ml ethanol which had been cooled to -78^0. The temperature of the solution was gradually increased to 0^0. A sodium ethoxide solution [prepared by adding 2.01 g Na (0.087 g-atom) to 50 ml 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 benzene was added. The dark blue solution was cooled to -10^0 for 12 hours. 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 $NaW(OC_2H_5)_6$ 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.

Analysis calculated for $NaW(OC_2H_5)_6$: 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. A sodium ethoxide solution with an ethoxide to tungsten ratio of 7:1 also gave a dark blue solution. However, the yellow compound isolated in the above manner had a significant amount of sodium ethoxide impurity.

Found: W, 25.32; OC_2H_5, 61.12. OC_2H_5/W ratio = 9.8/1.

Dimers of W(IV): $W_2Cl_4(OR)_4(ROH)_2$, R = CH_3, C_2H_5, 1-C_3H_7, 2-C_3H_7,- $W_2Cl_4(OCH_3)_4(CH_3OH)_2$: A 5.9 g sample of WCl_4 was added to 20 ml methanol that had been cooled to 0^0. The temperature of the solution was increased to 25^0. The grey-black solid gradually became yellow-green and the solution became green. After the mixture had been stirred for three hours, the yellow-green compound was removed by filtration, washed with methanol and dried under vacuum. The product was then added to 20 ml methanol and stirred at 25^0 for 12 hours. Further reaction did not occur. The compound was separated by filtration, washed with methanol and dried under vacuum.

Analysis calculated for $W_2Cl_4(OCH_3)_4(CH_3OH)_2$: 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 equivalents of cerium per g-atom W.

$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$: This compound was prepared by the same procedure as $W_2Cl_4(OCH_3)_4(CH_3OH)_2$ except that ethanol

was used in place of methanol. The dark green compound was recrystallized from a $CHCl_3$ and ethanol mixture. Yield 45%.

Analysis calculated for $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$: 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 equivalents of Ce(IV) per g-atom W.

$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$: This dark green compound was prepared by the same procedure as the previous complex except that 1-propanol was used.

Analysis calculated for $W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$: 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.

$W_2Cl_4(2\text{-}OC_3H_7)_4(C_3H_7OH\text{-}2)_2$: 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.

Analysis calculated for $W_2Cl_4(2\text{-}OC_3H_7)_4(C_3H_7OH\text{-}2)_2$: 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.

$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$:- A 2.26 g sample of $W_2Cl_4(OC_2H_5)_4$-$(C_2H_5OH)_2$ was dissolved in 20 ml $CHCl_3$. A solution of 1 ml pyridine in 10 ml $CHCl_3$ 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 -78^0. The compound was separated by rapid filtration, was washed with a small amount of $CHCl_3$ and dried under vacuum.

Analysis calculated for $W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$: 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.

$W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$:- A 4.38 g (0.011 mol) portion of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ was suspended in 20 ml ethanol. A potassium ethoxide solution [prepared by adding 0.438 g K (0.011 g-atom) to 15 ml ethanol] was added to the green mixture. The color became dark green and KCl separated from the solution. The mixture was stirred for two hours and the KCl was removed by filtration. The resulting solution was stored at -10^0 for 12 hours. The black crystalline product was filtered, washed with a small amount of ethanol and dried under vacuum.

Analysis calculated for $W_2Cl_2(OC_2H_5)_6(C_2H_5OH)_2$: W, 45.93; Cl, 8.85; OC_2H_5, 45.02.

Found: W, 46.00; Cl, 9.15; OC_2H_5, 41.10. The oxidation state determination required 1.96 equivalents of cerium per g-atom W. This compound decomposed with evolution of ethanol vapor. Commercial C, H analyses were not obtained.

Attempts to Prepare $W(OC_2H_5)_4$:- A 4.46 g sample (0.012 mol) of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ was suspended in 10 ml ethanol. A potassium ethoxide solution [prepared by treating 0.892 g K (0.023 g-atom) with 30 ml ethanol] was added to the mixture. The solution became black and KCl separated. The mixture was stirred for one hour then the KCl was removed by filtration. The blue-black filtrate was then evaporated to dryness. A black liquid residue was obtained. This residue was allowed to sublime at 110^0 and 0.1 torr. A very dark red liquid resulted from this treatment. Elemental analysis, ir and pmr spectra indicated that this compound was $W(OC_2H_5)_5$ with a small amount of an unidentified impurity.

Analysis calculated for $W(OC_2H_5)_5$: W, 44.97; OC_2H_5, 55.03.

Found: W, 45.17; OC_2H_5, 51.22.

Reaction of WCl_4 with Alcohols:- At 0^0, WCl_4 formed a black suspension in alcohols. After the temperature was increased to 25^0, 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.

Analysis calculated for $(C_2H_5)_4NW(OC_2H_5)_2Cl_4$: W, 33.69; Cl, 25.97.

Found: W, 34.00; Cl, 25.98. $\mu(297^0K)$ = 1.47 B.M.

Analysis calculated for $(C_2H_5)_4NW(OCH_3)_2Cl_4$: W, 35.51; Cl, 27.39.

Found: W, 35.66; Cl, 27.39. $\mu(297^0K)$ = 1.51 B.M.

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 Tungsten Compounds:- The W(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.

The W(V) dimers, $W_2Cl_4(OC_2H_5)_6$ and $W_2Cl_4(OC_3H_7)_6$ were slightly soluble in the parent alcohol and soluble in other organic solvents. These compounds were inert to water or dilute acids but were attacked by base. The compounds, $W_2Cl_2(OC_2H_5)_8$ and $W_2Cl_2(OC_3H_7)_8$, were very soluble in the parent alcohol and in other organic solvents. These complexes were readily decomposed by aqueous acid or base.

In general, the W(V) monomeric compounds were much more sensitive to air and moisture. The dialkoxo species, $C_5H_6NW(OR)_2Cl_4$ were soluble in alcohol and other organic solvents. The thiocyanate complex, $(C_2H_5)_4NW(NCS)Cl_5$ was insoluble in common organic solvents. The mixed compound, $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$, was similar to the dialkoxo species.

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 pyridine in 10 ml ethanol

saturated with HCl. The solution changed from a dark red to orange. No precipitate was observed after the solution was allowed to cool to -10^0. 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.

F. Spectroscopic Measurements

I.R. Spectra:- Near infrared spectra were recorded by means of a Unicam SP-200 prism instrument. Far infrared measurements were made by use of Perkin-Elmer model 301 and 457 spectrophotometers. Solid compounds were measured as Nujol mulls. In some cases, the spectra of samples, dissolved in an appropriate solvent, were also determined. Sodium chloride or cesium iodide plates were used between 4000 cm^{-1} and 650 cm^{-1}, cesium iodide plates from 650-300 cm^{-1} and polyethylene discs from 650-100 cm^{-1}.

Optical Spectra:- Solution spectra in the region of 8.0×10^3 cm^{-1} to 50.0×10^3 cm^{-1} were determined by means of Unicam SP-800 and Cary Model 14 spectrophotometers. Samples were dissolved in the appropriate solvent and transferred under nitrogen to dry cuvettes. Two methods were used to obtain solid reflectance spectra. A thick paste of the compound and Nujol was pressed between glass plates. Spectra were then recorded on the Cary Model 14 as if they were ordinary absorption spectra. Samples were also loaded into a flat-windowed adaptor for measurement on a Bausch and Lomb Spectronic 600 spectrophotometer equipped with a reflectance attachment.

Mass Spectra:- The mass spectra of some dimeric compounds were obtained by Dr. L. Shadoff, Dow Chemical Co., Midland, Michigan. Samples were sealed in melting point capillaries which were broken in the direct probe pumping chamber of a CEC21-110B mass spectrometer.

Magnetic Susceptibility Measurements:- The magnetic susceptibilities of solid compounds were determined by the Gouy method. The experimental apparatus for variable temperature measurements was similar to that of Vander Vennen.[73] The procedure was modified so that a stream of helium was passed over the sample tube. This action prevented the condensation of water and contamination of the sample. The diamagnetism of some samples, including $W(OC_2H_5)_5$ and $W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$, was confirmed by the sharp pmr spectra and the absence of an epr signal.

Proton Magnetic Resonance Spectra:- PMR spectra were recorded by use of a Varian A56/60 spectrometer, equipped with a variable temperature controller. Tetramethylsilane (TMS) was used as an internal standard.

Electron Spin Resonance Spectra:- ESR spectra were obtained with a Varian V-4502-04 spectrometer with 100 kHz modulation. The magnetic field was calibrated by use of a Hewlett-Packard 524C Frequency Counter. The g values were obtained from the measured magnetic field and the Klystron frequency.

G. Proton Magnetic Resonance

The theory and experimental applications of proton magnetic resonance have been treated in many recent review articles and textbooks.[74-75] No detailed discussion of these topics will be given here. The usefulness of the method is related to its two main features, the chemical shift and proton or nuclear spin-spin coupling. For diamagnetic alkoxide complexes, the spin-spin coupling constant is invariant (J_{H-H} = 7 cps). The chemical shift, which is sensitive to the environment about the nuclei or protons, is of primary concern. This quantity is related to the orientation and reactivity of the various alkoxide ligands. The chemical shift, δ , is defined by the equation:[75]

$$\delta = \frac{\nu_S - \nu_R}{\nu_0}$$

where ν_S and ν_R are the applied fields (in units of frequency, cps) necessary to cause the sample and reference protons to undergo resonance and ν_0 is the fixed frequency of the probe (for protons, ν_0 = 60 mc sec^{-1}).

H. Electron Spin Resonance

The basic theory and application of esr spectroscopy to transition metal complexes have been the subject of many excellent reviews and texts. The review by McGarvey[76] and the chapter by Kuska and Rogers in "Radical Ions"[77] are recommended.

An unpaired electron in a transition metal complex may interact with an external magnetic field (Zeeman interaction), with the nuclear spin (metal hyperfine) and with the ligand nuclear spin (ligand hyperfine or superhyperfine). ESR spectroscopy is used to study these phenomena. These effects are generally described by the spin Hamiltonian. For an electron in a complex with axial symmetry (X = Y = $\perp$, z = ||), the spin Hamiltonian can be written:

$$H = \beta[g_{||}S_zH_z + g_{\perp}(S_xH_x + S_yH_y)] + [A_{||}S_zI_z + A_{\perp}(S_xI_x + S_yI_y)],$$

where $g_{||}$ and $g_{\perp}$ are the spectroscopic splitting factors, β is the Bohr Magneton, H_x, H_y, H_z are the components of the magnetic field in the x, y, z directions; S_x, S_y, S_z are the components of the electron spin operator along the respective axes and I_x, I_y, I_z are the components of the metal nuclear spin along the respective axes.

The measurable parameters in ordinary esr spectra are the g values (position of absorptions) and A values (distance between metal hyperfine absorptions). For tungsten complexes, the low isotopic abundance [^{183}W I = 1/2 = 14.2%) generally prevents the resolution of metal hyperfine structure.

I. Magnetic Susceptibility

The calculation of the magnetic susceptibility was made by use of the equation:[78]

$$10^6\chi_g = \frac{F'\beta}{w_s}$$

where χ is the gram susceptibility (cgs units) of the sample, β is the tube constant, w_s is the weight of the sample in grams and F' is the force (in mgrams) exerted on the sample alone, that is, $F' = F - \delta$, where δ is the force on the tube.

The tube constant, β, must be determined by use of a substance of known susceptibility. In this work, $CuSO_4 \cdot 5H_2O$ was used. Its susceptibility is 5.92×10^6 cgs units at 25^0.

The molar susceptibility, χ_m, was found by multiplying the gram susceptibility by the molecular weight of the sample. The diamagnetism of the organic ligands and cations present forms an appreciable portion of the susceptibility of the complex. The susceptibility of the metal ion, χ_m', is obtained by adding to χ_m the Pascal's constants,[78] which are a measure of the diamagnetism of the ligands. The value of the magnetic moment is related to the square root of χ_m':

$$\mu_{eff} = 2.84\ (\chi_m'\ T)^{1/2}\ \text{B.M.}$$

The Curie-Weiss Law:

$$\chi_m' = \frac{C}{T + \theta}$$

is used to describe the variation with temperature of the magnetic susceptibility of normal paramagnetic substances. A plot of $1/\chi_m'$ against T gives a straight line whose intercept θ, is the Weiss constant.

The magnetic moment is often discussed in terms of spin and orbital contributions:

$$\mu_{eff} = g[J(J + 1)]^{1/2}$$

where $g = \frac{1 + [S(S + 1) - L(L + 1) + J(J + 1)]}{2J(J + 1)}$

and J, the total angular momentum, $= |L + S|, |L + S-1| \cdot\cdot |L - S|$. When a system has no angular momentum ($L = 0$) then $J = S$ and $g = 2.00$,

$$\mu_{eff} = 2[S(S + 1)]^{1/2} .$$

This is the so-called "spin only" formula.

The degeneracy of the d orbitals may not be completely removed by a ligand field. For this reason, orbital angular momentum remains to some extent with the t_{2g} orbitals. Figgis[79] has developed a method for estimating the orbital contribution to the magnetic moment of transition metal complexes. The degeneracy of the t_{2g} orbital may be removed by spin-orbit coupling or by a ligand field of

symmetry lower than cubic. Figgis defines k as a measure of the delocalization of the electron on the ligands. Δ is the separation between the orbital singlet and doublet of the t_{2g} term created by tetragonal distortion of the ligand field and ν is Δ/λ, where λ is the spin-orbit coupling constant. Figgis has calculated μ_{eff} as a function of kT/λ for different values of k and ν. If the experimental curve can be matched over a wide temperature range, values of k, Δ, ν and λ can be obtained. This method must be used cautiously, computer fits are desirable and too little or too great a dependence of μ_{eff} on temperature prevents quantitative correlations.

RESULTS AND DISCUSSION

This section is divided into two parts: A. W(V) monomeric complexes; B. W(V) and W(IV) dimeric complexes.

A. W(V) Monomeric Complexes

1. Preparation of Complexes

The reaction of WCl_5 with neutral, acidic (with HCl) and basic (with alkoxide ion) alcohol solutions was investigated. At -78^0, WCl_5 formed a blue-black mixture with the alcohols studied. When the temperature of the solution was increased to 0^0, dark green solutions were obtained. The addition of a pyridine-alcohol mixture or a pyridinium chloride solution resulted in the formation of the light green tetrachlorodialkoxotungstate(V) complexes, $C_5H_6NW(OR)_2Cl_4$, R = CH_3, C_2H_5. When larger cations, such as tetraethylammonium chloride, were added to this WCl_5 alcohol solution, a mixture of salts of the anions $W(OR)Cl_5^-$ and $W(OR)_2Cl_4^-$ was isolated.[81]

Only mixed oxoalkoxo complexes were isolated from the reaction of WCl_5 with 1 or 2-propanol. The light blue-green complex, $(C_5H_6N)_2WOCl_5$, was prepared by the addition of pyridinium chloride to a solution of WCl_5 in 2-propanol

saturated with HCl. The method of preparation of this compound reported by Funk[62] could not be successfully repeated. Funk added pyridinium chloride to a hot solution of WCl_5 in methanol.

In acidic (with HCl) alcohol solutions, WCl_5 formed an unstable anion, $W(OR)Cl_5^-$. The size of the cation was critical in the isolation of this species. No solid complex was obtained with the pyridinium cation. However, the yellow complexes, $(C_2H_5)_3NHW(OR)Cl_5$, R = CH_3, C_2H_5, were prepared by the use of the triethylammonium cation. The pentachloroalkoxotungstate(V) complexes were unstable and decomposed in the solid state with evolution of alkyl halide vapor. One of the solid products of this decomposition reaction was identified as the tetrachlorooxotungstate(V) complex. Rillema[72] found that the rate of alkyl halide evolution decreased as the sizes of the cation and the alkoxide ligand were increased.

Attempts to prepare monomeric complexes of the type, $W(OR)_nCl_{6-n}^-$ with n > 2 were unsuccessful. The green WCl_5 alcohol solutions were made basic with alkoxide ion. When alcohol solutions of the cations, $(C_2H_5)_4NCl$ or $(C_2H_5)_4NOR$, were added to this reaction solution with the OR^-/W ratio greater than 2:1, the precipitate was contaminated with dark red or brown crystalline material. These highly colored complexes were diamagnetic dimers (see Results and Discussion, Part B). In these basic alcohol solutions, dimerization appeared to be the dominant reaction.

Several new thiocyanate complexes of W(V) were also prepared. The reaction of WCl_5 with $(C_2H_5)_4NSCN$ in chloroform yielded the dark brown $(C_2H_5)_4NW(NCS)Cl_5$. Attempts to prepare other substituted chlorothiocyanate complexes of W(V) were unsuccessful. The mixed alkoxo-thiocyanate compound, $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$, was prepared by the addition of $(C_2H_5)_4NSCN$ to an ethanol solution of WCl_5 which had been treated with NH_4SCN. This compound decomposed with evolution of ethyl chloride. The solid complex gradually changed from a light yellow-green to dark green. However, the solid residue was unidentified.

The esr and far ir spectra of these W(V) monomers indicated that the compounds possessed axial symmetry.

2. Electron Spin Resonance Spectra

The esr spectra were determined for solid samples and solutions of the W(V) complexes at 77^0K and at room temperature. These results are listed in Table I and representative spectra are shown in Figures 1 and 2.

The frozen solution spectra of the W(V) complexes could be resolved into parallel and perpendicular components. Thus, axial symmetry is indicated--D_{4h} symmetry for the dialkoxide complexes and C_{4v} symmetry for $(C_5H_6N)_2WOCl_5$ and for $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$. In each case, $g_{||}$ was found to be greater than $g_{\perp}$. A similar observation is reported for $WOX_5^=$, X = Cl, Br, complexes.[19] The spectra of the solid samples and solutions of the complexes at room

Table I. ESR parameters for W(V) complexes.[a]

Compound	Medium	Temp. °K	$\langle g \rangle$	$g_{\|\|}$	$g_{\perp}$
$(C_5H_6N)_2WOCl_5$	Solid	297	1.76		
	CH_3NO_2	77	(1.78)	1.79	1.77
$C_5H_6NW(OCH_3)_2Cl_4$	Solid	297	1.73		
	CH_3OH	77	(1.72)	1.75	1.70
	CH_3NO_2	77	(1.74)	1.78	1.72
$C_5H_6NW(OC_2H_5)_2Cl_4$	Solid	297	1.75		
	C_2H_5OH	297	1.76		
		77		1.76	1.70
	CH_3NO_2	77	(1.75)	1.79	1.73
$(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$	Solid	297		1.79	1.72
	CH_3NO_2	77	(1.75)	1.78	1.73
$(C_2H_5)_4NW(NCS)Cl_5$	Solid	297	1.78		

[a] ( ) = calculated values.

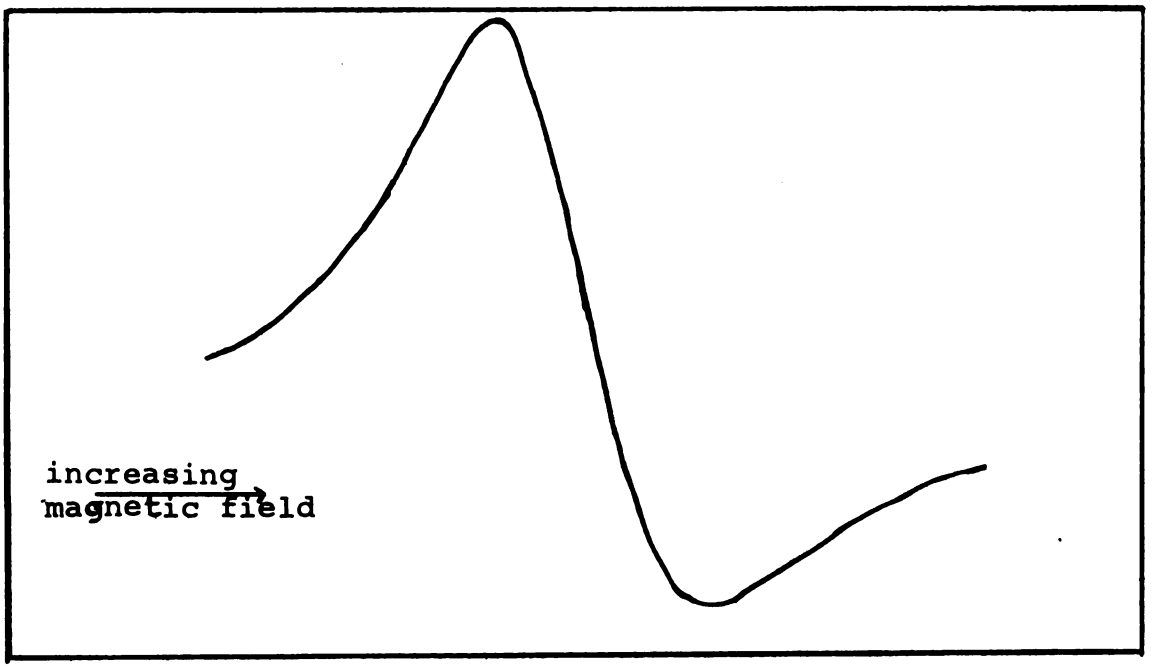


Figure 1. Electron spin resonance spectrum of solid $C_5H_6NW(OCH_3)_2Cl_4$ at 297°K.

