THE PREPARATION AND PROPERTIES OF SOME d^1 MOLYBDENUM AND TUNGSTEN COMPOUNDS

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This is to certify that the

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DONALD PAUL RILLEMA

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Carl H. Brubaker, Jr.
Major professor

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ABSTRACT

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By

D. Paul Rillema

Solutions of WCl_5 in alcohols were investigated. The solutions were acidic with HCl, neutral, or basic with alkoxide ion. A number of tetrachlorodialkoxo and pentachloroalkoxotungstates(V) were prepared and characterized. A yellow compound, $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$, was isolated from ethanol solutions which had been saturated with HCl. The pentachloroalkoxotungstate(V) decomposed by the elimination of alkyl chloride to give a mixture of solid materials which probably contain tetrachloroxotungstate(V). Neutral solutions which were evaporated to dryness produced dimeric compounds, $[W(OCH_3)_3Cl_2]_2$.

Molybdenum pentachloride underwent similar reactions with alcohols. A direct preparation of tetrachlorodiethoxomolybdate(V) was found. The compound, believed to be the pentachloroethoxomolybdate(V) salt of a tetraalkylammonium cation, was isolated at -78^0. The compound rapidly evolved ethyl chloride and formed the salt of the tetrachloroxomolybdate(V).

Electronic properties of the compounds were extensively investigated. Some of the three possible d-d transitions from $B_2 \rightarrow E$, $B_2 \rightarrow B_1$, and $B_2 \rightarrow A_1$ were found. These transitions and state assignments were made on the basis of C_{4v} symmetry for $MoOCl_4^-$ and $W(OR)Cl_5^-$ ions and D_{4h} symmetry for dialkoxide complexes. According to esr measurements, only trans alkoxides were present.

The $g_\perp$ value changed as ligands were displaced on the C_{4v} axis of symmetry, for $W(OCH_3)Cl_5^-$ $g_\perp = 1.50$ and for $W(OCH_3)_2Cl_4^-$ $g_\perp = 1.73$. For $[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$ in nitromethane glass, $g_{||} = 1.970$, $g_\perp = 1.923$, $A = +70 \times 10^{-4}\ cm^{-1}$, $B = +30 \times 10^{-4}\ cm^{-1}$, and the isotopic contact term, K, is $-39.6 \times 10^{-4}\ cm^{-1}$. In addition, an esr signal was detected for $[(C_2H_5)_4N](WCl_6)$ in the powder.

Magnetic moments of tungsten complexes showed variations as the spacings between the B_2 and E states changed. The effective magnetic moment was approximately 1.36 for monoalkoxo complexes and about 1.53 for dialkoxo compounds.

In addition to the typical C-O stretch at $\sim 1080\ cm^{-1}$ and cation absorptions in the infrared region, for infrared vibrations were recorded in the range 650 - 80 cm^{-1}. The M-OR stretch has been assigned and several trends which depend on the nature of the alkoxide, halide, and metal were found.

THE PREPARATION AND PROPERTIES OF SOME d^1 MOLYBDENUM AND TUNGSTEN COMPOUNDS

By

D. Paul Rillema

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To my wife, Necia

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INTRODUCTION

The chemistry of molybdenum(V) and tungsten(V) is essentially described by their ability to form a metal-oxygen double bond. At room temperature the pentahalo salts of of both transition metals react violently with solvents containing the OH group and form oxo products. Similar species are obtained by abstraction of oxygen from acetone[1,2], dimethylsulfoxide[1], dioxane[2,3], sulfur dioxide[4], and tetrahydrofuran.[2,3] In an extreme case, Kepert and Mandyczewski[5] formulated a compound as $(Ph_3AsCl)^+(MoOCl_4)^-$ rather than the previously reported adduct, $MoCl_5 \cdot Ph_3AsO$.

Consequently, the more numerous molybdenum(V) and tungsten(V) complexes contain a metal-oxygen double bond. These complexes generally are of the anionic form, MOX_5^{2-} where X = Br, Cl, F, and SCN.[4,6] The anionic species is prepared by dissolving the pentahalo compound or reducing some M(VI) product[7,8] in strongly acidic HX solutions. These solutions stabilize monomeric MOX_5^{2-} ions and allow their precipitation with NH_4^+, Na^+, K^+, Rb^+, and Cs^+ cations.