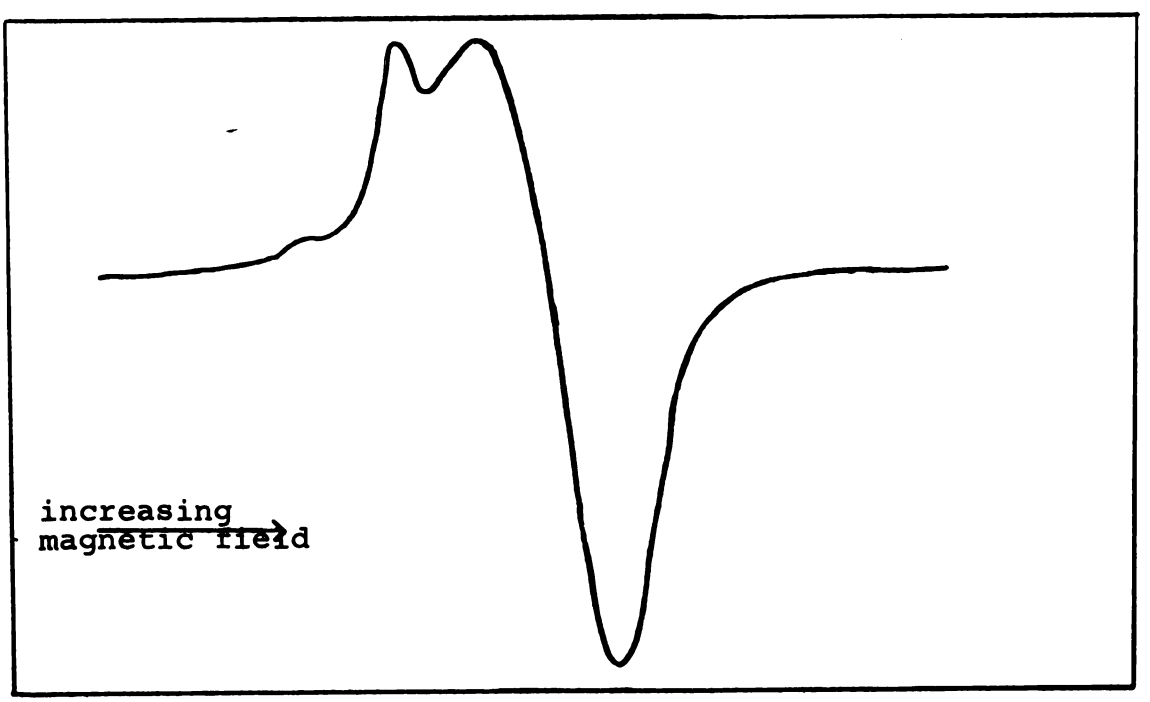


Figure 2. Electron spin resonance spectrum of $C_5H_6NW(OCH_3)_2Cl_4$ in CH_3NO_2 at 77°K.

temperature consisted of a single broad absorption (half width ~ 100 gauss). No suitable solvent was found for $(C_2H_5)_4NW(NCS)Cl_5$.

An absorption in the frozen solution spectra of these compounds was thought to be the hyperfine component of the parallel band due to ^{183}W (I = 1/2, 14.28%). However, the broad absorptions of the isotopes with I = 0 prevented any definite assignment.

3. Infrared Spectra

The infrared absorptions of these complexes are listed in Table II. Representative traces of the spectra are shown in Figures 3 to 7.

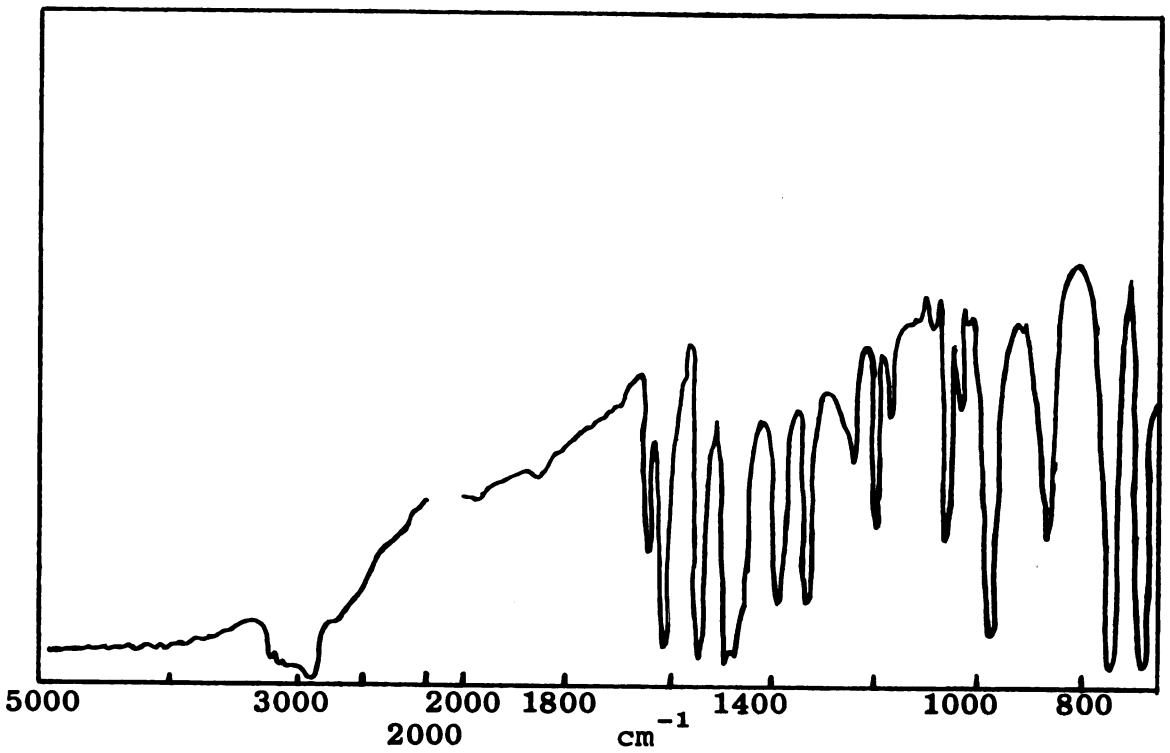
The evidence of C_{4v} or D_{4h} point group symmetry for these complexes was indicated by the position and number of the observed far ir vibrations. The dialkoxo compounds exhibited a trans alkoxide arrangement (D_{4h}). This symmetry required only five normal modes. The cis configuration (C_{2v}) would require a large number (13) of normal modes.

The metal-chlorine stretching frequency at about 300 cm^{-1} and the metal-chlorine deformation vibrations at 165 cm^{-1} were assigned by comparison with tungsten hexachloro[49] and oxochloro[32] complexes. Absorptions of the tungsten alkoxide complexes in the region 500-600 cm^{-1} are probably M-O-C stretching vibrations. A band at 400 cm^{-1} in the ethoxide complexes may be an O-C-C deformation.

Table II. Infrared absorption frequencies of W(V) monomers.[a] (With possible assignment.)

$(C_5H_6N)_2WOCl_5$			$C_5H_6NW(OCH_3)_2Cl_4$		
606	(s)		559,542	(s)	ν(W-O)
387	(s)		389,360	(w)	
309,294	(s)	ν(W-Cl)	317	(sh)	
231,238	(s)		289	(s)	ν(W-Cl)
197,203	(s)		255	(s)	
161	(s)	ν(Cl-W-Cl)	1060	(s)	ν(C-O)
970	(s)	ν(W = O)			
$C_5H_6NW(OC_2H_5)_2Cl_4$			$(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$		
594	(s)	ν(W-O)	595	(s)	ν(W-O)
416	(m)	ν(C-C-O)	480	(w)	δ(N-C-S)
286	(s)	(broad) ν(W-Cl)	410	(m)	
231	(m)		350	(m)	
154	(s)	ν(Cl-W-Cl)	315	(sh)	
1060,1095		ν(C-O)	285	(s)	ν(W-Cl)
			2020	(s)	
$(C_2H_5)_4NW(NCS)Cl_5$			2085	(m)	ν(C-N)
500	(w)	δ(N-C-S)	1990	(sh)	
320	(s)	ν(W-Cl)	900	(w)	ν(C-S)
2120	(m)		1060,1090		ν(C-O)
1980	(s)	ν(C-N)			
2020	(sh)				
1920	(m)				
1830	(w)				
890	(w)	ν(C-S)			

[a] Plus all cation bands; w = weak; m = medium; s = strong; sh = shoulder.



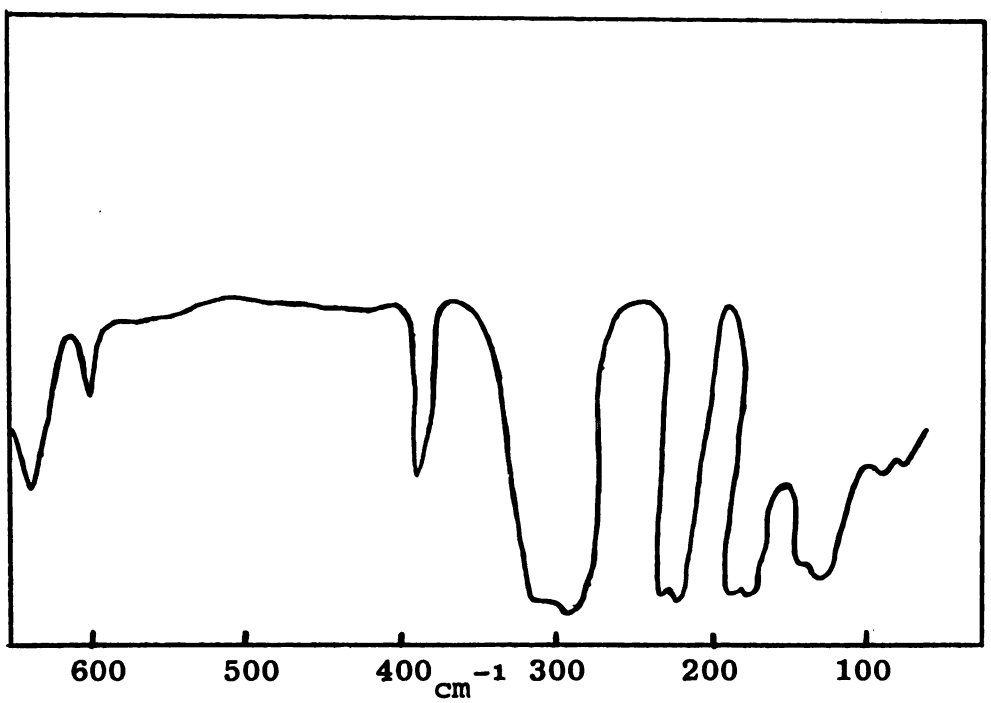
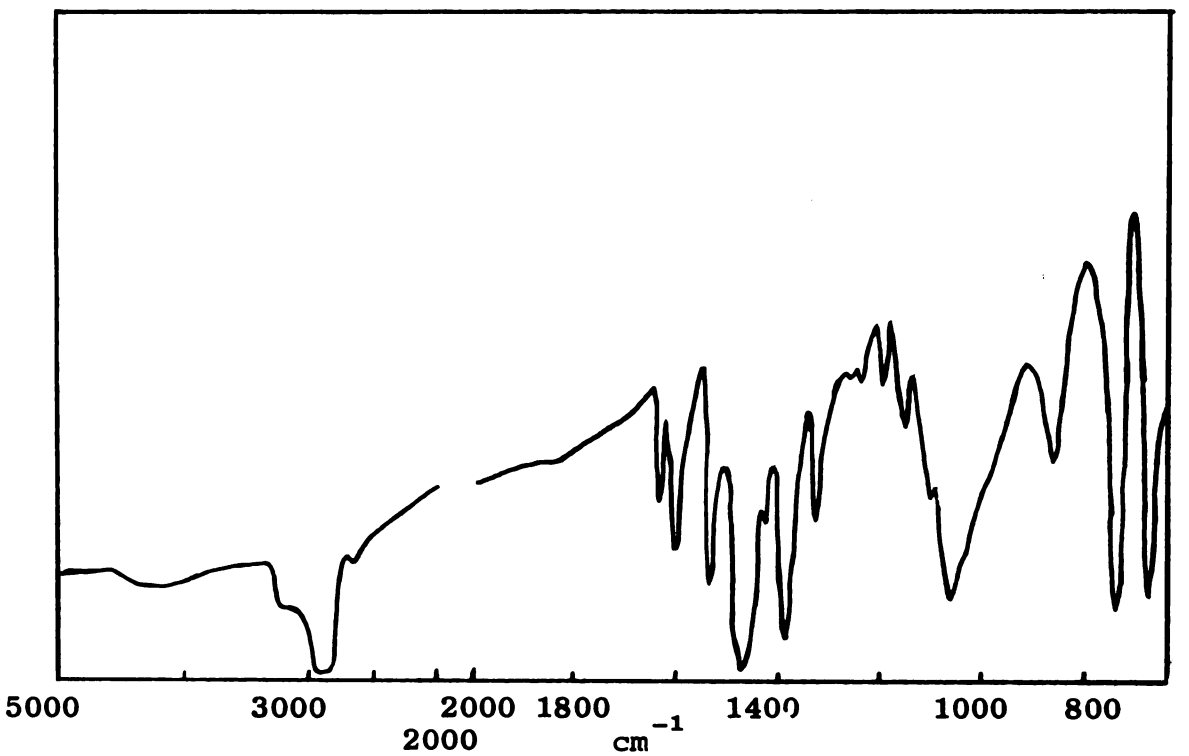


Figure 3. Infrared spectrum of $(C_5H_6N)_2WOCl_5$.



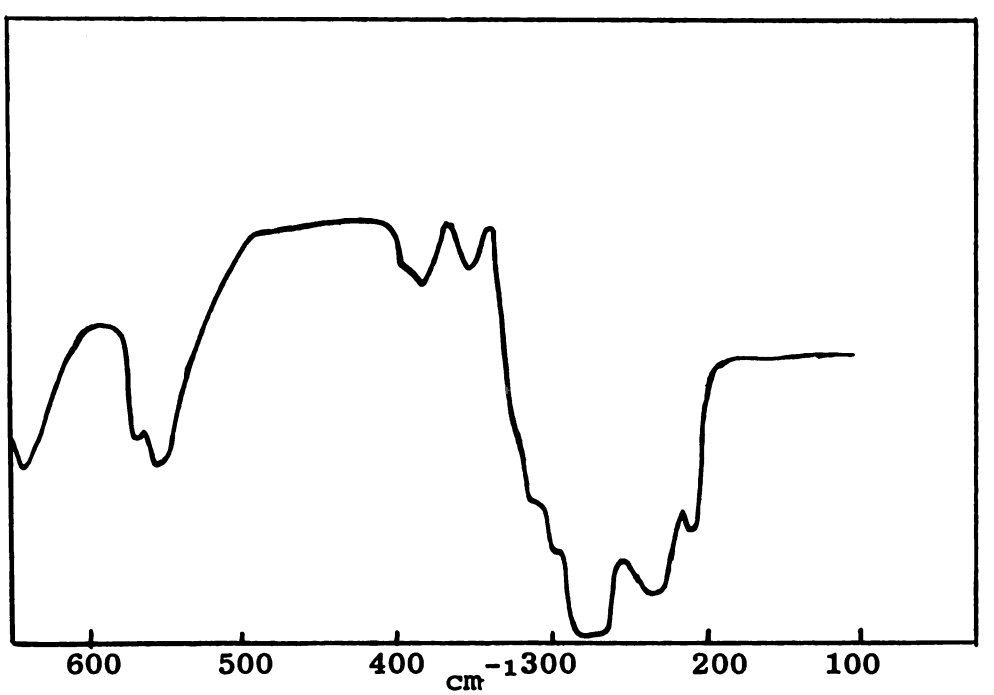
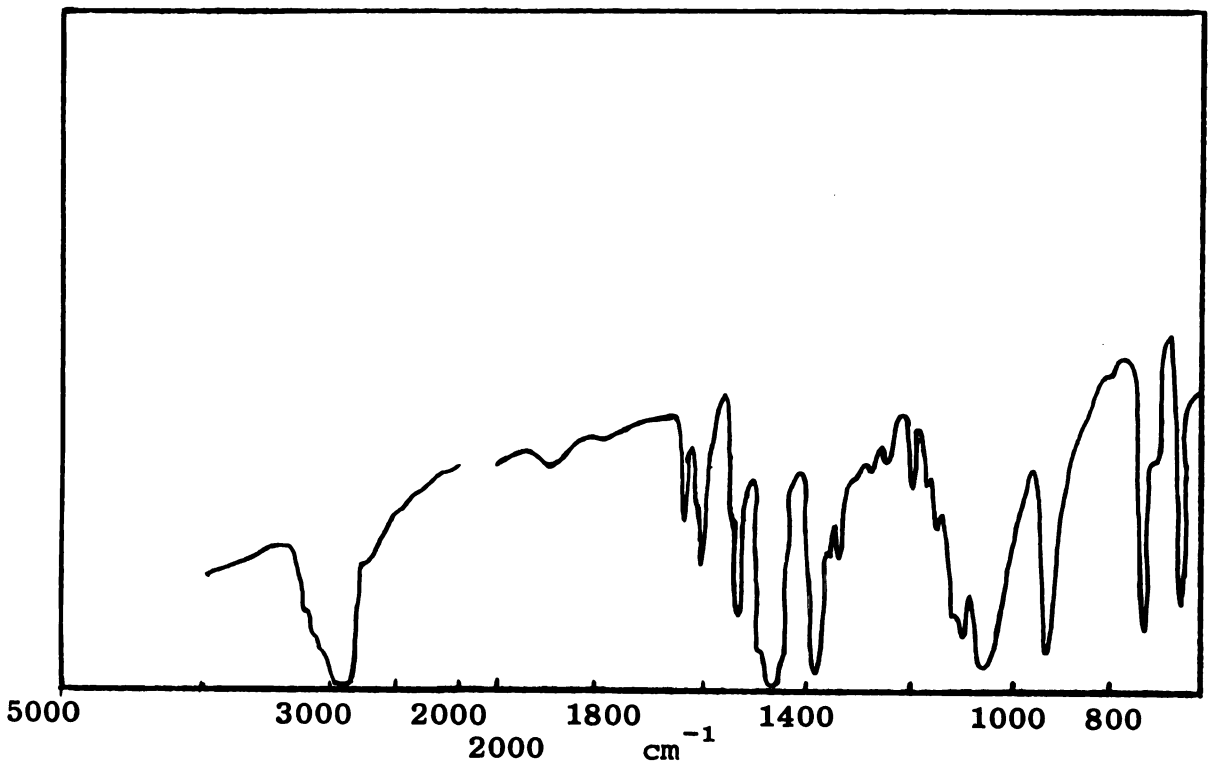


Figure 4. Infrared spectrum of $C_5H_6NW(OCH_3)_2Cl_4$.



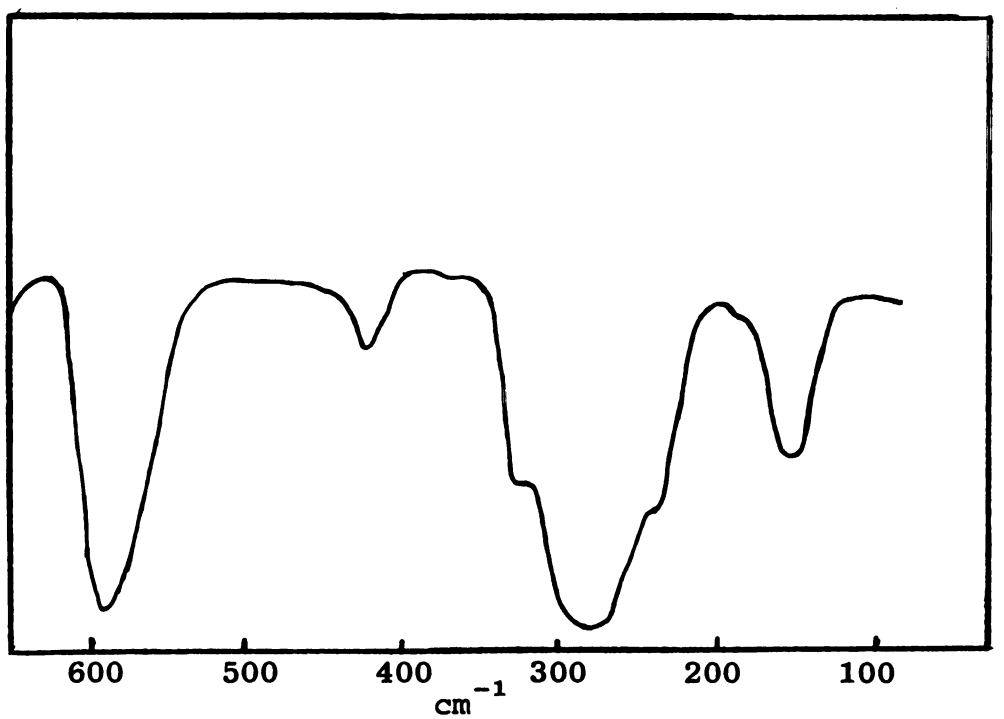


Figure 5. Infrared spectrum of $C_5H_6NW(OC_2H_5)_2Cl_4$.

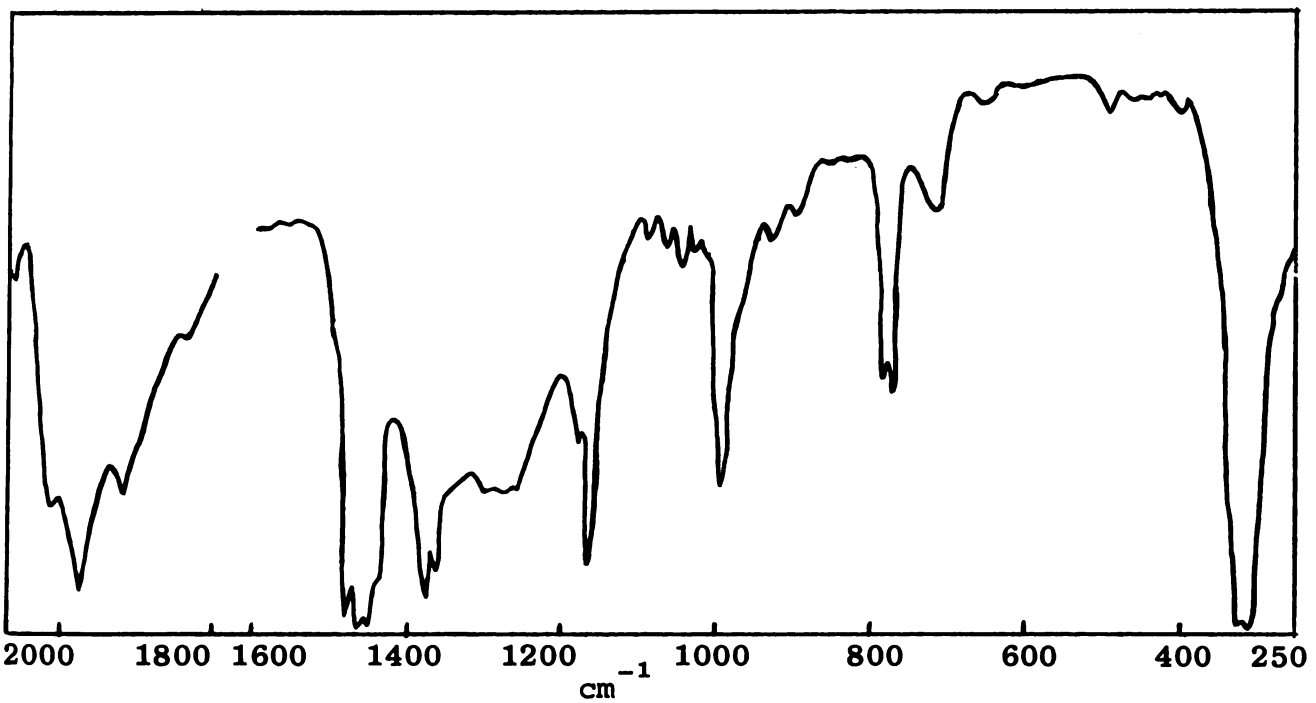


Figure 6. Infrared spectrum of $(C_2H_5)_4NW(NCS)Cl_5$.

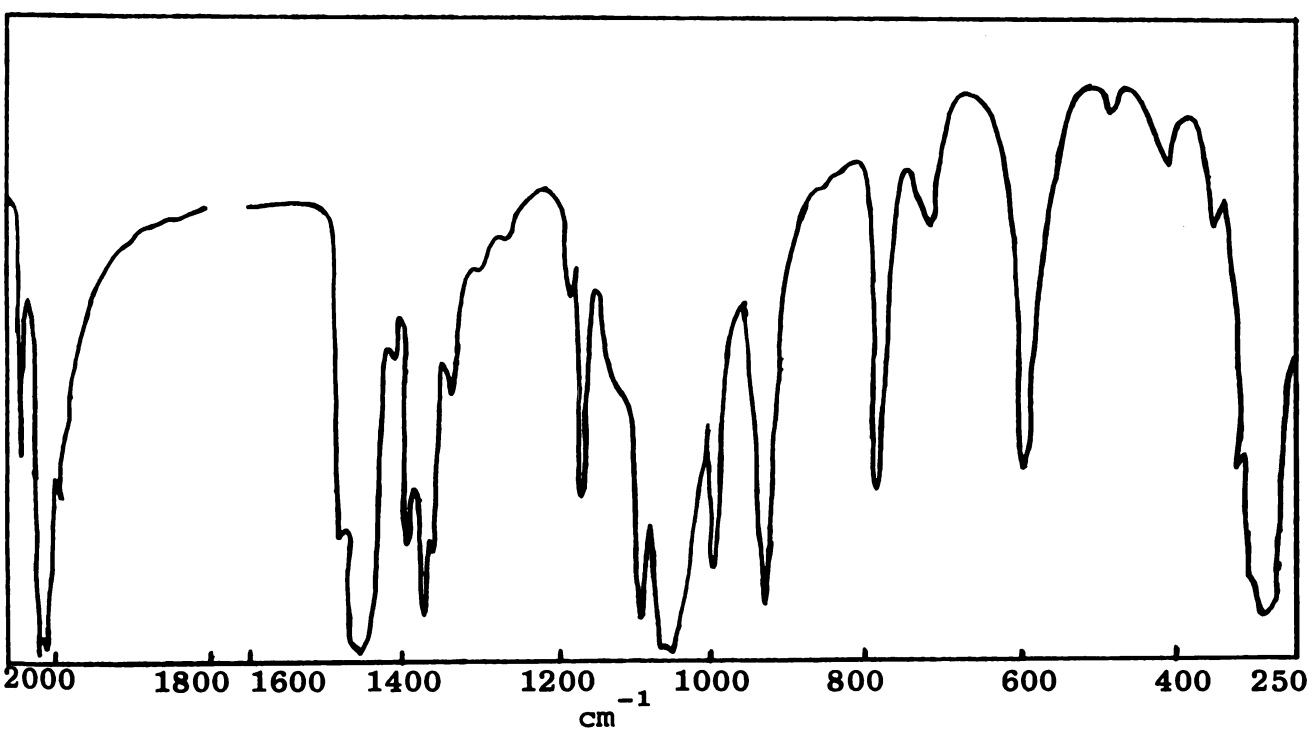


Figure 7. Infrared spectrum of $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$.

Near ir spectra (5000-650 cm^{-1}) of the tetrachlorodialkoxotungstate(V) and pentachlorooxotungstate(V) complexes indicated that pyridinium ion was present rather than pyridine ligand. Cation bands due to $(C_2H_5)_4N^+$ were also identified in the spectra of tetraethylammonium salts. The alkoxide complexes have strong bands in the region (1000-1100 cm^{-1}) where the C-O stretching vibration occurs.[82] No O-H vibration at 3500 cm^{-1} was observed, as one would expect with alkoxide rather than alcohol ligands bound to the metal.

The C-N stretching,[83] the C-N-S bending[84] and C-S stretching[85] vibrations at 2150-2050, 500-400 and 880-690 cm^{-1}, respectively, have been used to differentiate between thiocyanato (S-bonded) and isothiocyanato (N-bonded) complexes. For an N-bonded complex, an increase in the covalent character of the coordinate bond results in a decrease of the C-N stretching frequency and an increase in both the C-S stretching and N-C-S bending vibrations from those observed for the free thiocyanate ion. The ir spectra of the W(V) complexes indicated the presence of N-bonded thiocyanate ligands.

The C-N stretching frequencies of the W(V) compounds are located at 2000-1950 cm^{-1}. These bands are lower than the free thiocyanate value (2050 cm^{-1}). Weak absorptions near 900 cm^{-1} and 500 cm^{-1} are believed to be the C-S stretching and N-C-S bending vibrations. These bands are at higher frequencies than the free thiocyanate values. Similar results were reported for the N-bonded niobium and tantalum

hexaisothiocyanates, $K_2M(NCS)_6$.[34] The presence of more than one absorption band in the C-N region for these W(V) complexes can be explained by assuming the M-N-C bond to be bent rather than linear.

An interesting comparison can be made between the C-N stretching frequencies of $(C_2H_5)_4NW(NCS)(OC_2H_5)Cl_4$ at 2020 cm^{-1} and $(C_2H_5)_4NW(NCS)Cl_5$ at 1970 cm^{-1}. The lower value for the latter complex is an indication of a more covalent nitrogen bond to the tungsten atom. The mixed alkoxo-thiocyanate complex apparently has a more ionic M-N bond. Its ir spectrum in the C-N region is similar to that for $WO(NCS)_5^{=}$. For this reason, the ethoxide and thiocyanate ligands are probably in a <u>trans</u> configuration.

4. <u>Magnetic Moments</u>

The magnetic susceptibilities of the W(V) complexes were measured at room temperature, at 77°K and in some cases at 195°K. These results are listed in Table III. The compounds exhibited normal field independent paramagnetism. The weak temperature dependence of the magnetic moments is reflected in the small negative values of the Weiss constant.

Ir and esr spectra of these complexes suggest that the degeneracy of the ground state was removed by axial distortion to give tetragonal symmetry. This is the basic requirement for the use of the Figgis calculations.[80] Because of the nearly constant magnetic moments, only

Table III. Magnetic properties of W(V) compounds.

Compound	Temp. (^{0}K)	χ'_m x 10^6 cgs units	μ (B.M.)	θ (^{0}K)
$(C_5H_6N)_2WOCl_5$	297	1000.4	1.54	-2
	77	3834.0	1.54	
$C_5H_6NW(OCH_3)_2Cl_4$	297	913.9	1.48	-1
	195	1358	1.46	
	77	3166	1.40	
$C_5H_6NW(OC_2H_5)_2Cl_4$	297	957	1.51	+1
	195	1501	1.53	
	77	3775	1.50	
$(C_5H_6)_4NW(NCS)Cl_5$	297	417.5	1.00	-35
	77	1244	0.88	
$(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$	297	919.7	1.49	-1
	77	3544	1.48	

qualitative conclusions were obtained. For the oxychloride and dialkoxide complexes, ν is greater than 10, Δ ranges from 8,000 to 11,000 cm^{-1} and λ is approximately 500 cm^{-1}. Other workers[86] have found similar values for other oxyhalide compounds.

The low value of the magnetic moment for $(C_2H_5)_4NW(NCS)Cl_5$ is a reflection of the weak ligand field of the thiocyanate ion. The weak axial component of the ligand field does not increase the spacing of the degenerate t_{2g} orbitals and the large spin-orbit coupling constant leads to a magnetic moment well below the spin-only value. The magnetic moments of the other complexes increase as the number of alkoxide groups increases. By analogy with the oxo complexes, a strong tungsten oxygen multiple bond would provide a strong axial distortion to increase the spacing of the t_{2g} orbitals. Then, the spin-orbit contribution to the magnetic moment is lowered.

5. Visible and Reflectance Spectra

The electronic spectra in solution and the reflectance spectra of the solid complexes were determined. The results are listed in Table IV. Sketches of the spectra are shown in Figures 8 to 11.

The symmetry of the compounds can be used to assign the absorption bands. The splitting of the d orbitals by either C_{4v} or D_{4h} symmetry result in the same arrangement of the orbitals. The ordering of the orbitals from lowest

Table IV. Electronic absorption spectra of W(V) compounds.

Compound	Medium	Electronic Absorptions maxima x 10^3 cm^{-1} (ϵ in parentheses)
$(C_5H_6N)_2WOCl_5$	solid	12.8, 14.1, 15.6 (sh), 17.3 (sh), 23.8
$C_5H_6NW(OCH_3)_2Cl_4$	solid	11.1, 13.9, 24.1
	methanol	11.2(12), 14.3(15), 25.0 (~15), 30.8(>10^3), 35.0 (>10^3)
$C_5H_6NW(OC_2H_5)_2Cl_4$	solid	12.4, 14.5, 25.6
	ethanol	11.4(12), 13.9(13), 25.0(60), 30.8(600), 34.5(~10^3)
$(C_2H_5)_4NW(NCS)Cl_5$	solid	17.8, 19.6, 24.1
$(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$	solid	17.1, 18.5, 23.5, 26.0 (sh)
	solid (after two weeks)	14.3, 17.2, 18.2

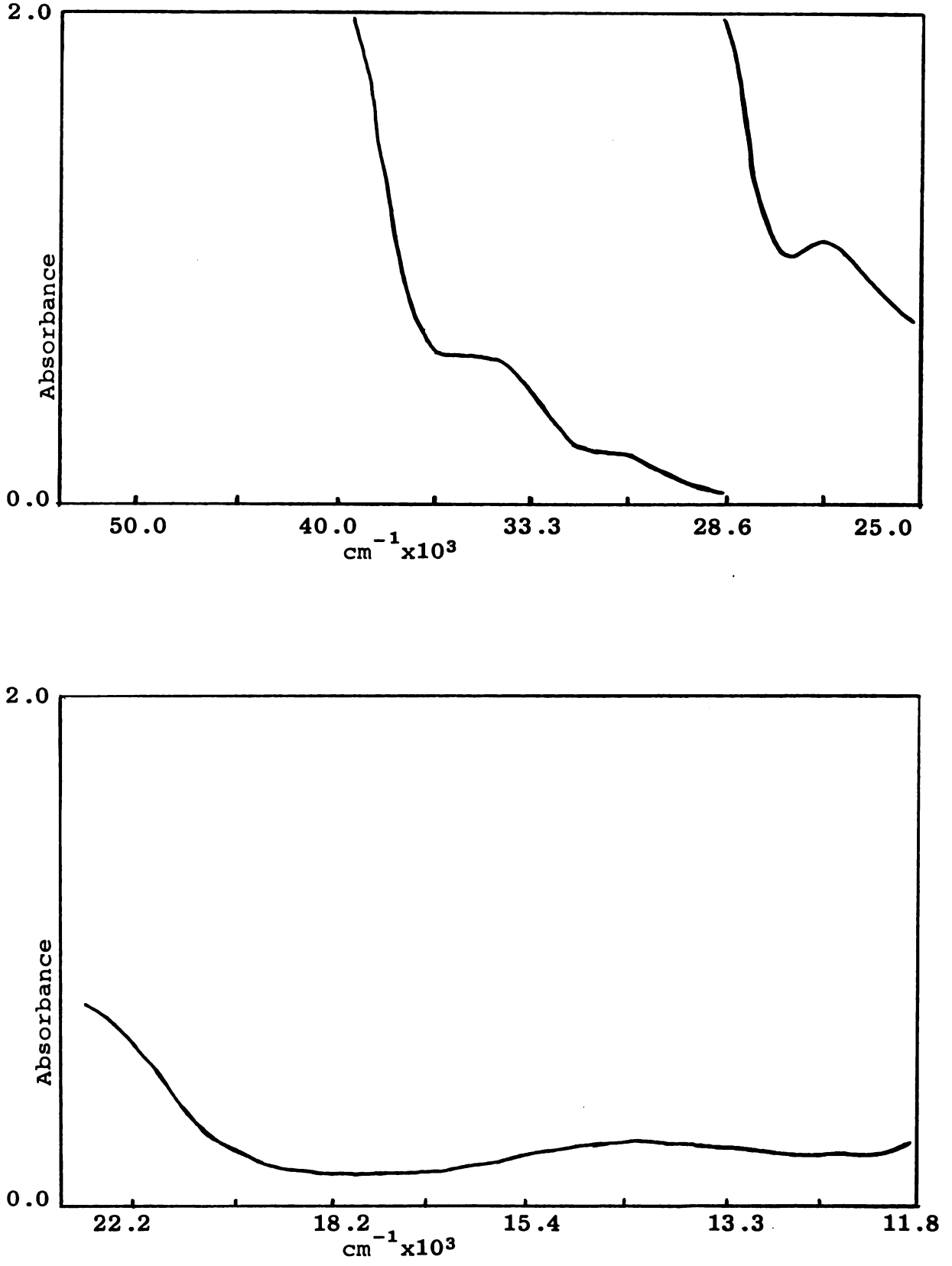


Figure 8. Solution spectrum of $C_5H_6NW(OC_2H_5)_2Cl_4$ in ethanol.

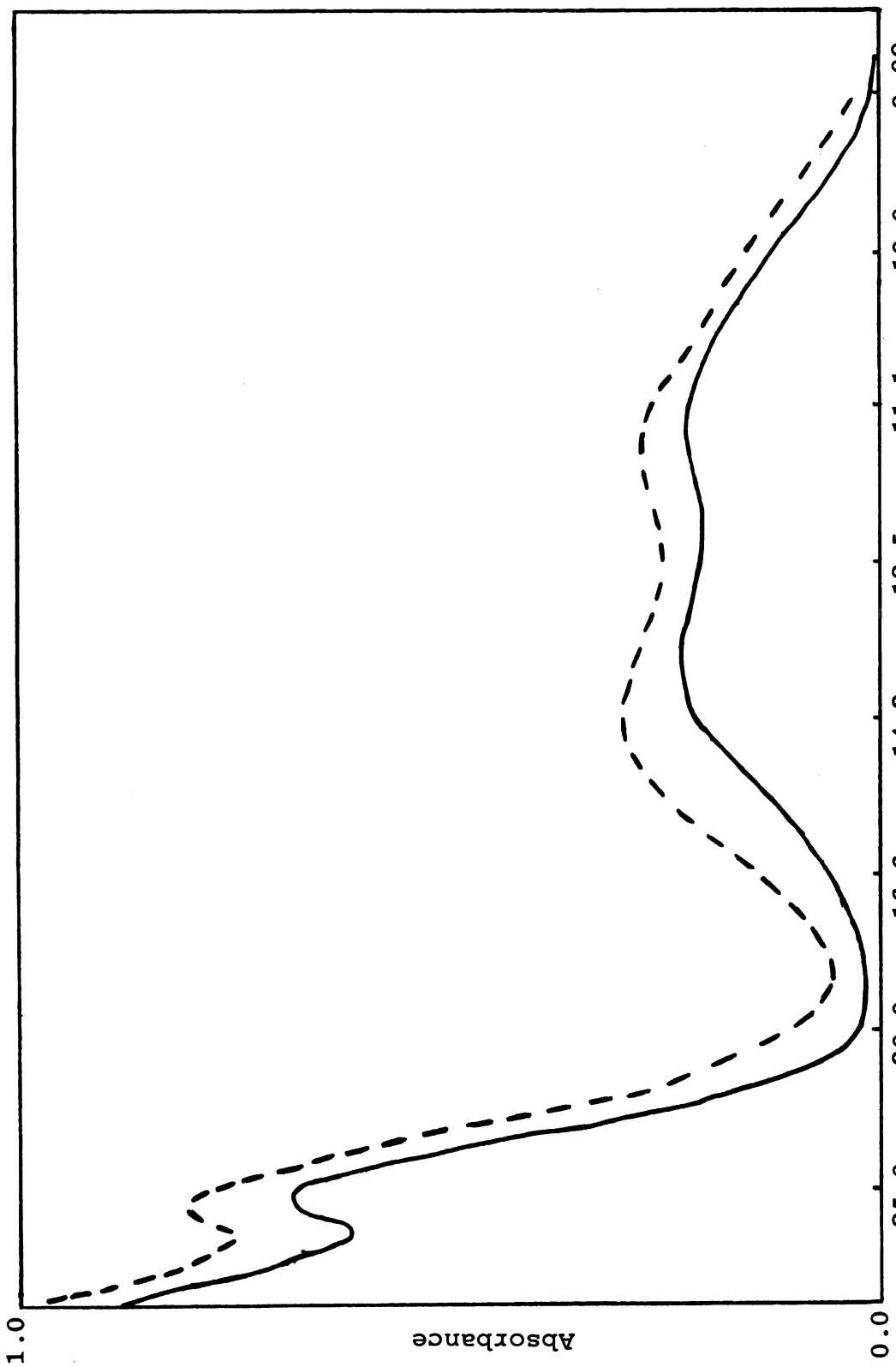


Figure 9. Solution spectrum of $C_5H_6NW(OCH_3)_2Cl_4$ (------) in methanol; and $C_5H_6NW(OC_2H_5)_2Cl_4$ (———) in ethanol.