Since these compounds contain one unpaired d electron, properties due to the electron comprise the greatest part of studies which have been made.

Gray and Hare[9,10] devised a molecular orbital scheme to account for the electronic spectrum of $MoOCl_5^{2-}$. The ligand field transitions, $B_2 \rightarrow E$ and $B_2 \rightarrow B_1$, were assigned to bands at 14,050 and 22,500 cm^{-1} respectively. The three ultraviolet absorptions were considered to be transitions from a π bonding orbital which is largely associated with the oxygen atom to either nonbonding or antibonding orbitals essentially d in character. The assignments were: $B_2 \rightarrow E(II)$ at 28,010 cm^{-1}, $B_2 \rightarrow B_2(I)$ at 32,260 cm^{-1}, and $B_2 \rightarrow E(III)$ at 40,000 cm^{-1}. These transitions are respectively: the e_π electron to the nonbonding b_2 orbital(d_{xy}), the e_π electron to an antibonding e_π^* orbital-(d_{xz} or d_{yz}), and the e_π electron to an antibonding orbital, $b_1^*(d_{x^2-y^2})$. Inherent in the calculation of the energy scheme is the assumption that π bonding occurs between the metal and oxygen but none between the metal and chloride. Neglect of the latter's π bonding capability is the reason for the claim of Allen <u>et al</u>.[4] that the molecular orbital diagram does not qualitatively explain the electronic spectra of $MoOBr_5^{2-}$, $WOCl_5^{2-}$, and $WOBr_5^{2-}$.

Electron spin resonance spectra (esr) of these species were recorded by a number of workers.[7-20] Representative magnetic tensors are given in Table 1. In addition to the hyperfine structure, ligand hyperfine structure is reported for bromide[11], chloride[21], fluoride[22], and the nitrogen atom of the thiocyanate ligand.[23]

Table 1. Magnetic tensor elements for some molybdate and tungstate complexes

Complex	$\langle g \rangle$	$g_{\parallel}$	$g_{\perp}$	$\langle a \rangle^a$	A^a	B^a	Ref.
$(MoOBr_5)^{2-}$	1.993 ±0.002	2.090 ±0.002	(1.945) ±0.002	41.7	66.0 ±0.5	(30) ±0.5	11
$(MoOCl_5)^{2-}$	1.950 ±0.002	1.972 ±0.004	1.942 ±0.005	47.1 ±0.7	74.6 ±0.9	30.8 ±3.6	7
$(MoOF_5)^{2-}$	1.905	1.874	1.911	62.2	92.93	45.13	12
$[MoO(SCN)_5]^{2-}$	1.935 ±0.02	1.928 ±0.005	1.944 ±0.005	45.0 ±2.7	68.3 ±4.5	34.5 ±4.5	15
$[MoO(NCS)_5]^{2-}$	1.940 ±0.003			44.4 ±3			16
$[Mo(OCH_3)_2Cl_4]^-$	1.9453 ±0.0008	1.9673 ±0.0002	1.934 ±0.002	46.93 ±0.08	75.1 ±0.1	33.0 ±0.3	14
$(WOBr_5)^{2-}$	1.830 ±0.002	1.940 ±0.002	(1.775) ±0.002		91 ±20		11
$(WOCl_5)^{2-}$	1.773 ±0.002	1.804 ±0.002	(1.758) ±0.002		127 ±10		11
$(WOF_5)^{2-}$		1.589	1.767				13

[a]Units of $cm^{-1} \times 10^{-4}$; ( ) = calculated values.

Magnetic moments for the molybdenum compounds are very close to spin only values. However, for tungsten complexes considerable spin orbit coupling is indicated by moments which range from 1.35 - 1.55 B.M. Both molybdenum and tungsten compounds obey the Curie-Weiss law with small values of θ.[4]

In addition to electronic properties, metal-ligand vibrations have also been measured. A. Sabatini and I. Bertinis'[24] work is summarized in Table 2. In a complex such as MOX_5^{2-}, which has C_{4v} symmetry, there should be four A_1 and four degenerate E modes which are infrared active. The A_1 vibrations include two M-X vibrations, one M-O stretch and one O-M-X, X-M-X deformation. The modes that are bases for the E representation are pairs of M-X stretching modes, two pairs of X-M-X bending modes, and a pair of O-M-X bending vibrations.