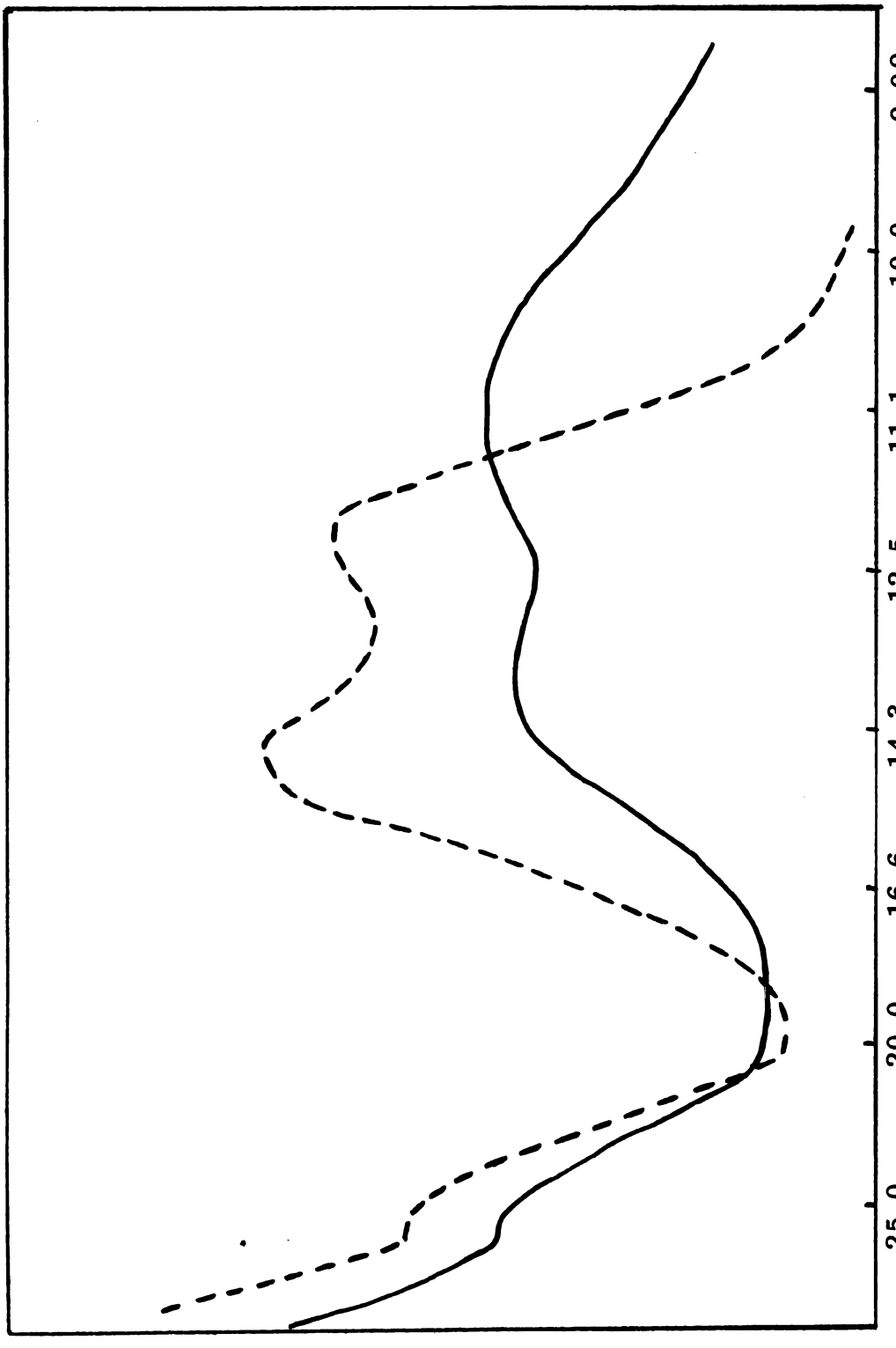


Figure 10. Solid reflectance spectrum of $C_5H_6NW(OCH_3)_2Cl_4$ (———); and $C_5H_6NW(OC_2H_5)_2Cl_4$ (- - - - - -).

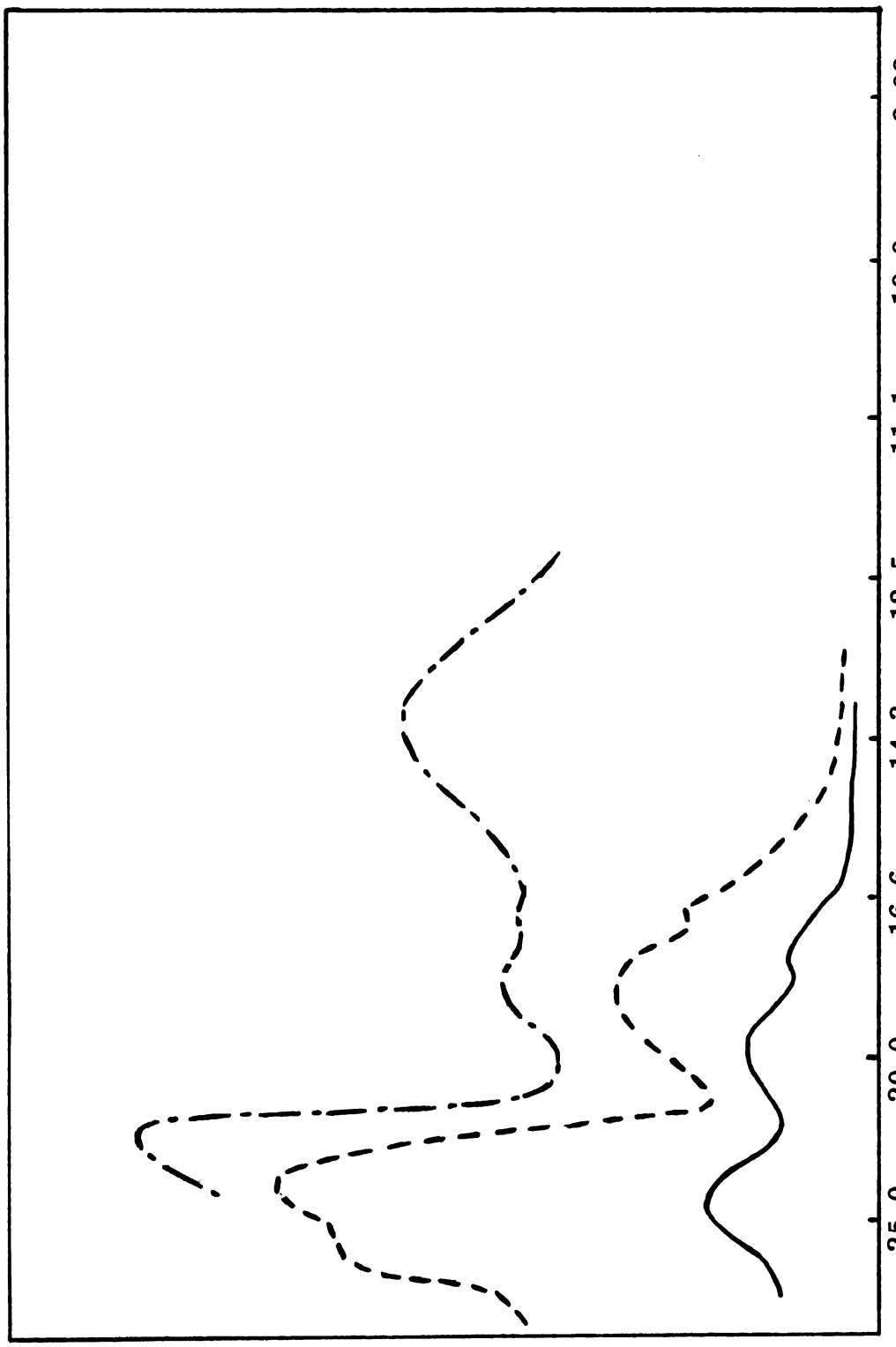


Figure 11. Solid reflectance spectrum of $(C_2H_5)_4NW(NCS)Cl_5$ (————); $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$ (- - - -), and $(C_2H_5)_4NW(OC_2H_5)(NCS)Cl_4$ after two weeks (— - — - —).

to highest energy are the b_2 (dxy), the degenerate e (dxz, dyz), the b_1 (dx^2-y^2) and the a_1 (dz^2). Thus three d-d transitions are spin allowed. Molar absorptivities for these Laporte forbidden bands should be low (~10).

For the tungsten oxo or dialkoxo compounds, the bands at ~12.0 x 10^3 cm^{-1} and ~14.0 x 10^3 cm^{-1} are probably the B_2 ⟶ E transition. The two transitions are probably due to a removal of the degeneracy of the E state. The B_2 ⟶ B_1 transition may be located at ~23.0 x 10^3 cm^{-1}. The other d-d transition is probably obscured by the charge-transfer bands at higher energy.

The absorption bands for the thiocyanate complexes are located at about 16.0 x 10^3 cm^{-1} and also indicate the low ligand field strength of the thiocyanate ion. The t_{2g} orbital is not split to a great extent since these values are close to the 10Dq value for WCl_6^- at 21.7 x 10^3 cm^{-1}. After the compound had stood in a sealed tube for two weeks, the spectrum of $(C_2H_5)_4NW(NCS)(OC_2H_5)Cl_4$ showed a strong band in the region of 14.0 x 10^3 cm^{-1}. This band was absent from the spectrum of a freshly prepared sample and is probably due to the presence of oxychloride decomposition products.

B. W(V) and W(IV) Dimeric Complexes

1. Preparation of Complexes

Color changes were observed during the titration of WCl_5 alcohol solutions with alkoxide ion solutions. Table V summarizes these results for an ethanol solution. Similar changes occurred in methanol and 1-propanol. No further colors were noted for alkoxide to tungsten ratios greater than 6:1. The visible spectra of these solutions were characterized by intense charge transfer bands which gradually shifted into the visible region with greater alkoxide concentration.

Table V. WCl_5 in basic ethanol solutions.

Ratio $^-OC_2H_5/W$	Color
0	green
2:1	red-brown
4:1	dark-brown
6:1	blue

A new preparative method was developed to isolate the complexes present in these basic alcohol solutions. A WCl_5 sample was allowed to react with the neutral alcohol, then a stoichiometric amount of alkoxide ion dissolved in alcohol was added. After filtration to remove the sodium or potassium

chloride that was formed, the resulting solution was allowed to reflux for 1-2 hours. The complex crystallized after the reaction solution was allowed to cool to -10^0. The red, diamagnetic complexes, $W_2Cl_4(OR)_6$, R = C_2H_5, 1-C_3H_7 were isolated from solutions with an alkoxide to tungsten ratio of 2:1. The ethoxide complex, $W_2Cl_4(OC_2H_5)_6$, was previously prepared by the prolonged alcoholysis of WCl_6.[57] Brown, diamagnetic complexes $W_2Cl_2(OR)_8$, R = C_2H_5, 1-C_3H_7, were prepared when the WCl_5 alcohol solution was treated with an alkoxide solution where $^-OR/W = 4:1$.

A red-black liquid, $W(OC_2H_5)_5$, was obtained after a WCl_5 ethanol solution was treated with an ethoxide solution with $^-OC_2H_5/W = 5:1$. Vacuum distillation was necessary to obtain this compound in a pure form. A yellow, paramagnetic solid, probably $NaW(OC_2H_5)_6$, was isolated after an alkoxide solution with $^-OC_2H_5/W = 6:1$ was added to the neutral WCl_5 ethanol solution. This complex was unstable and satisfactory elemental analyses were not obtained.

Solid W(IV) chloride alkoxides, $W_2Cl_4(OR)_4(ROH)_2$, and solutions containing W(V) species were obtained when WCl_4 was allowed to react with the various alcohols. 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 possibility that the starting material was contaminated with WCl_5 can be discounted. The WCl_4 was purified by heating under vacuum at 325^0. Under these conditions, WCl_5 would have sublimed away from the tetrahalide.

The compounds, $W_2Cl_4(OR)_4(ROH)_2$, were the only stable W(IV) species 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. The reason for the instability of the tetraethoxide may be similar to that postulated for the niobium analogue. Bradley[87] has suggested the cause for the instability of the tetraalkoxide of niobium in the presence of alcohol,

$$2\ Nb(OR)_4 + 2ROH \longrightarrow 2\ Nb(OR)_5 + H_2.$$

A similar reaction may be involved in the tungsten tetraethoxide decomposition. The main product from attempts to prepare $W(OC_2H_5)_4$ was the pentavalent derivative, $W(OC_2H_5)_5$. However, Wentworth and Brubaker[88] successfully prepared $Nb(OC_2H_5)_4$, which may indicate that Bradley's argument is not valid.

The W(IV) alkoxoalcohol complexes are very similar to the W(III) compounds, $W_2Cl_4(OR)_2(ROH)_4$, R = CH_3, C_2H_5, C_3H_7, prepared by Clark and Wentworth.[64] However, products different from those reported by Clark and Wentworth were isolated from the reaction of the ethoxo-ethanol compounds with pyridine. A brown, air-sensitive material was reported[64] as the result of the reaction of the W(III) complex with pyridine. An orange compounds, $W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$, was isolated from the analogous reaction of the W(IV) ethoxo-ethanol compound.

The dimeric formulation for these W(V) and W(IV) compounds is supported by mass spectra and molecular weight determinations. The diamagnetism and far ir and pmr spectra of the chloro-alkoxo compounds suggest that the structure of these complexes may be a chloride bridged bioctahedron.

2. Mass Spectra and Molecular Weight Determinations

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. The same formulation for the other compounds is suggested by the similarity of their chemical and physical properties.

Molecular weight determinations in benzene (cryoscopic method) were performed by Galbraith Laboratories, Inc. The results for the compounds, $W_2Cl_4(OC_3H_7)_6$ (1040) and for $W_2Cl_4(OC_3H_7)_4(C_3H_7OH)_2$ (1013) were higher than the calculated molecular weights, 864 and 866, respectively. Partial dissociation of the complexes in solution is a possible explanation of these results. Conductivity data were not obtained for these solutions.

3. Magnetic Susceptibility and Oxidation State Determinations

All of the compounds formulated as dimers were diamagnetic. A chloride bridged bioctahedral structure was proposed for $W_2Cl_4(OC_2H_5)_6$ by Klejnot.[57] The other W(V) and W(IV) dimeric compounds prepared in this study probably have similar structures. Thus, the diamagnetism can be explained in terms of metal-metal bonding resulting from overlap of orbitals on adjacent tungsten atoms. If the

tungsten ions are shifted from the centers of their octahedra toward each other, as is observed for the niobium and tungsten tetrahalides, then overlap would be even more favorable. The oxidation state determinations confirmed the formulation of these complexes as W(V) or W(IV) derivatives.

4. Infrared Spectra

The infrared features of the W(V) and W(IV) dimers are listed in Tables VI and VII. Sketches of the spectra are given in Figures 12 to 19.

These compounds have near ir absorptions characteristic of bound alkoxide in the 1000-1100 cm^{-1} region. The complexity of the spectra in this region may be an indication of non-equivalent alkoxide groups and has been interpreted as evidence for bridging and terminal alkoxide groups.[82] However, the far ir spectra of these compounds tend to support a chloride bridged formulation.

An absorption at about 250 cm^{-1} may be a W-Cl bridge vibration in these W(V) and W(IV) dimers. Similar bands for the dimers, WCl_5 (246 cm^{-1}) and WCl_4 (237 cm^{-1}) have been assigned as bridging chloride vibrations.[43] The terminal W-Cl vibration at about 300 cm^{-1} is in the same region as the W(V) monomers. The presence of a bridging metal-chlorine vibration about 50 cm^{-1} below the terminal vibration was also noted for polymeric cobalt complexes.[8]

Table VI. Infrared absorption frequencies (cm^{-1}) of dimeric tungsten species (with possible assignment).

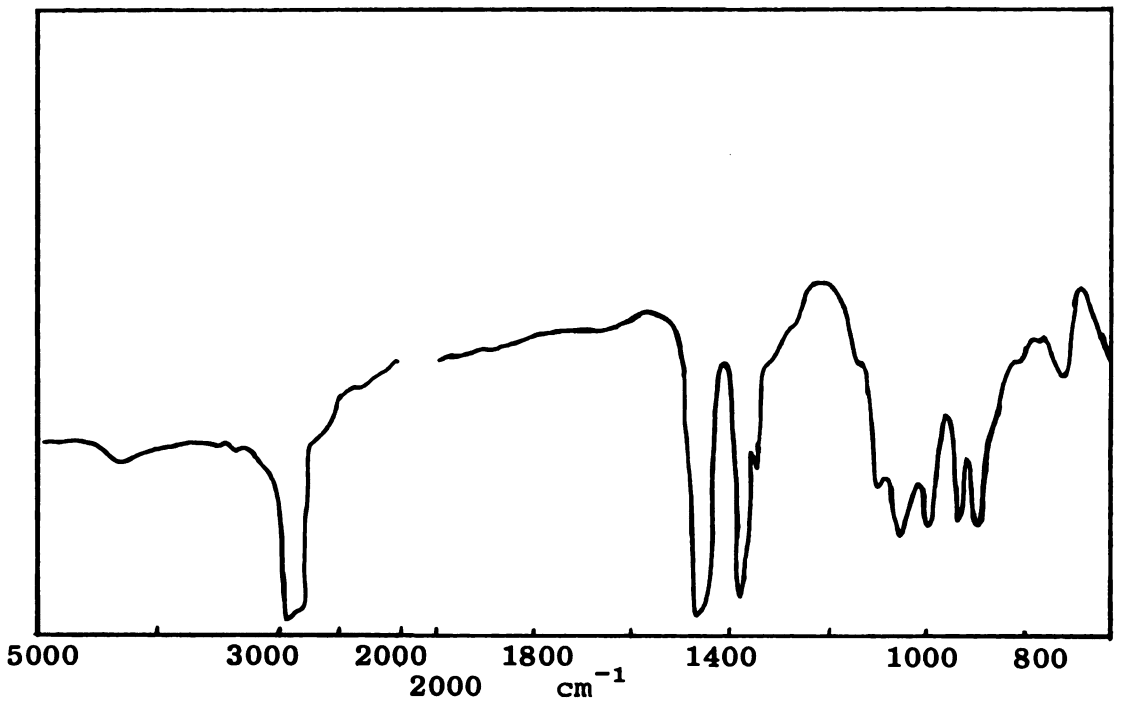
$W_2Cl_2(OC_2H_5)_8$		$W(OC_2H_5)_5$	
600 (s)	ν (W-O)	615 (s)	ν (W-O)
519 (s)	ν (W-O)	582 (s)	ν (W-O)
387 (m)	ν (O-W-O)	550 (sh)	
282 (s)	ν (W-Cl)		
228 (m)	ν (W-Cl)		
$W_2Cl_4(OC_3H_7)_6$		$W_2Cl_4(OCH_3)_4(CH_3OH)_2$	
652 (m)		575 (m)	ν (W-O)
619 (s)	ν (W-O)	532 (s)	ν (W-O)
575 (s)	ν (W-O)	476 (s)	
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)			
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$		$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$	
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)		

Table VI. (Continued)

$W_2Cl_4(2\text{-}OC_3H_7)_4(C_3H_7OH\text{-}2)_2$		$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$	
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)	(W-O)
449 (m)		476 (m)	ν (O-W-O)
407 (m)		449 (w)	
307 (sh)	ν (W-Cl)	397 (w)	
294 (s)		315 (sh)	ν (W-Cl)
250 (m)	ν (W-Cl)	291,296 (vs)	ν (W-N)
194 (w)		280 (s)	
		230 (m)	ν (W-Cl)
$W_2Cl_4(OC_2H_5)_6$		205 (w)	
		185 (w)	
617 (s)	ν (W-O)		
515,497 (s)	ν (W-O)		
395 (m)	ν (O-W-O)		
304 (s)	ν (W-Cl)		
284 (s)			
258 (m)	ν (W-Cl)		

Table VII. Features of infrared spectra of W(V), W(IV) compounds (1000-1100 cm^{-1}).

Compound	
$W_2Cl_4(OC_2H_5)_6$	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)
$W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$	1010(s), 1095(s) 1020(s), 1060(sh), 1095(m) $CHCl_3$ sol'n.
$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$	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)



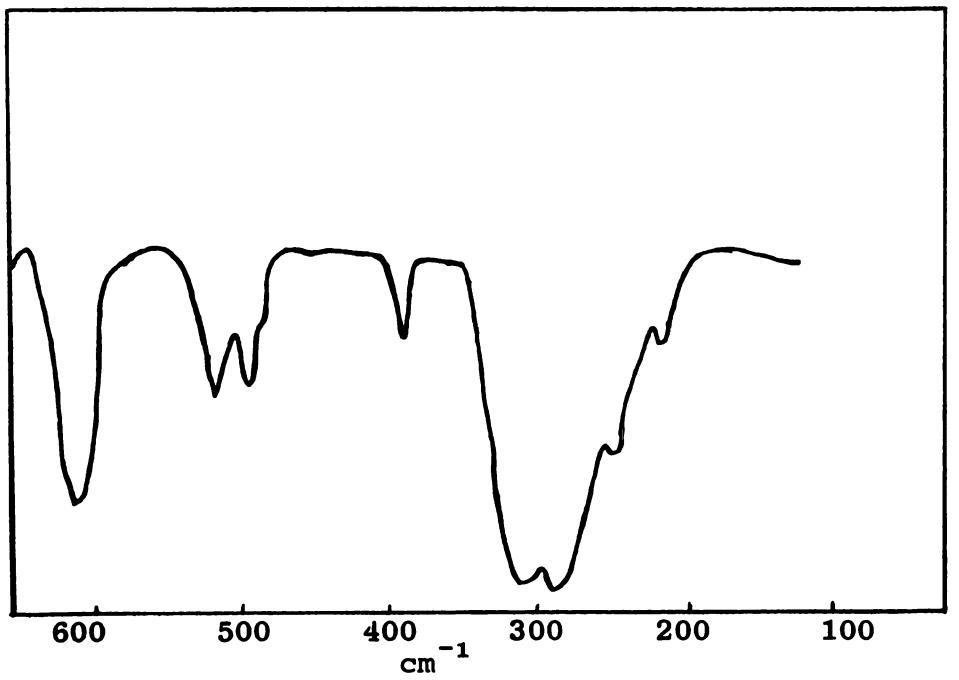
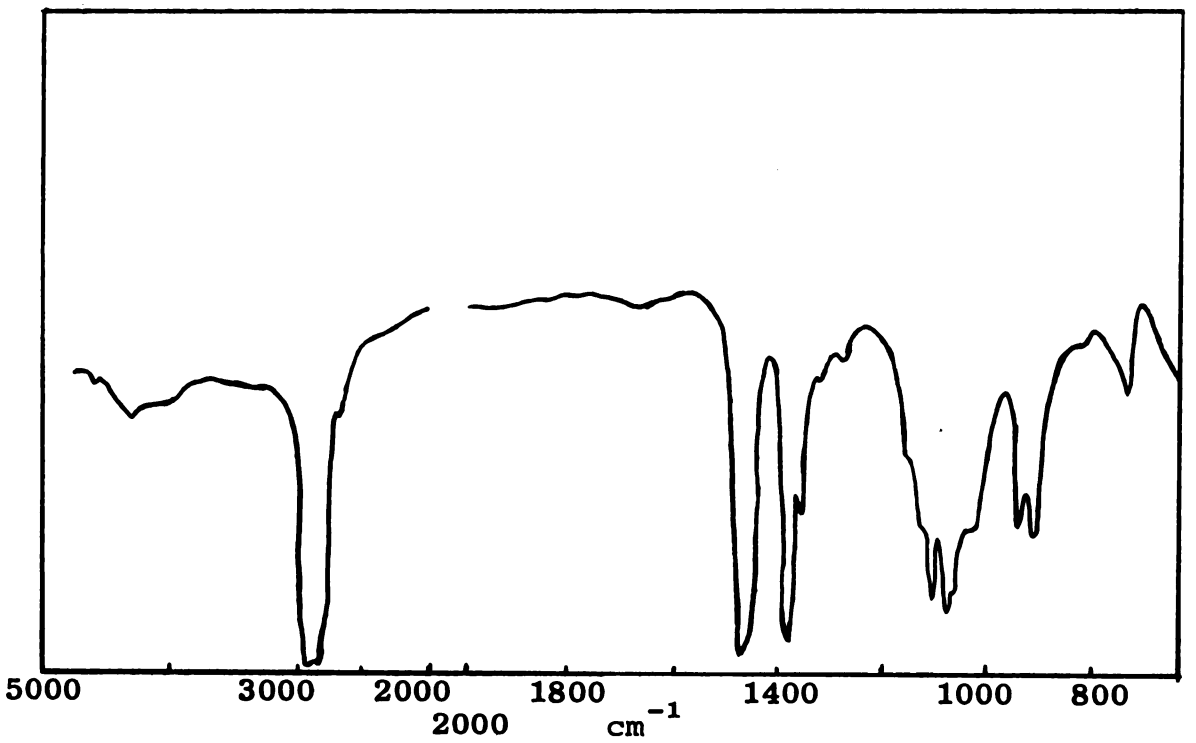


Figure 12. Infrared spectrum of $W_2Cl_4(OC_2H_5)_6$.



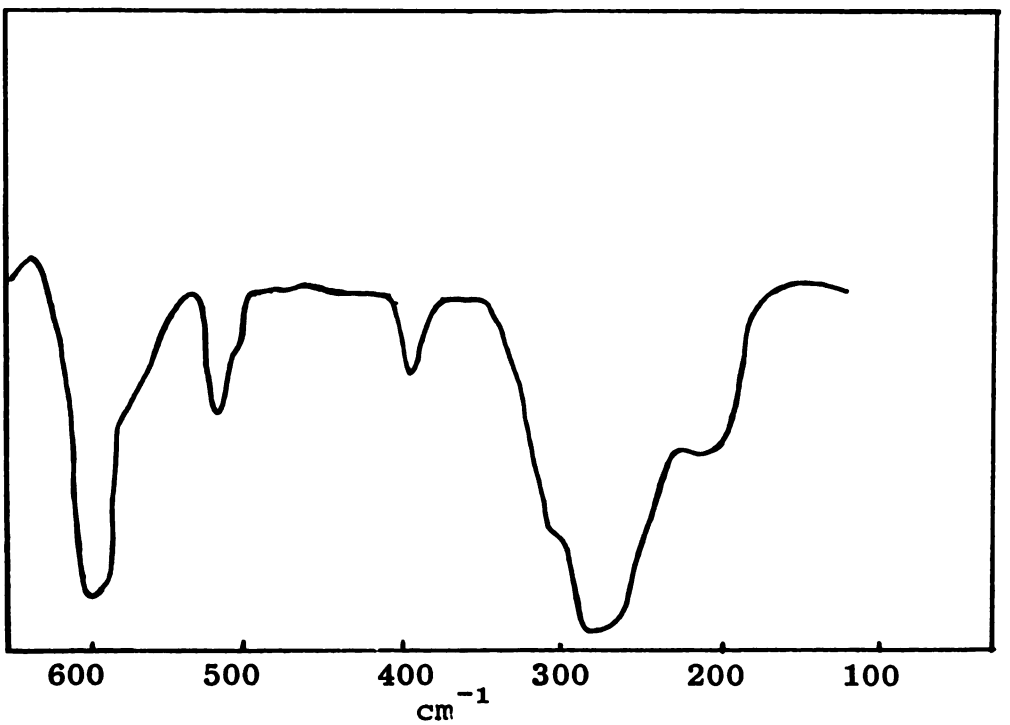
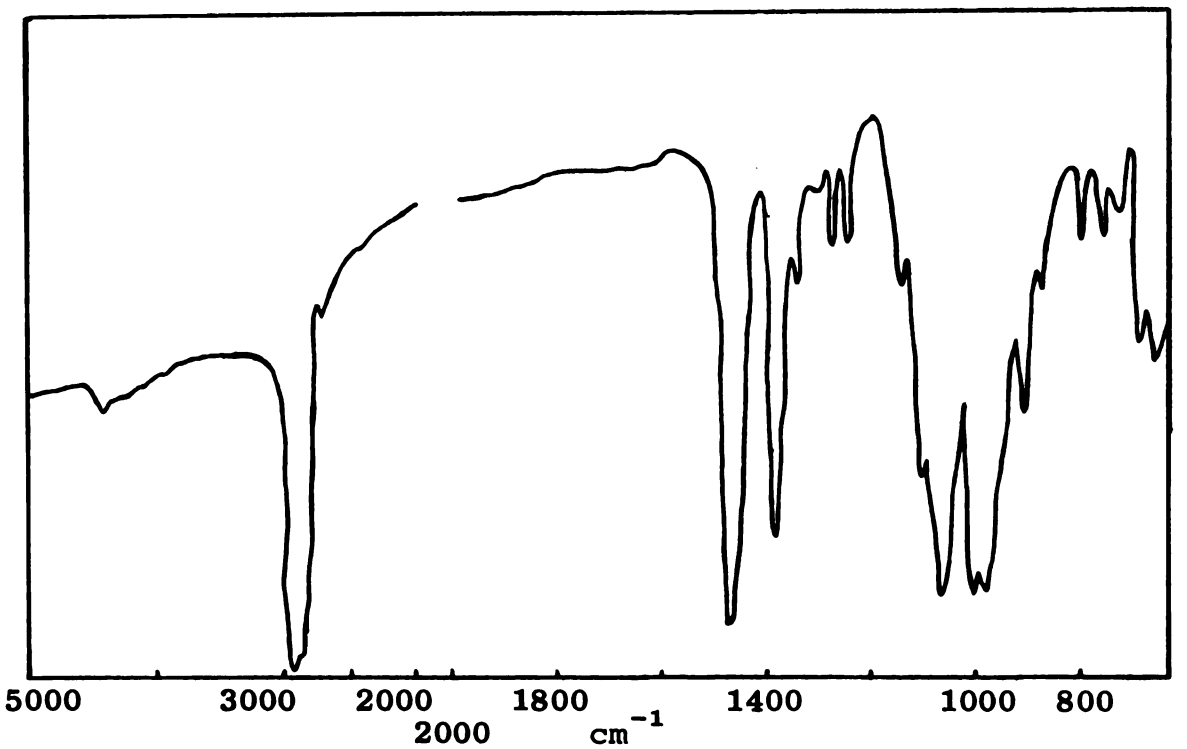


Figure 13. Infrared spectrum of $W_2Cl_2(OC_2H_5)_8$.



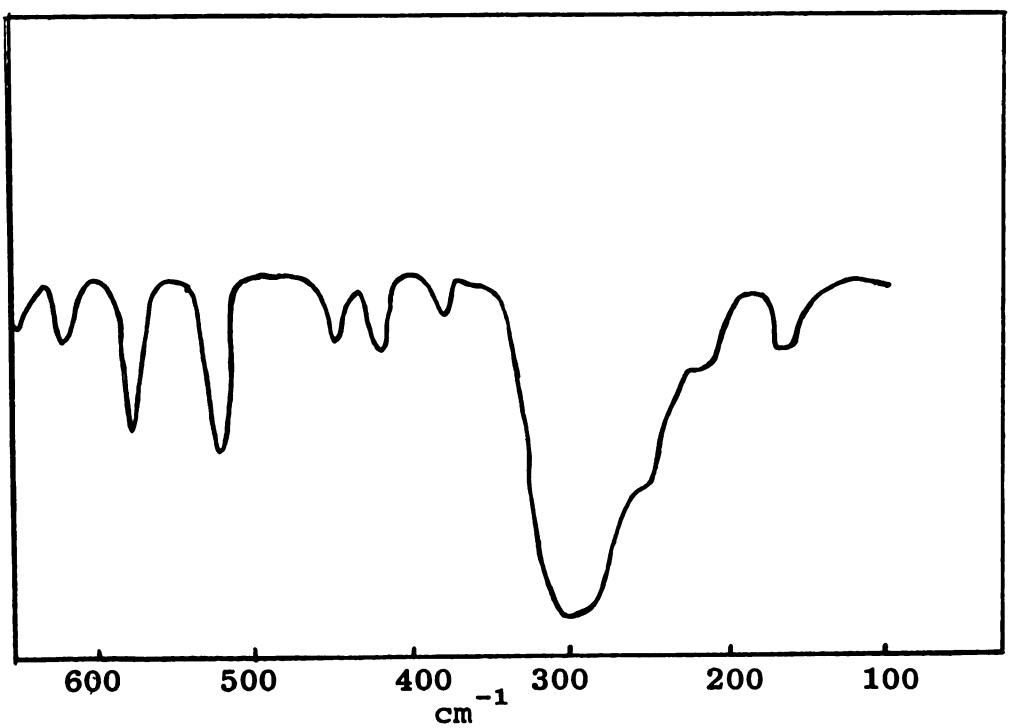
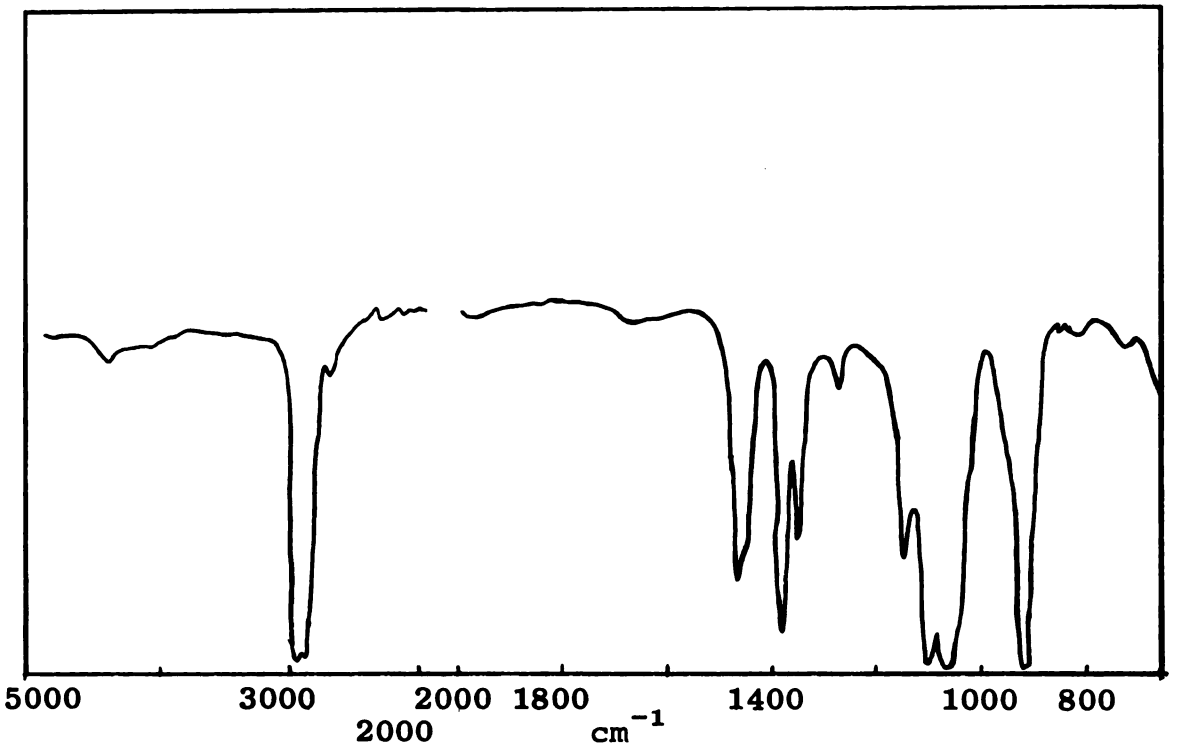


Figure 14. Infrared spectrum of $W_2Cl_4(OC_3H_7)_6$.



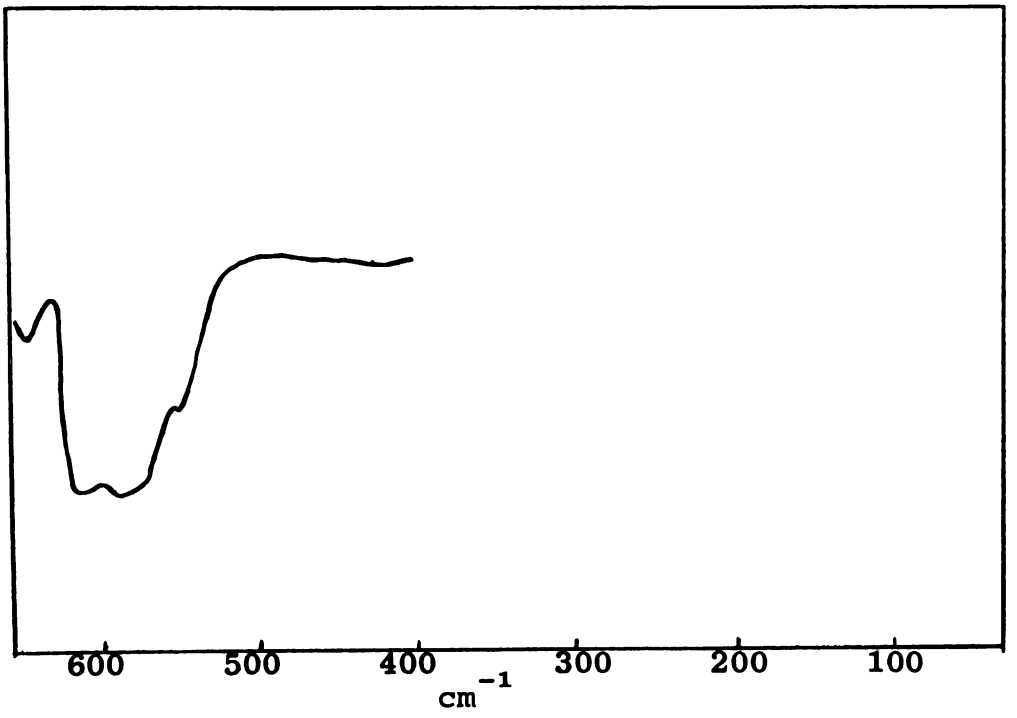
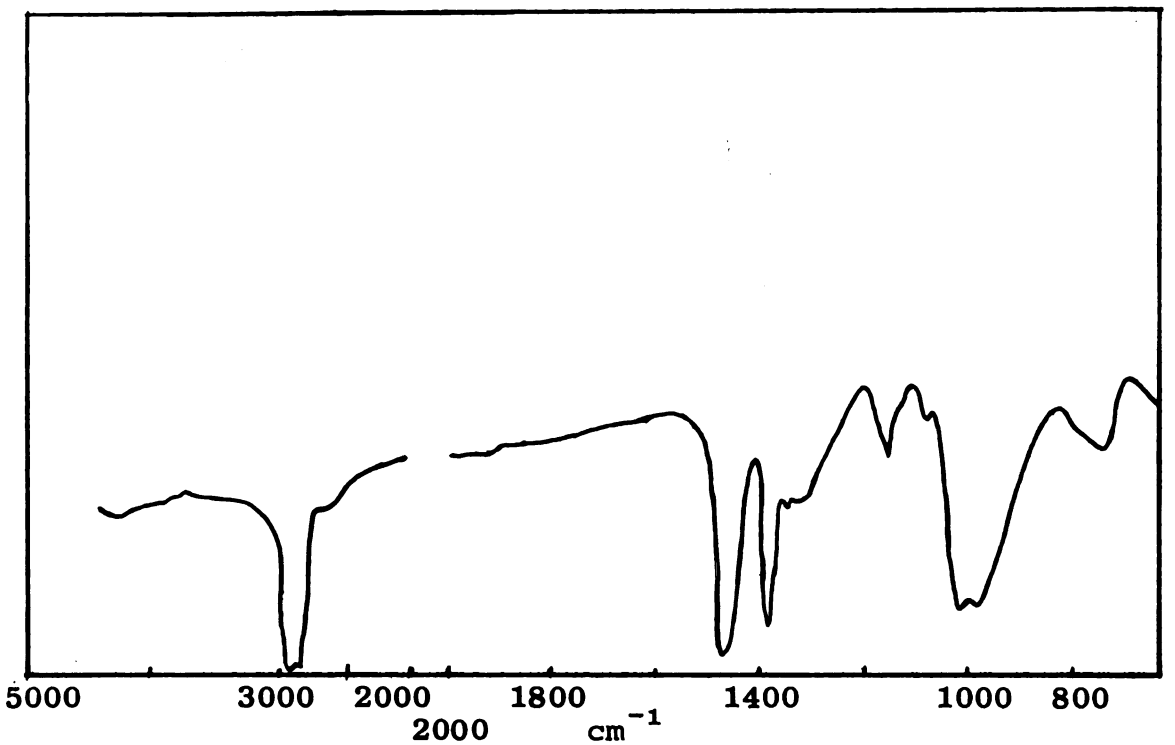


Figure 15. Infrared spectrum of $W(OC_2H_5)_5$.