If one adds pyridine or quinoline to an aqueous acid solution of $WOCl_5^{2-}$ or $WOBr_5^{2-}$, one precipitates $(pyH)(WOX_4)$ or $(qH)(WOX_4)$ respectively,[25,26] where py = pyridine and q = quinoline. The molybdenum analogues are prepared in liquid sulfur dioxide which contains the appropriate cationic halide. Molybdenum pentachloride is presumably first solvolyzed to give $MoOCl_3$ which then picks up halide ion[4] to give $MoOCl_4^-$. Magnetic and electronic properties are similar to the MOX_5^{2-} species. Electron spin resonance properties remain uninvestigated.

Table 2. Infrared absorption frequencies of MOX_5^{2-} with possible assignment.[a]

$Cs_2(MoOCl_5)$				$Cs_2(MoOBr_5)$			
952 vs	M-O str.	178 m	Cl-M-Cl def.	948 vs	M-O str.	136 w	Br-M-Br def.
329 s	M-Cl str.	86 m	Cl-M-Cl def.	246 vs,b	M-Br str.	125 w	Br-M-Br def.
320 sh	M-Cl str.			209 mw	M-O rock	118 w	Br-M-Br def.
227 m	M-O rock			195 m	M-O rock		
$Cs_2(WOCl_5)$				$Cs_2(WOBr_5)$			
957 vs	M-O str.	174 ms	Cl-M-Cl def.	960 vs	M-O str.	143 w	Br-M-Br
333 w	M-Cl str.	164 mw	Cl-M-Cl def.	220 s	M-Br str.	119 m	Br-M-Br
309 s,b	M-Cl str.	84 m	Cl-M-Cl def.	202 s	M-O rock		
230 ms	M-O rock						

[a] s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

Even more stringent conditions are required in systems where formation of oxo complexes is to be avoided. Strictly anhydrous conditions are employed.

Hexahalo compounds are prepared by various procedures. The tetraethylammonium salt of hexachloromolybdate(V) is prepared by the reaction of $MoCl_5$ and $[(C_2H_5)_4N]Cl$ in methylene chloride.[27] A similar procedure produced $[(C_2H_5)_4N](WBr_6)$ from WBr_5 and $[(C_2H_5)_4N]Br$ in chloroform.[28] The compound formed by reduction of WCl_6 in thionyl chloride was WCl_6^-. It was precipitated with tetraethylammonium ion.[29,30] Brisdon et al.[27] assigned values of 10 Dq for $MoCl_6^-$ at 21,700 cm^{-1}, WCl_6^- at 23,300 cm^{-1}, and WBr_6^- at 18,900 cm^{-1}. In addition Dowsing and Gibson[17] report that $[(C_2H_5)_4N](MoCl_6)$ gives a room temperature electron spin resonance spectrum with $g_{||} = 1.977$ and $g_{\perp} = 1.935$. It was argued that considerable distortion of the lattice took place because Jahn-Teller distortion is too small to account for a signal under those temperature conditions.

The compound, $[(C_2H_5)_4N](WCl_6)$, exhibits antiferromagnetism and has a room temperature magnetic moment of approximately 0.8 B.M.[29] The magnetic moment of $[(C_2H_5)_4N](WBr_6)$ is reported as 1.28 B.M.[28]

A final property of concern is a tungsten-chloride stretch assigned at 305 cm^{-1}.[30]

A different non oxo system investigated by several authors involved reactions of MX_5 compounds with amines. Reduction of molybdenum pentachloride in primary and secondary amines yielded complexes of the type $MX_4 \cdot L_2$ whereas adducts, $MX_5 \cdot L$, formed with tertiary amines.[31] In contrast to molybdenum, both tungsten pentachloride and pentabromide reacted with primary amines to give $WX_2(NHR)_3$ products. However, reduction products were produced with secondary and tertiary amines.[32]

Pyridine and acetonitrile cause reduction of both molybdenum and tungsten pentachlorides.[33-35] Brown and Ruble[36] synthesized compounds by the reaction of $MoCl_5$, WCl_5, and WBr_5 with 2,4,6-trimethylpyridine and benzonitrile in methylene chloride. Based on conductance data the compounds were formulated as $(MX_4L_2)X$. A similar formulation was given by Boorman <u>et al</u>.[37] for compounds WCl_5py_2, WCl_5bipy and WCl_5diphos which were prepared by reaction of WCl_6 with the appropriate ligand in benzene or carbon tetrachloride. The abbreviations: py = pyridine; bipy = 2,2'-bipyridyl; and diphos = 1,2-bis(diphenylphospino)-ethane.