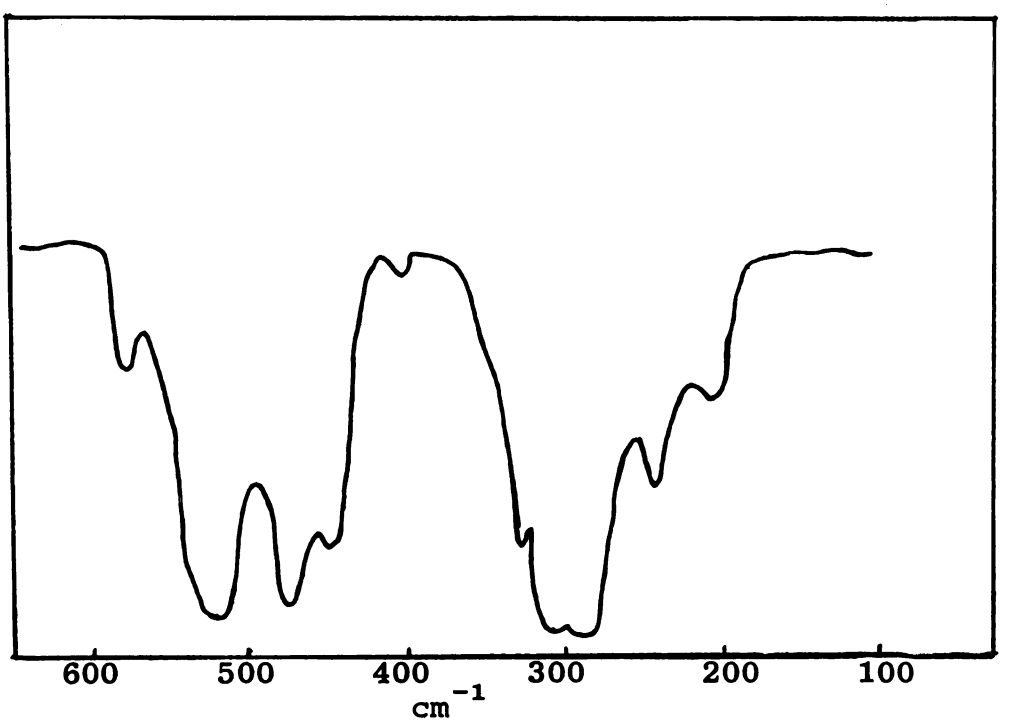
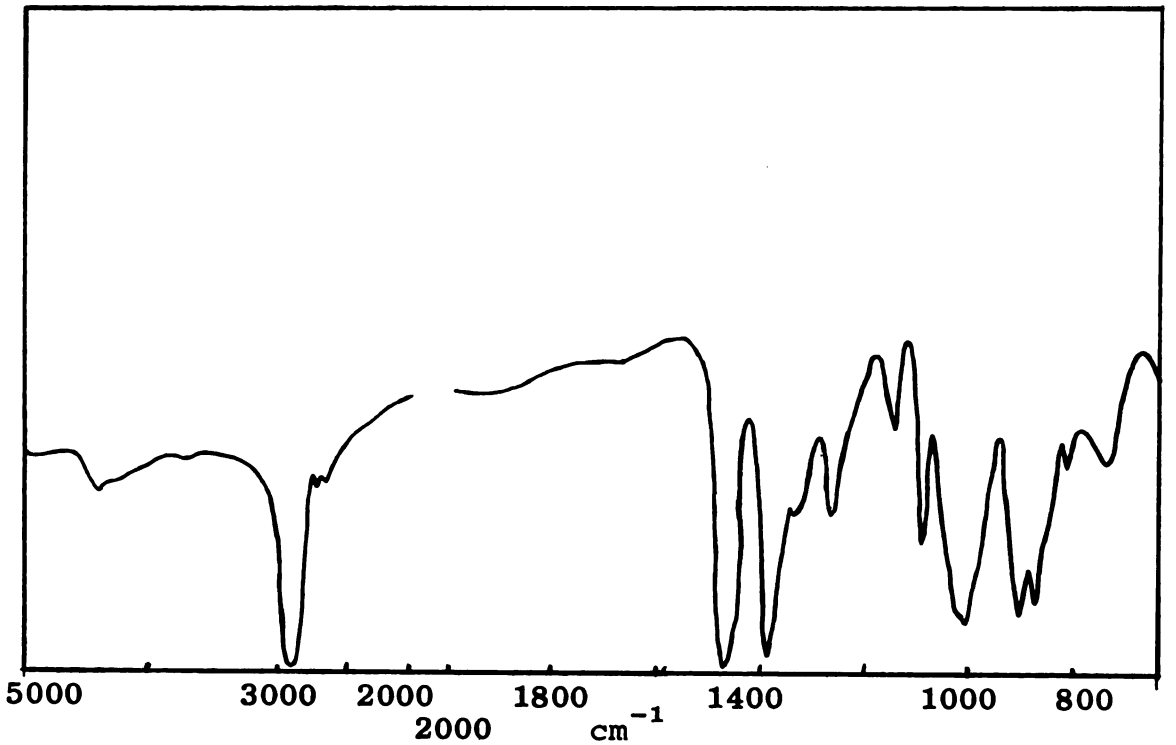


Figure 16. Infrared spectrum of $W_2Cl_4(OCH_3)_4(CH_3OH)_2$.



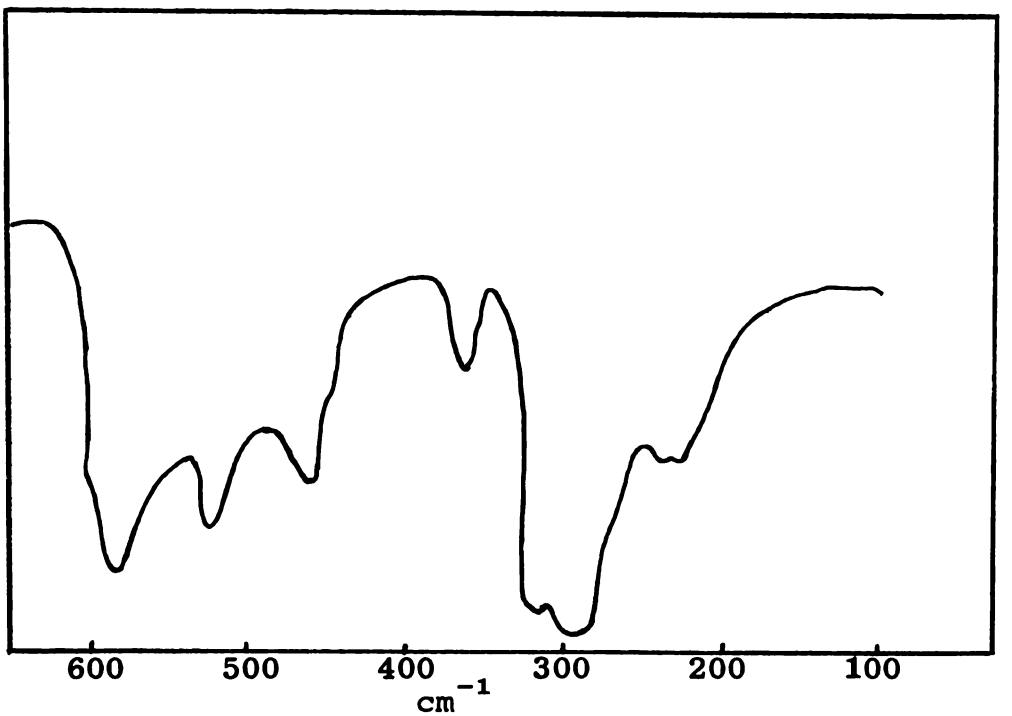
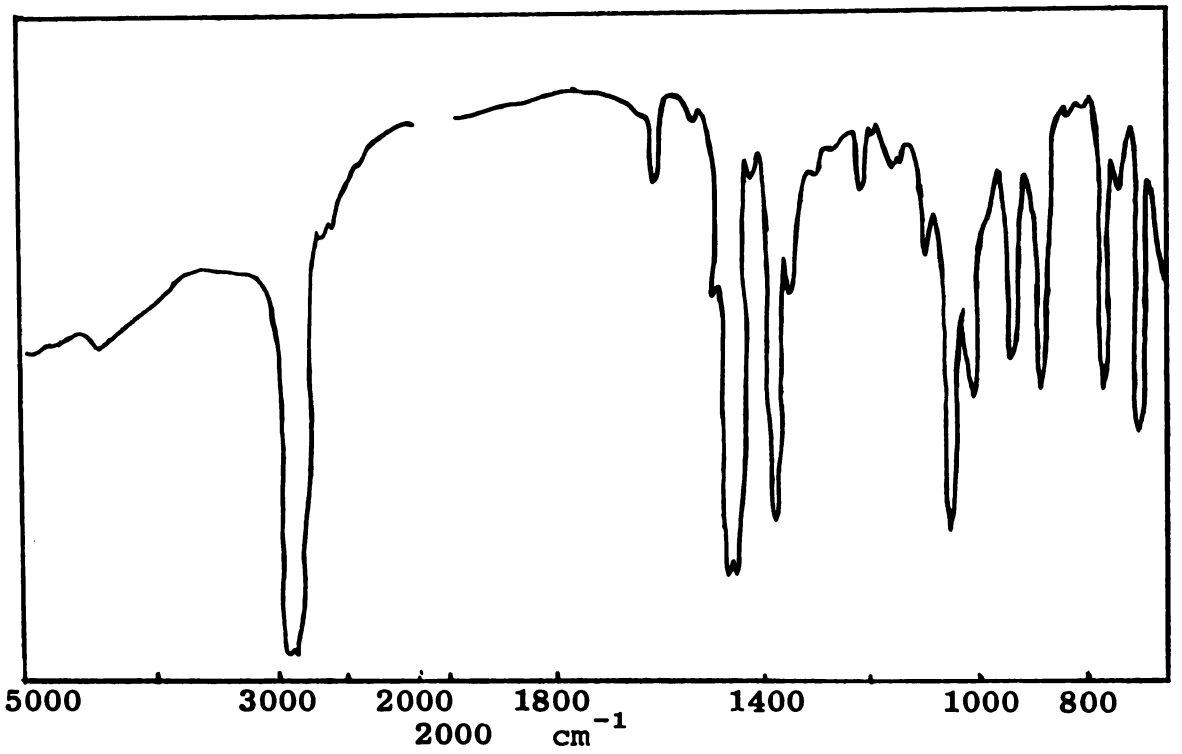


Figure 17. Infrared spectrum of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$.



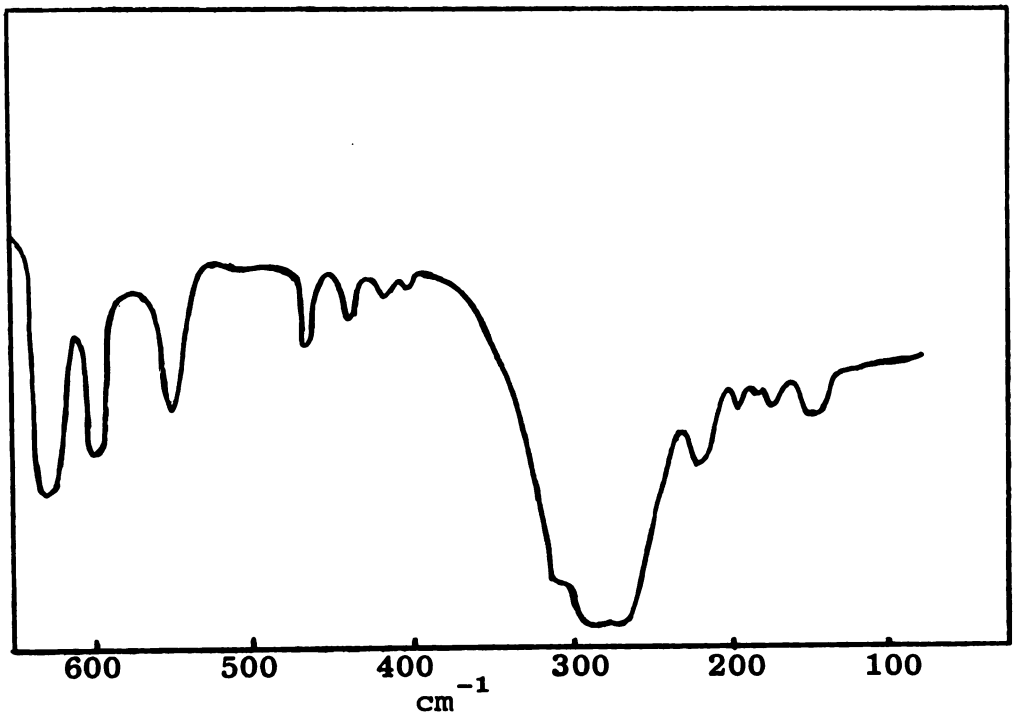
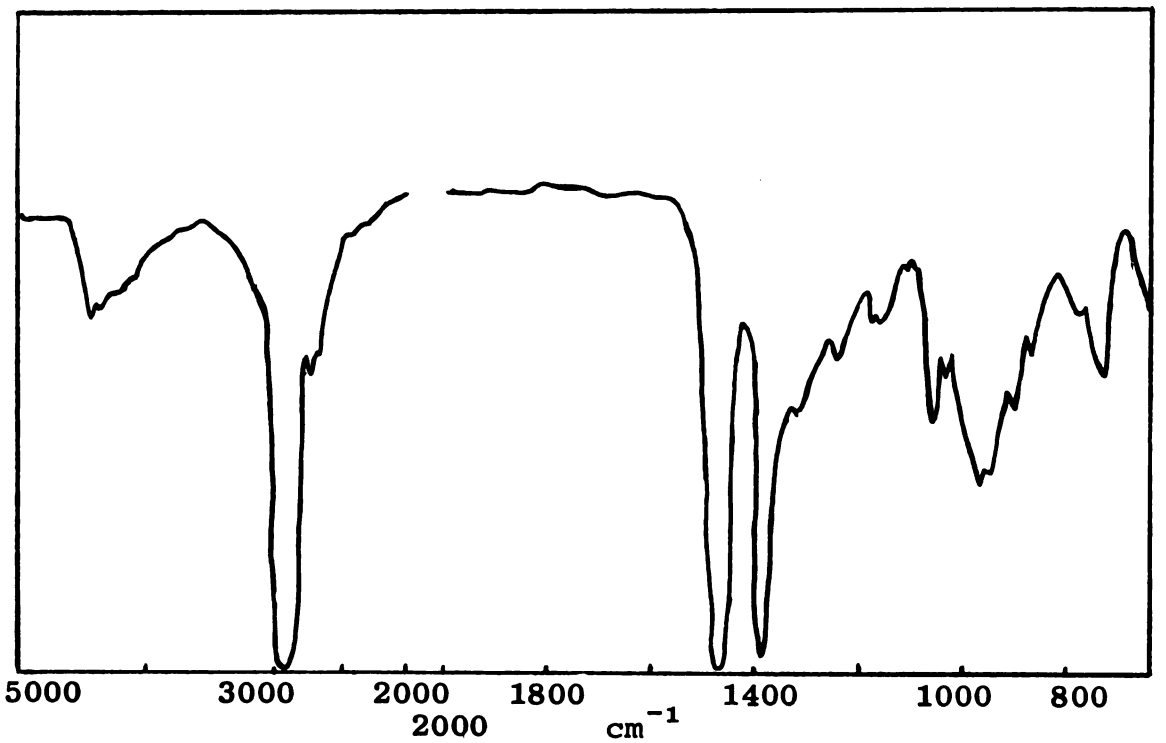


Figure 18. Infrared spectrum of $W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$.



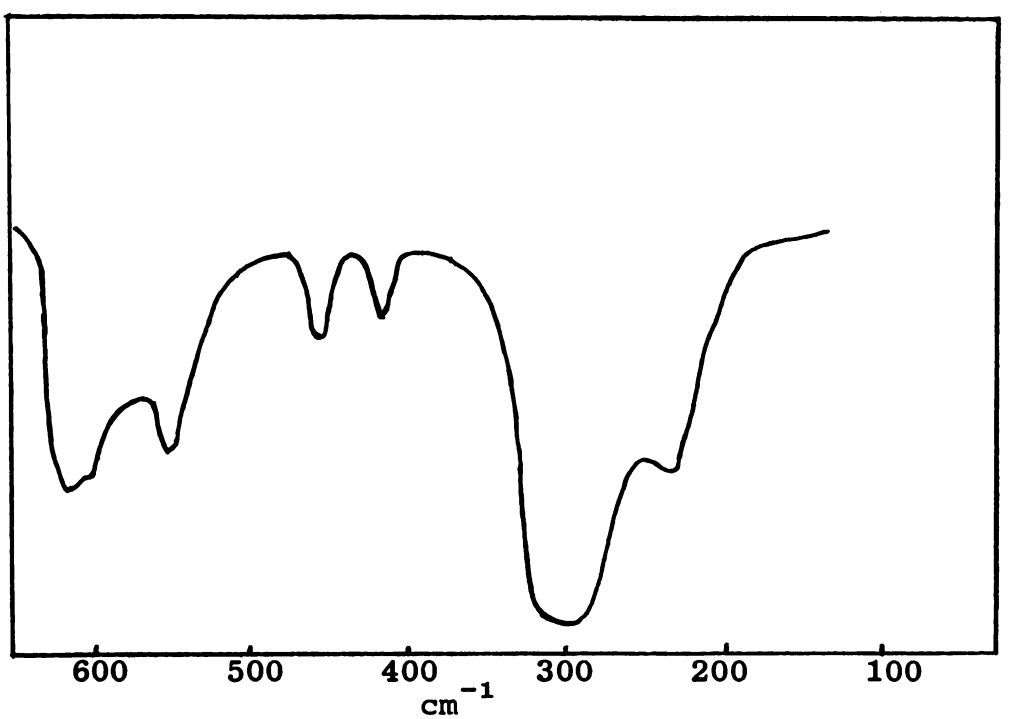


Figure 19. Infrared spectrum of $W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$.

Attempts were made to displace the chloride ions from the chloro alkoxide dimers. Samples were dissolved in alcohol and a saturated solution of KI in alcohol was added. No precipitation occurred even after heating. The relative inertness of the chloride ions to solvolysis and precipitation of KCl may be an indication of chloride bridging. On the basis of similar chemical evidence, Wentworth and Brubaker[88] suggested a chloride bridged structure for the dimer, $Nb_2Cl_2(OC_2H_5)_6(C_5H_5N)_2$.

Tentative assignments of the far ir absorptions were based on previous work with monomeric W(V) alkoxides (see this section Part A). In general, the W-O stretching frequency was observed between 600-500 cm^{-1} and the W-Cl and W-N stretch about 300 cm^{-1}. As the alkoxide increased in size, the metal oxygen stretch increased in frequency. This trend was also noted for monomeric W(V) alkoxides.[90] No apparent change in the W-Cl stretching frequency occurred when the oxidation state changed.

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. Some type of proton exchange is apparently present in these W(IV) alkoxoalcohol complexes.

5. Proton Magnetic Resonance Spectra

The pmr absorptions of the dimers are listed in Table VIII. The spectra are presented in Figures 20 to 25.

Table VIII. PMR spectra of W(V) and W(IV) dimers.[a] (Relative intensities in brackets).

Compound	Solvent	τ $-CH_3$ ppm	τ $-CH_2$ ppm
$W_2Cl_4(OC_2H_5)_6$	CCl_4	1.03(2)	4.57(2)
		1.38(1)	5.83(1)
$W_2Cl_2(OC_2H_5)_8$	CCl_4	.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)
$W_2Cl_4(OC_2H_5)_4(C_5H_5N)_2$[b]	$CHCl_3$	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°.

[b] Reacted with TMS; resonance measured against $CHCl_3$ (7.27 ppm).

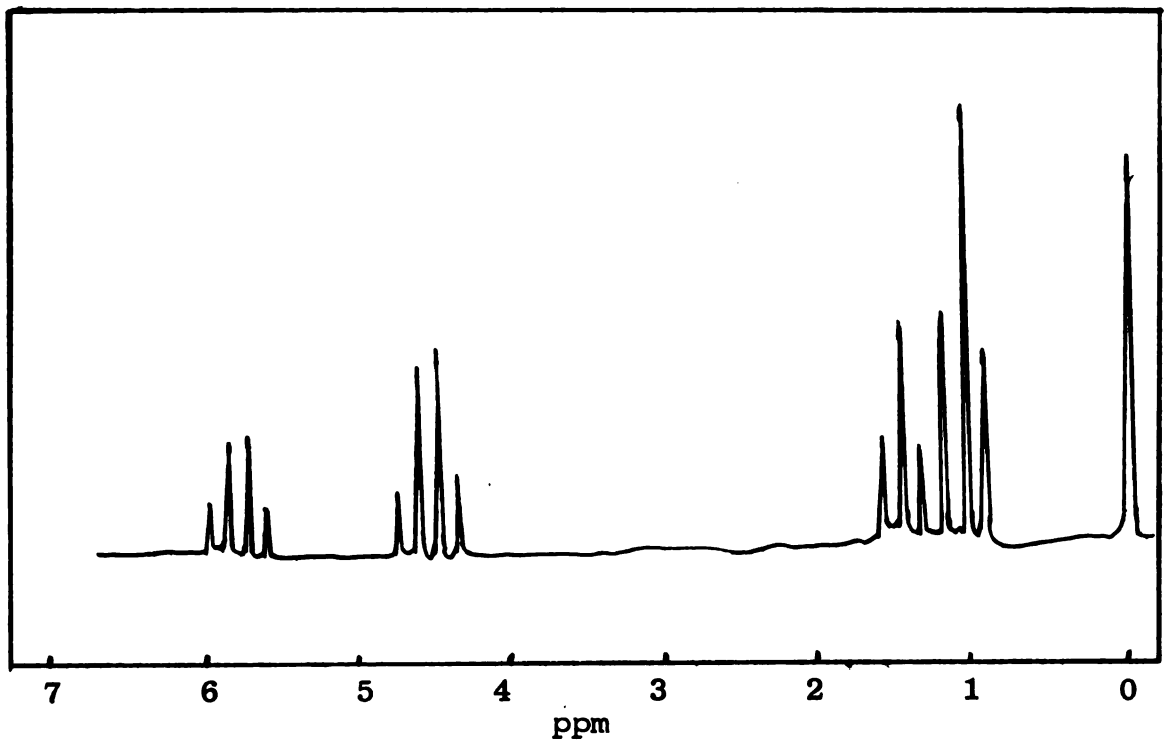


Figure 20. Proton magnetic resonance spectrum of $W_2Cl_4(OC_2H_5)_6$ in CCl_4.

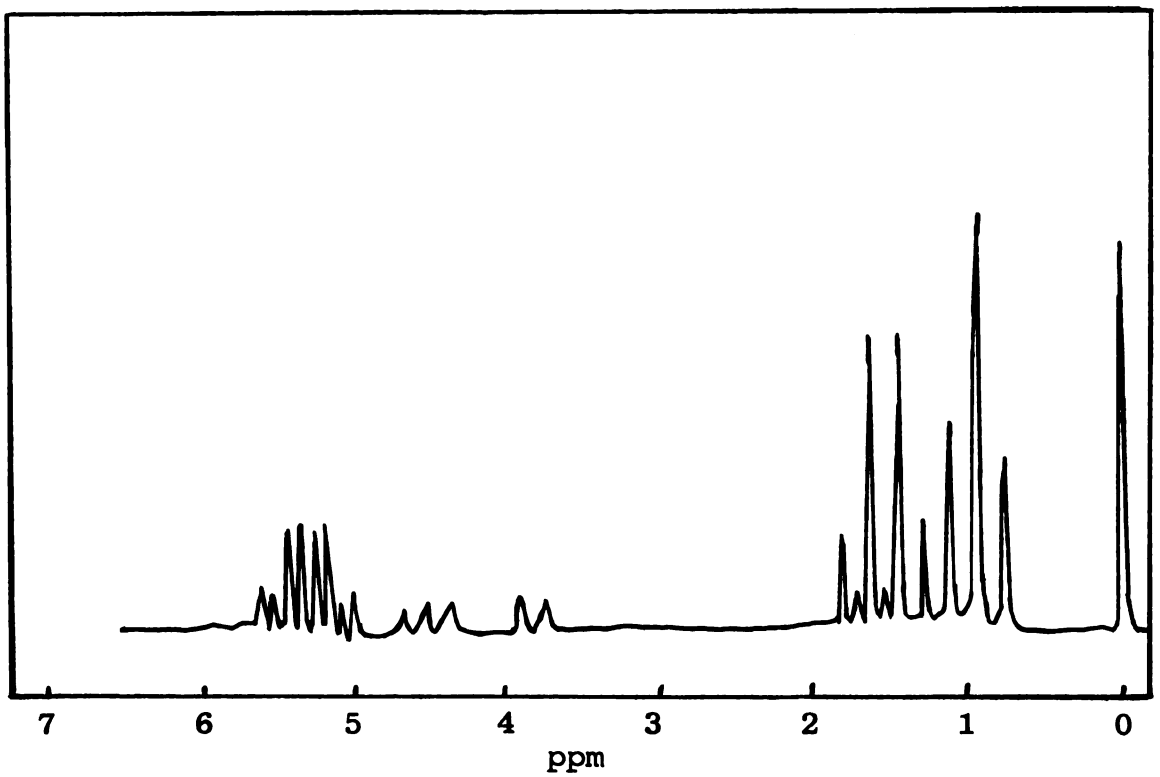


Figure 21. Proton magnetic resonance spectrum of $W_2Cl_2(OC_2H_5)_8$ in CCl_4.

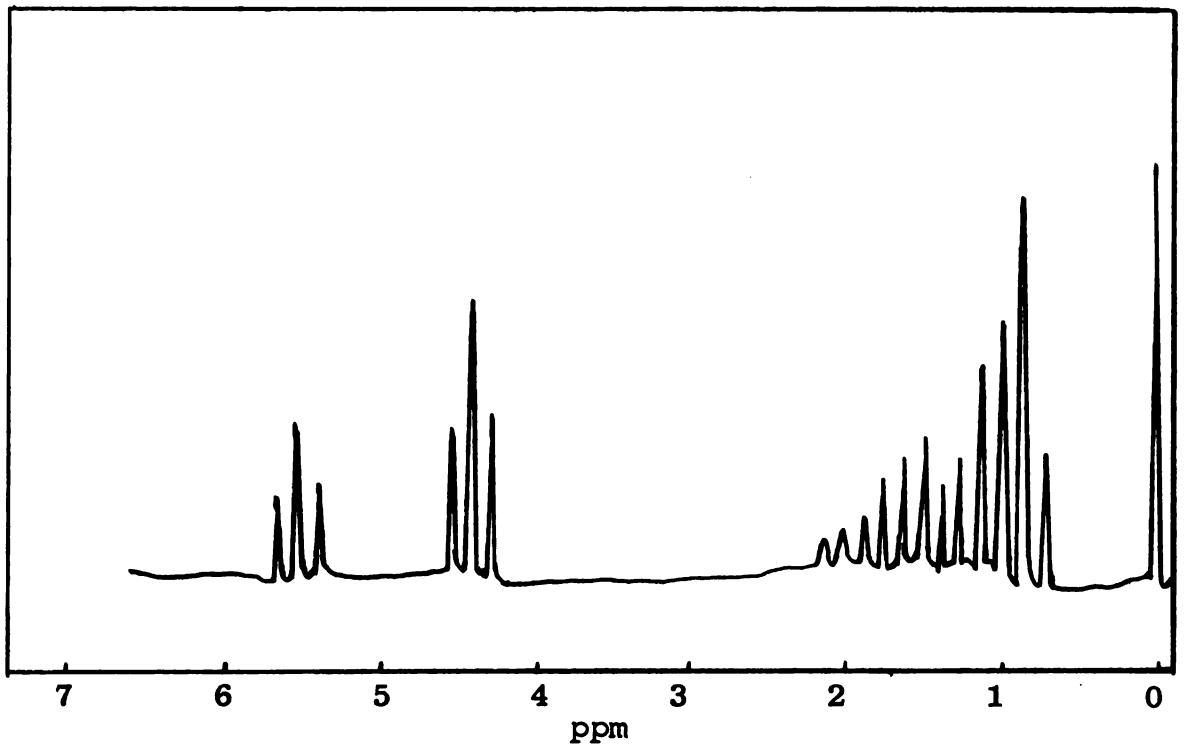


Figure 22. Proton magnetic resonance spectrum of $W_2Cl_4(OC_3H_7)_6$ in CCl_4.

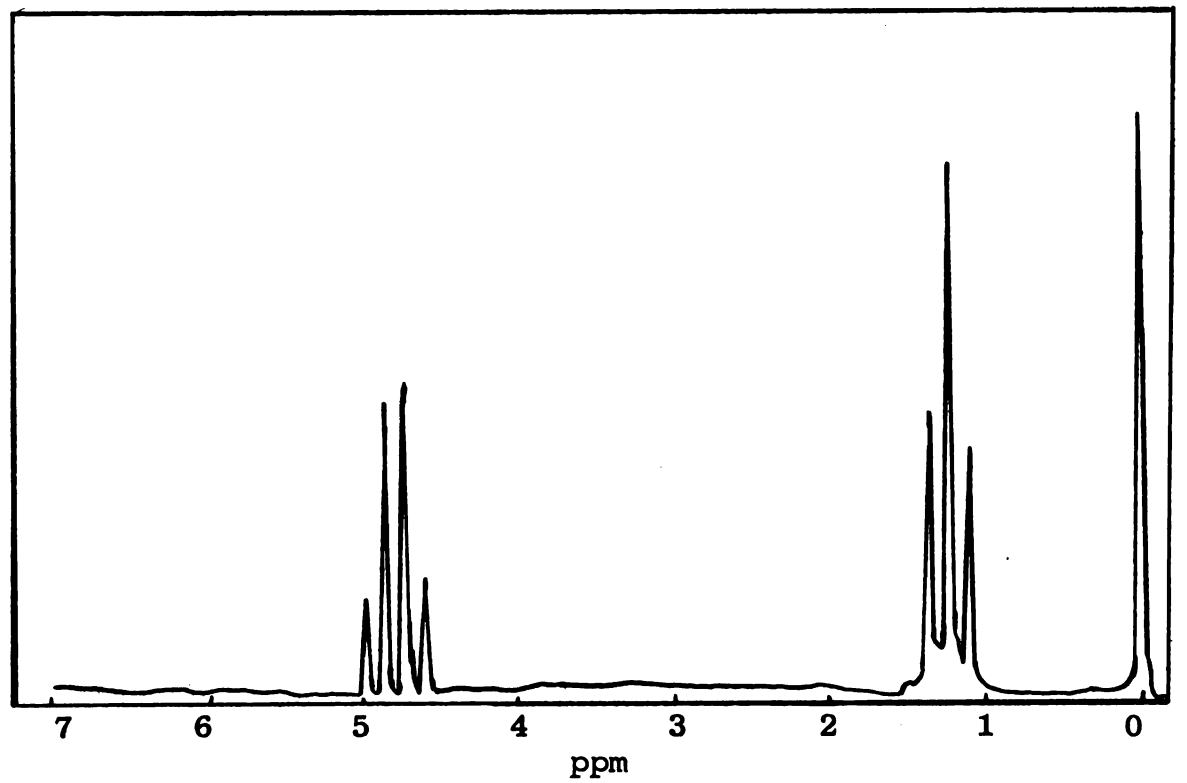


Figure 23. Proton magnetic resonance spectrum of $W(OC_2H_5)_5$ in CCl_4.

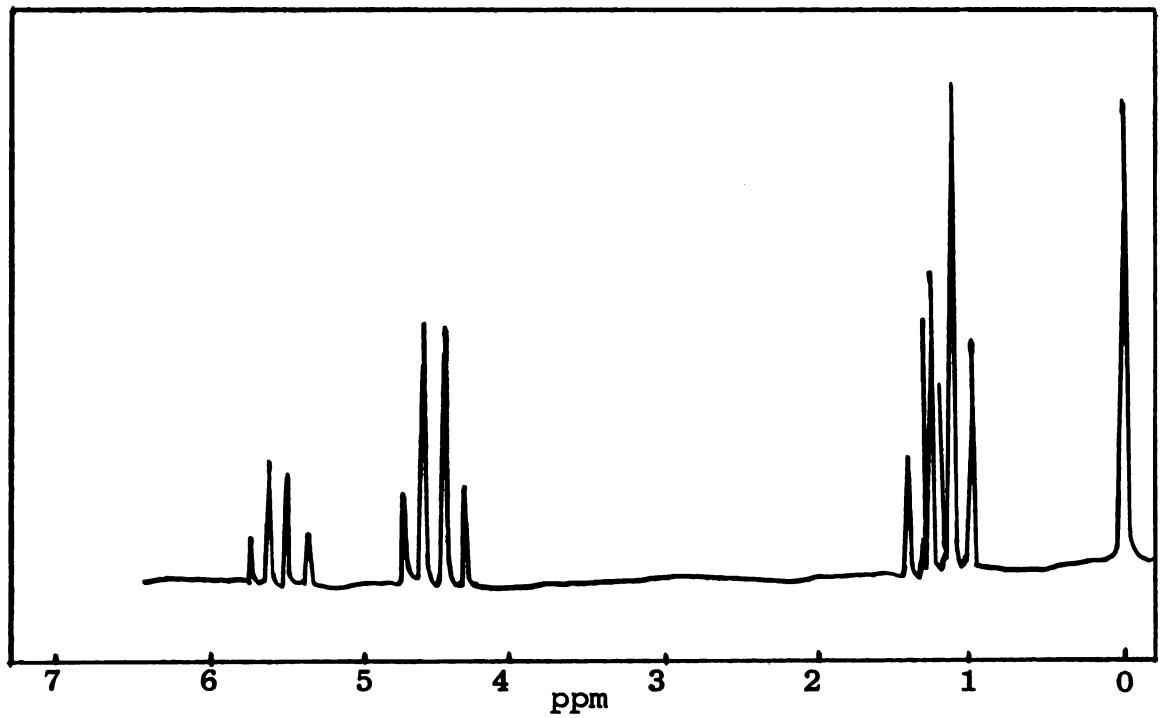


Figure 24. Proton magnetic resonance spectrum of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ in $CHCl_3$.

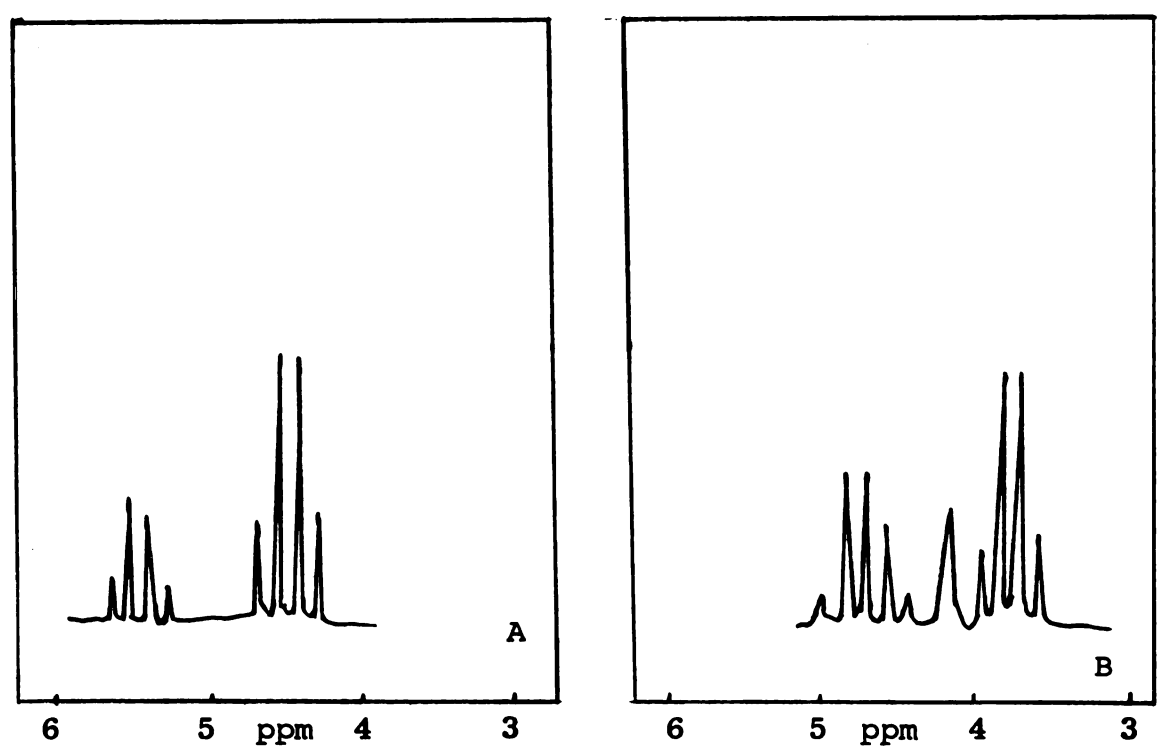


Figure 25. A. Low field pmr spectrum of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$.
B. with DMSO after 15 minutes.

Klejnot[57] reported that the pmr spectrum of $W_2Cl_4(OC_2H_5)_6$ showed two groups of signals with an intensity ratio of 2:1, indicating four and two ethoxide groups in two different environments. These results were confirmed in this work and a similar 2:1 intensity ratio was observed for all other complexes with six alkoxide or alcohol and four chloride ligands. The chloride-bridged bioctahedral structure proposed by Klejnot is shown in Figure 26.

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 possible structure for $W_2Cl_2(OC_2H_5)_8$ is shown in Figure 27. A comparison of the propoxide derivatives was not possible because pure $W_2Cl_2(OC_3H_7)_8$ was not obtained. The pmr and ir spectra are not sufficiently diagnostic to decide absolutely on the nature of the bridging groups. An X-ray structure determination would be required to resolve this question.

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, $W_2Cl_4(OC_2H_5)_6$,[57] $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ and $W_2Cl_4(OC_2H_5)_2(C_2H_5OH)_4$.[64] The pmr spectra of the W(III)[64] and W(IV) alkoxoalcohol complexes did not show a resonance due to the hydroxyl protons of the bound alcohol. Presumably, the lack of an observable signal in the pmr spectrum is the result of proton

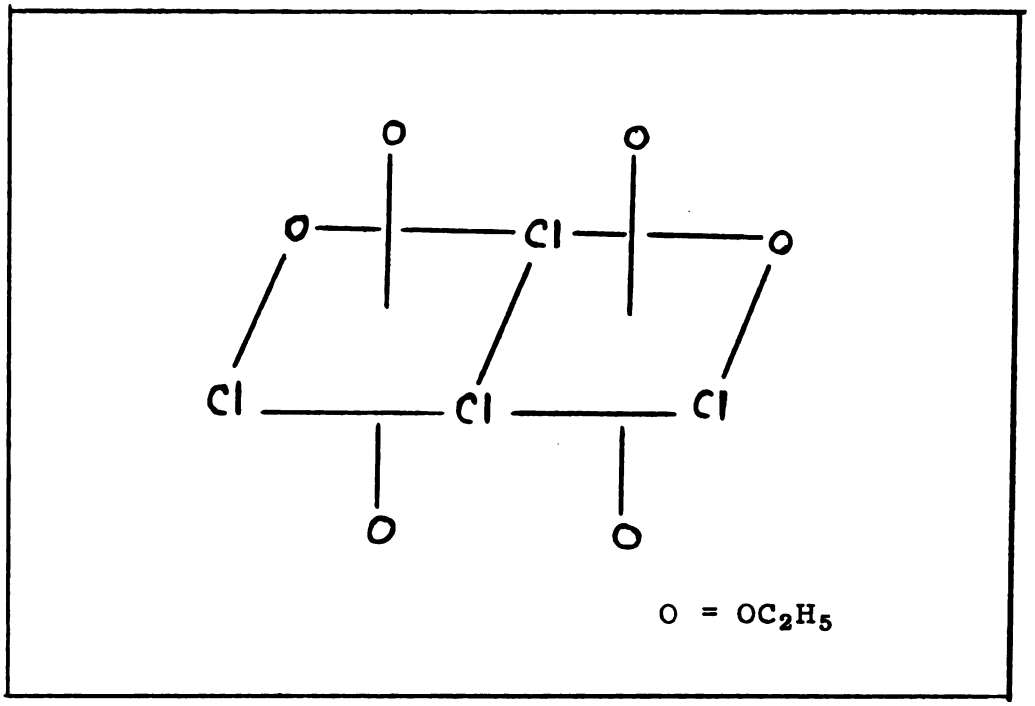


Figure 26. Proposed structure for $W_2Cl_4(OC_2H_5)_6$.

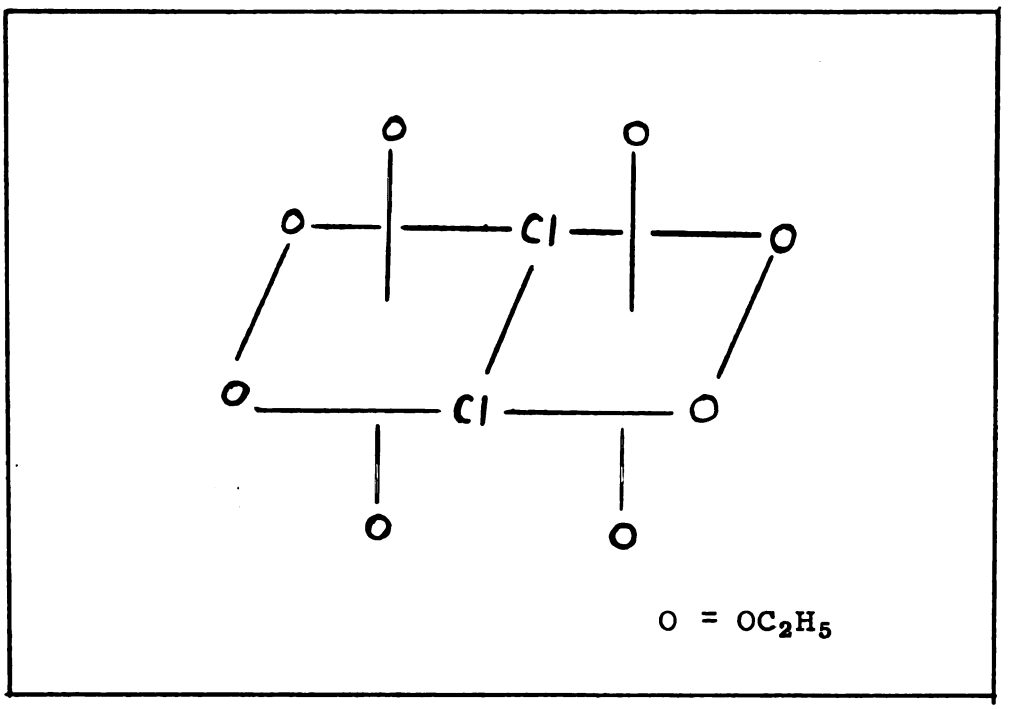


Figure 27. Proposed structure for $W_2Cl_2(OC_2H_5)_8$.

exchange occurring at a very fast rate.