Magnetic moments are lower for amine substituted compounds than spin only values; yet moments are similar to values reported for other Mo(V) and W(V) compounds.[38] Only for $WX_2(NHR)_3$ compounds were magnetic moments so low (μ_{eff} = 0.3 B.M.) that bridging between chloride ligands was proposed. In this case, bridging was further substantiated by molecular weight data.

The absorption coefficients (~200 $\underline{M}^{-1}cm^{-1}$) for $(MX_4L_2)X$ compounds were higher than normal for d-d transitions. The bands, however, did occur in the visible region which is normally associated with these types of transitions. It is unfortunate that electron spin resonance parameters have not been determined because the data would aid the understanding of the bonding and the stereochemistry of the complexes.

The final molybdenum(V) and tungsten(V) complexes receiving attention were complexes which contain alkoxide as ligand. Klejnot[39] examined the reduction of WCl_6 in methanol and ethanol. He isolated two products, a blue compound, $W(OR)_2Cl_3$, and a red product, $W_2(OR)_6Cl_4$, R = CH_3 and C_2H_5. Nuclear magnetic resonance evidence and dipole data led to the prediction of chloride bridging in the dimeric compounds.

Funk and coworkers[40-42] found that molybdenum pentachloride and tungsten pentachloride behaved similarly in methanol solutions. At low temperature and with continual cooling, the adduct, $MCl_3(OCH_3)_2 \cdot 3CH_3OH$, was isolated. Addition of pyridinium chloride to a methanol solution of the adduct or pyridine to a reaction solution of MCl_5 in methanol precipitated $(pyH)[M(OCH_3)_2Cl_4]$. Solutions which were made basic with pyridine yielded dimeric products $[M(OCH_3)_3Cl_2]_2$ and $[M(OCH_3)_4Cl]_2$. Although concentrated solutions of the tetrachloroalkoxotungstate(V) anion were stable at room temperature, similar solutions of molybdenum rapidly formed oxo compounds. Some compounds isolated were $MoO(OCH_3)_3 \cdot \frac{1}{2}CH_3OH$, $MoOCl_3 \cdot 2CH_3OH$, and $(pyH)(MoOCl_4 \cdot CH_3OH)$.

The pyridinium salt of pentachloroxotungstate(V) could be isolated by boiling a reaction solution of WCl_5 in methanol until a clear green solution was obtained. Addition of pyridinium chloride and cooling caused $(pyH)_2(WOCl_5)$ to separate.

Funk and Schauer[43] described the alcoholysis of WBr_5 and its reactions with phenols to give $W(OR)_2Br_3$ and $W(OR)_3Br_2 \cdot ROH$ and with aldehydes to give $WBr_2(OH)_3 \cdot$aldehyde. They reported that WBr_5 gives permanent deep red methanol solutions at low temperature. However, at room temperature, the red solution becomes yellow, then green, and finally blue. No compound was isolated from these solutions.

The only characterizations of the tungsten complexes were given for $(pyH)[W(OCH_3)_2Cl_4]$ and $(pyH)_2(WOCl_5)$. Magnetic moments were reported as 1.48 and 1.52 B.M. respectively. A C-O stretch for the former was reported at 1060 cm^{-1} and pyridinium infrared structure was noted for each compound.

Due to the incompleteness of the work, McClung <u>et al</u>.[44] synthesized four compounds, $(pyH)[Mo(OCH_3)_2Cl_4]$, $(qH)[Mo(OCH_3)_2Cl_4]$, $[(CH_3)_4N][Mo(OCH_3)_2Cl_4]$, and $(pyH)[Mo(OC_2H_5)_2Cl_4]$. The general procedure for the preparation of the methoxide compounds involved slow addition of methanol to the solid molybdenum pentachloride which was contained in a closed flask at -78^0. The desired cation was dissolved in methanol and the solution added slowly to precipitate the tetrachloromethoxomolybdate(V) anion. The ethoxide analogue was prepared by alkoxide exchange of $(pyH)[Mo(OCH_3)_2Cl_4]$ in ethanol.

Properties of the complexes were more thoroughly investigated. Magnetic moments were near spin only values. Electron spin resonance spectra indicated axial symmetry. A typical example of $g_{||}$ and $g_{\perp}$ values along with measured hyperfine values is given in Table 1. The authors concluded trans stereochemistry predominated. Consequently, the complex belongs to the point group, D_{4h}. On this basis electronic transitions were assigned. These were a $B_2 \rightarrow E$ at 14,000 cm^{-1} and $B_2 \rightarrow B_1$ at 23,000 cm^{-1}. The $B_2 \rightarrow A_1$ transition was masked by the charge transfer band. McClung's[45] conclusion was that the alkoxides had properties very similar to pentachloroxomolybdate(V) compounds.

Several problems remained unresolved. McClung[45] reported that a more complicated process existed with the solvent, ethanol. If ethanol were substituted for methanol under similar preparative conditions of $Mo(OCH_3)_2Cl_4^-$, he obtained a mixture of products which he was unable to resolve. The preference of trans stereoisomerization rather than cis was still not obvious. Bradley[46] had found that the cis isomer was formed for transition metal alkoxides in their maximum oxidation state.

The measurement of metal-ligand vibrations would offer a clue to the formation of the favored species with a metal-oxygen double bond. The effective charge on the metal atom is related to the electron density which is in turn related to the energy of a vibration. Thus, it may be that the lower the effective charge on the metal ion, the more stable the species.

There is other information which can be gained from a metal-ligand vibration study. Chloride bridging was proposed for $[Nb(OR)Cl_5]_2$ by Wentworth[47] and $[W(OR)_3Cl_2]_2$ by Klejnot.[39] Bridging vibrations occur ~50 cm^{-1} below terminal vibrations. Thus, a vibration study should distinguish between bridging chloride or alkoxide.

In complexes as $M(OR)_nCl_{6-n}$, it would seem possible to vary n from zero to six. One might synthesize complexes with n < 2 in acidic solutions. Basic solutions produced dimers but no studies were reported where complexes with n > 2 had been isolated. Complexes where n varied from zero to six would not only be synthetically desirable, but also theoretically informative. The properties would unfold trends in electronic transitions, magnetic moments, and magnetic tensor parameters for various ligand field symmetries. These would then produce a basis for predicting properties of other uncharacterized systems. An additional high light would be the production of a molecular orbital diagram which would have some general application for transition metal complexes.

The initial transition metal ion chosen for study was tungsten(V). Tungsten pentachloride is more basic than molybdenum pentachloride, is stable to oxygen abstraction in methanol, and is a congener of molybdenum. Thus, its chemistry would also offer insight into the molybdenum system. Furthermore, additional characterization of known tungsten alkoxide complexes still remained necessary.

EXPERIMENTAL

Materials

Tungsten Pentachloride: - Tungsten pentachloride was prepared by the method of G. E. Novikov, N. V. Andeeva, and O. G. Polyachenok.[48] Climax Molybdenum's tungsten hexachloride was purified by sublimation before it was treated with red phosphorus. The tungsten pentachloride that formed was sublimed to insure its purity.

Tungsten Pentabromide: - Tungsten pentabromide was obtained from Alfa Inorganics, Inc. The compound was used without further purification.

Molybdenum Pentachloride: - Commerical molybdenum pentachloride was fractionally sublimed to remove impurities.[49] Two sublimations were usually required.

Solvents: - Methanol was dried by distillation in the presence of magnesium. The magnesium was activated with iodine according to the prescription of Lund and Bjerrium.[50] Absolute ethanol was dried by distillation in the presence of sodium ethoxide and diethylphthalate; *n*-propanol was dried by distillation in the presence of sodium propoxide.

Nitromethane was dried by distillation in the presence of Drierite. The distillate was then passed over a Dowex 50W-X8 resin to remove basic impurities.[51] Thionyl chloride was reagent grade.

Ethyl ether was stored over sodium. Chloroform and methylene chloride were dried by distillation in the presence of phosphorus pentoxide.