The presence of the alcohol ligands in the W(IV) ethoxoethanol compound was demonstrated by an exchange experiment with dimethylsulfoxide (DMSO). With excess DMSO, the bound alcohol of $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ is replaced, resulting in appropriate shifts in the spectrum. As the unbound alcohol appears, the signal due to its hydroxyl proton becomes apparent (Figure 25). Quantitative correlations of signal intensity to possible structures of the complex were not made because the reaction and the equilibria involved are not understood.

Bradley and Holloway[54] have proposed an edge-shared bioctahedral structure for niobium and tantalum pentaalkoxides. The pmr spectrum of $[Ta(OCH_3)_5]_2$ above 40^0 gave one peak at 5.78 ppm. At -58^0, the single methyl resonance splits into 3 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[91] was similar. At 35^0, $W(OC_2H_5)_5$ has a simple pmr spectrum, probably due to rapid intramolecular exchange between terminal and bridging ethoxide groups. Low temperature studies (to -80^0) 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.

At -50^0, the pmr spectrum of a dilute $CHCl_3$ solution of $W_2Cl_4(OC_2H_5)_6$ did not show any splitting of the two methylene peaks. It is possible that different alkoxide groups could be resolved at lower temperatures. However, this compound and other chloro-alkoxide complexes were not sufficiently soluble in the proper solvents (n-pentane or carbon disulfide) for this type of low temperature study.

6. Optical Spectra

The optical spectra in solution and the solid reflectance spectra were determined and the results are listed in Table IX sketches of representative spectra are shown in Figures 28 to 30.

The assignment of these bands is not possible because of the dimeric nature of the compounds. The molar absorptivities of the bands in the visible region are too high for simple d-d transitions. The visible spectra may arise from transitions between mixed metal orbitals. The W(IV) compounds have two well defined shoulders on the high energy side of the band at 13.5×10^3 cm^{-1}. This feature is absent in the spectra of Wentworth's W(III) complexes.[64]

König[17] has suggested that the compound, $K_4W_2OCl_{10}$ is a mixed valence W(III)-W(V) system. Its visible spectrum exhibited an intense band at 19.1×10^3 cm^{-1} ($\epsilon \cong 20,000$).

Table IX. Electronic absorption spectra of dimeric tungsten compounds. (ϵ in parentheses.)

Compound		Absorption Maxima ($cm^{-1} \times 10^{-3}$)
$W_2Cl_4(OC_3H_7)_6$	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(2480)
$W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$	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)

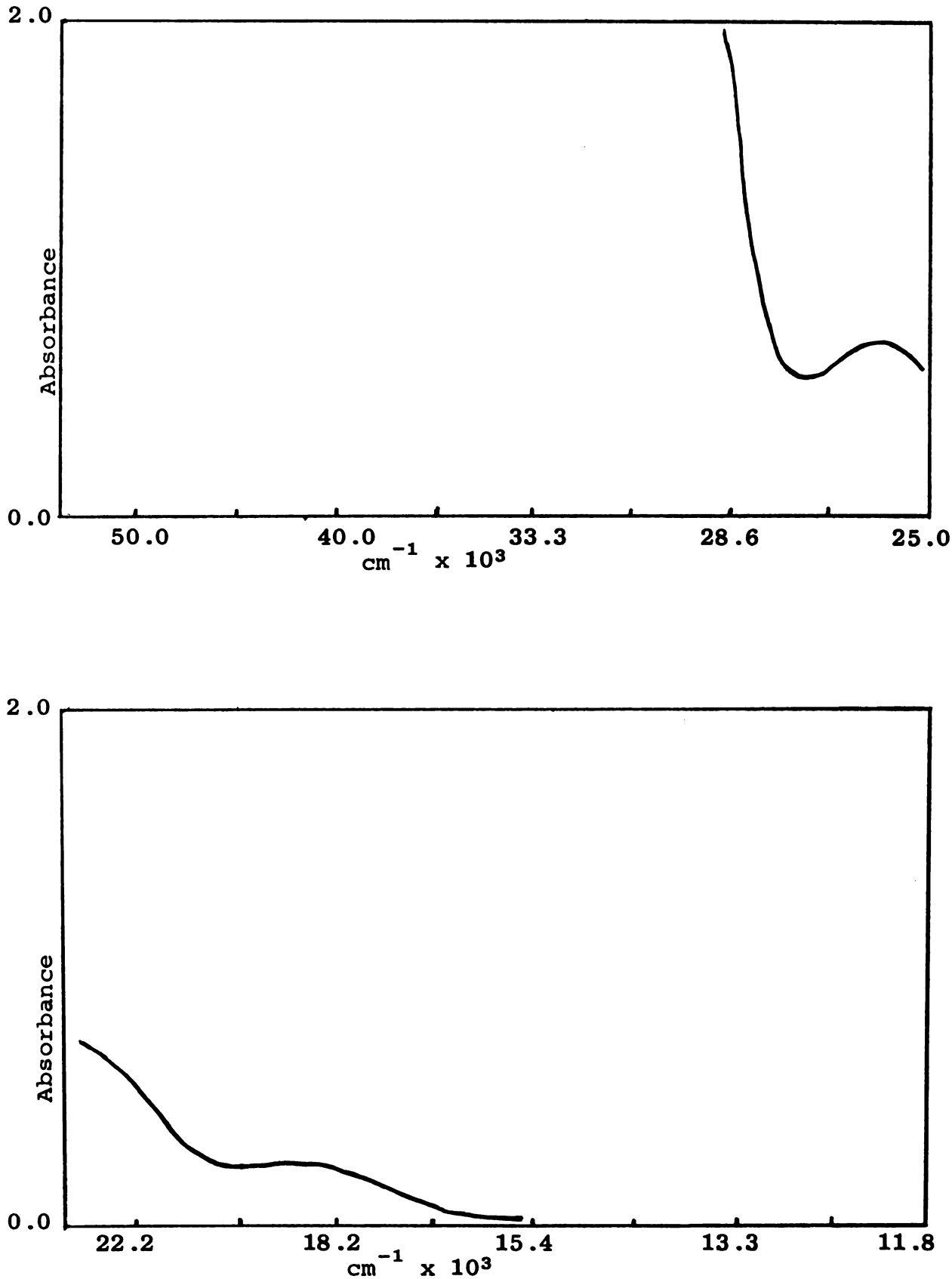
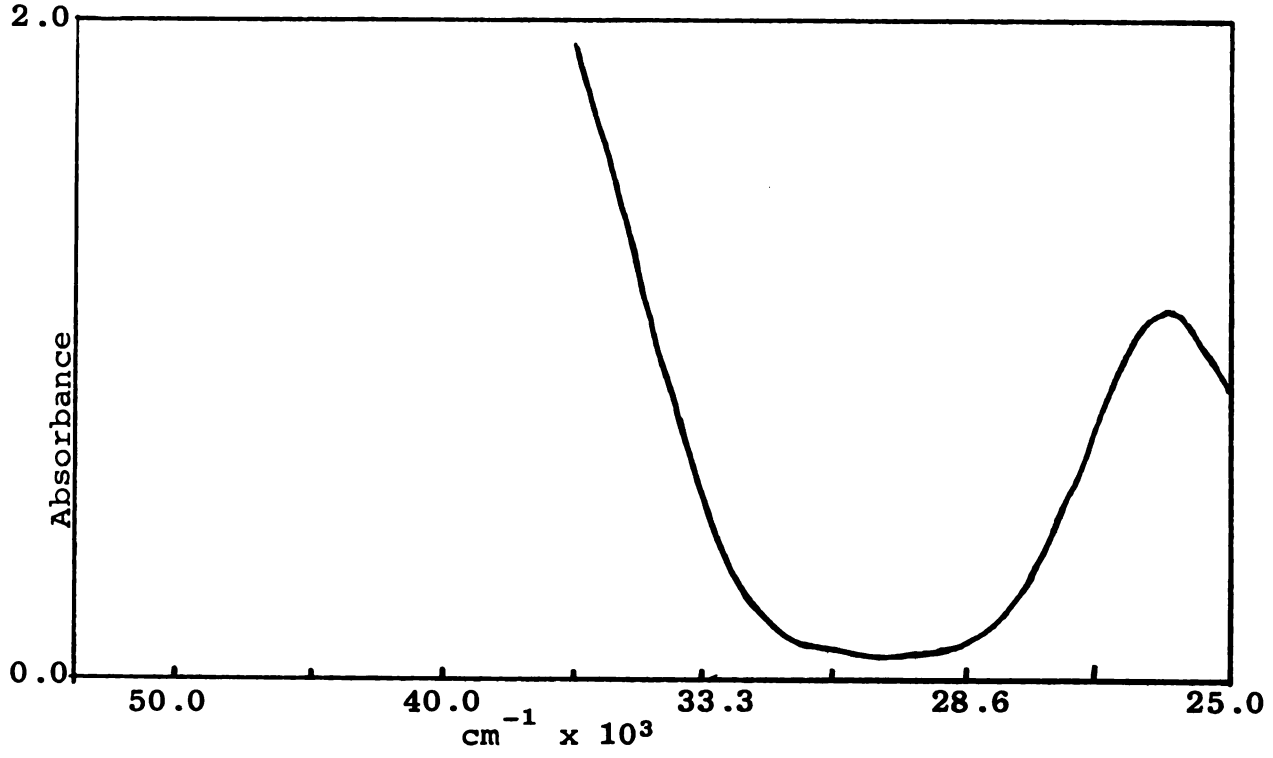


Figure 28. Solution spectrum of $W_2Cl_4(OC_3H_7)_6$ in benzene.



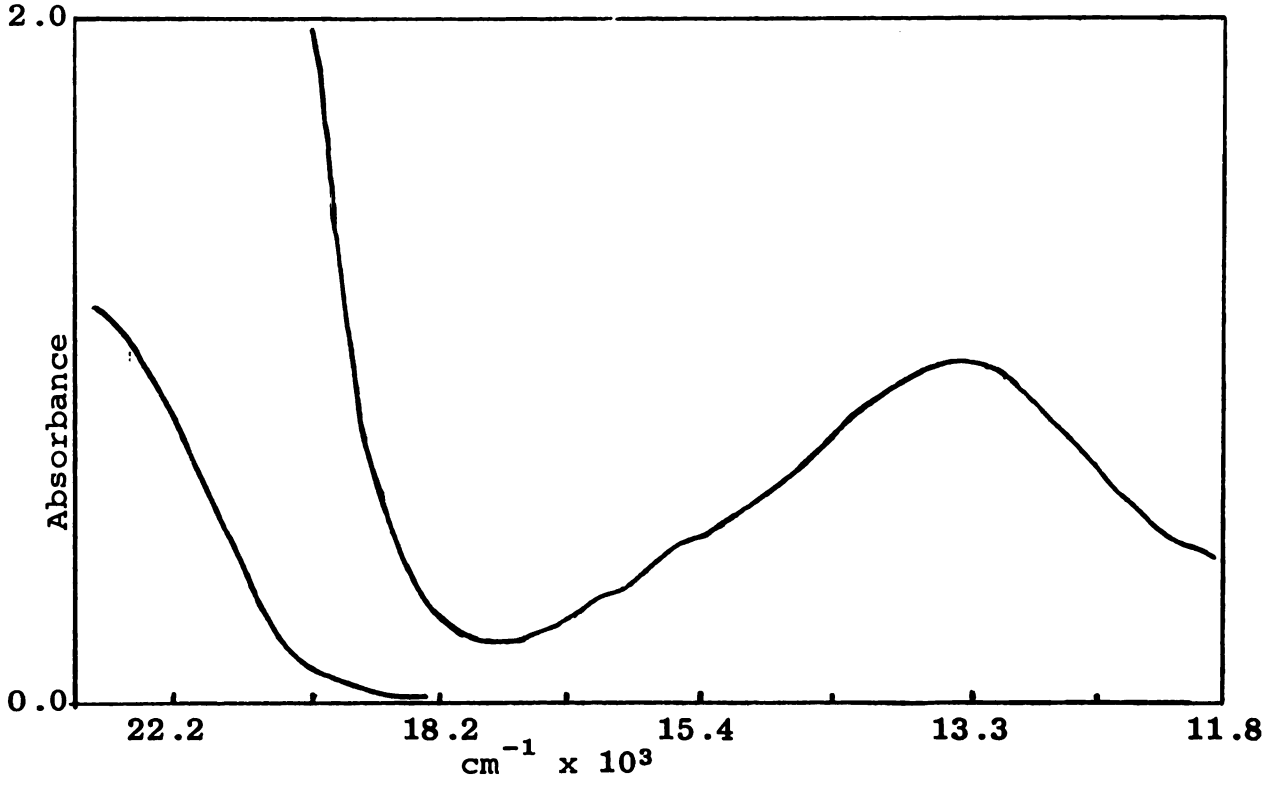


Figure 29. Solution spectrum of $W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$ in benzene.

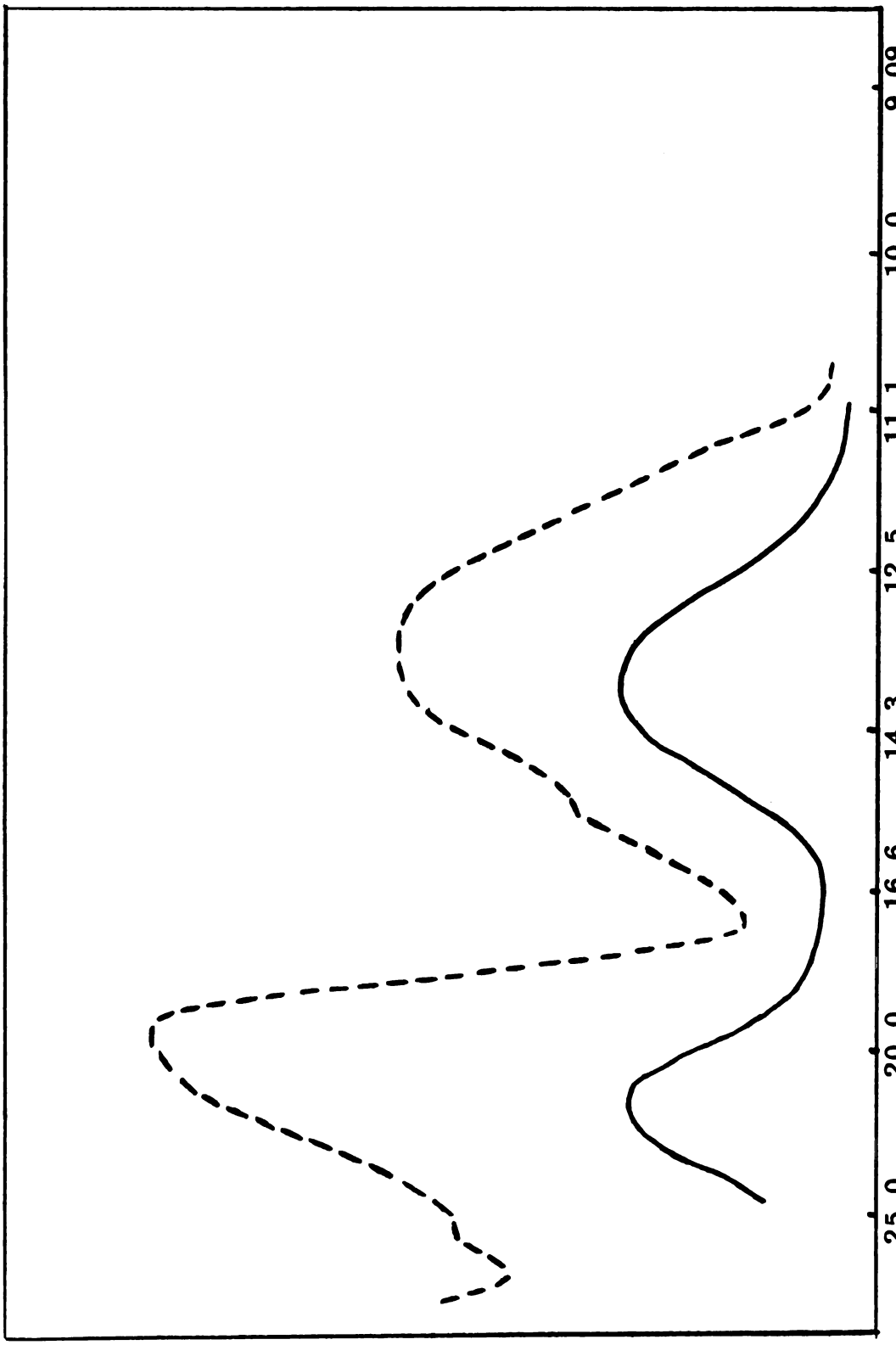


Figure 30. Solid reflectance spectrum of $W_2Cl_4(1\text{-}OC_3H_7)_4(C_3H_7OH\text{-}1)_2$ (-----) and $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$ (———).

Bands of comparable intensity in the visible region are often encountered in mixed valence compounds.[89] Since a similar band was not found in the spectra of the W(IV) or W(V) dimers, a mixed valence formulation is unlikely.

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APPENDIX

APPENDIX

A. Molybdenum(V) and Molybdenum(IV) Complexes

The physical and chemical properties of the dialkoxo complexes of W(V) are quite similar to the comparable Mo(V)[63] compounds. Therefore, it was of interest to prepare Mo(V) and Mo(IV) complexes for comparison with the other tungsten compounds isolated in this work. In particular, Mo(V) chlorothiocyanate and Mo(IV) alkoxide compounds would be desirable.

1. Reaction of $MoCl_4$ with Ethanol

At 0^0, $MoCl_4$ formed a dark red solution in ethanol. One portion of this reaction solution was treated with an ethanol solution of $(C_2H_5)_4NCl$. A light red precipitate formed immediately. Elemental analysis and ir spectra indicated that this product was an ethoxide complex, $(C_2H_5)_4NMo(OC_2H_5)_2Cl_4$.

Analysis calculated for $(C_2H_5)_4NMo(OC_2H_5)_2Cl_4$: Mo, 20.96; Cl, 30.97.

Found: Mo, 20.86; Cl, 32.00.

A strong band at 990 cm^{-1} (ν Mo = 0) probably indicated oxychloride contamination. The red color may be due to a mixed

valence Mo(IV)-Mo(V) complex since the Mo(V) dialkoxo complex is light green.

Another portion of the $MoCl_4$-ethanol reaction solution was allowed to cool to -10^0 for 4 hours. A dark red crystalline product was obtained. The ir spectrum of this compound was similar to the W(IV) complex, $W_2Cl_4(OC_2H_5)_4(C_2H_5OH)_2$. Elemental analysis indicated that a pure compound was not isolated.

Analysis calculated for $MoCl_4(OC_2H_5)_4(C_2H_5OH)_2$: Mo, 31.68; Cl, 23.43.

Found: Mo, 31.39; Cl, 30.56.

Molybdenum tetrachloride did not react with the alcohols studied in the same manner as tungsten tetrachloride. Attempts to prepare Mo(IV) alkoxide complexes were unsuccessful because of oxygen abstraction and possible disproportionation reactions.

2. Attempts to Prepare Thiocyanate Complexes of Molybdenum(V)

A dark green, air sensitive material was isolated when $MoCl_5$ was substituted for WCl_5 in the preparation of $(C_2H_5)_4NW(NCS)Cl_5$ (see Experimental section). Unless vigorous stirring was maintained, a dark amorphous product was obtained instead of the green powder. Elemental analysis indicated that the molybdenum compound was not pure.

Analysis calculated for $(C_2H_5)_4NMo(NCS)Cl_5$: Mo, 20.58; Cl, 38.43.

Found: Mo, 21.90; Cl, 38.56.

Attempts to purify this complex or to find an improved method of preparation were unsuccessful.

The rapid oxygen abstraction by $MoCl_5$ in alcohols interferred with the preparation of Mo(V) alkoxo-thiocyanate complexes. No examples of mixed complexes of this type were isolated.


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