Tetraalkylammonium Salts: - All substituted ammonium salts were Eastman Organic Chemicals' White Label grade. Water was removed by recrystallization of the salt from an acetone-methanol mixture and/or dried in an oven at 100^{0}.

Nitrogen, Hydrogen Bromide, and Hydrogen Chloride: - Liquid Carbonic's oil pumped, prepurified nitrogen was passed over copper turnings at 600^{0} and BTS catalyst to remove oxygen impurities. The nitrogen was then passed through drying towers of calcium chloride and Drierite for removal of water.

Anhydrous HCl and HBr were used directly from the cylinder.

Analytical Methods

Preparation of Compounds for Analyses: - A weighed portion of a compound was dissolved in an ammonium hydroxide-hydrogen peroxide solution. Excess hydrogen peroxide was destroyed by boiling. The solution was cooled and diluted in a volumetric flask.

Tungsten[52] or Molybdenum[53] Analysis: - An aliquot of the solution of molybdate or tungstate was diluted and about a ten fold excess of a solution of 4g of 8-hydroxyquinoline in 100 ml of absolute ethanol was added. The solution was heated to boiling and then acidified with glacial acetic acid. A yellow precipitate formed, was filtered, washed with a little hot water, and dried in the oven at 110^0. The precipitate was weighed as $MO_2(C_9H_6OH)_2$.

Bromide or Chloride Analysis: - An aliquot of the solution for halide analysis was diluted and acidified with sulfuric acid. The halide content was determined by potentiometric titration with a 0.1 M silver nitrate solution. The Beckman-Model G pH meter served as the potentiometer, silver-silver chloride as the electrodes, and a 0.1 M NaCl solution as the primary standard.

Alkoxide Analysis: - A weighed quantity of compound was added to a dichromate solution which was acidified with sulfuric acid. Simultaneous precipitation of tungstic acid occurred with oxidation of M(V) to M(VI) and oxidation of the alcohol. Excess dichromate was treated with KI and the iodine liberated was determined with thiosulfate.[54] Difficulties arose in the treatment of all tetraalkylammonium salts except those with the tetramethylammonium ion. The other cations precipitated some dichromate and some precipitated iodide.

Carbon, Hydrogen and Nitrogen Analyses: - Spang Microanalytical Laboratory, Ann Arbor, Michigan, performed these analyses.

Apparatus and General Methods of Procedure

Reaction vessels, storage tubes, and fritted discs for filtering were all glass with stopcocks and ground glass joints. The former allowed control of the inert atmosphere, nitrogen, and the latter insured a closed system. Glassware was cleaned in an alkali bath, washed, dried in an oven at 110^0, evacuated while it was cooling, and filled with nitrogen. When vessels were opened, nitrogen was rapidly forced through the stopcock to keep atmospheric air from entering. This general procedure allows more manipulating freedom than can be obtained in a dry box. The dry box was used primarily for pulverizing, storing and weighing starting materials.

Most solvents were continually allowed to reflux under nitrogen and were distilled in approximately 150 ml quantities. A Soxhlet extractor was converted to a collection vessel by sealing a 120^0, three way stopcock in place of the siphon tube. A 24/40 ground glass joint was sealed to the third end of the stopcock. Thus, dry solvent was readily available, easily collected, and delivered without contact with air. An aliquot of dry solvent was then removed from the collection flask with a dry pipet of the desired quantity. Nitrogen was rapidly forced through the flask as the sample was withdrawn.

Filtrations were effected by suction.

Notation

B, B is a tetraalkylammonium cation, for example $[(CH_3)_4N]^+$.

R, R is an alkyl group, for example CH_3.

Preparation of Tungsten(V) Compounds from WCl_5

I. The Tetraalkylammonium hexachlorotungstates(V), $B(WCl_6)$:

Twenty ml of ROH was presaturated with HCl at 0^0. This solution and 5.4g (0.015 mole) of tungsten pentachloride were cooled to -78^0 before mixing. A green-black suspension formed which turned yellow-brown upon warming to 0^0. Addition of a solution of 0.015 mole BCl in 20 ml of ROH precipitated a green compound. The compound was washed with a 5:1 ethyl ether-ethanol solution, then ethyl ether and was dried under vacuum.

a. $B = (C_2H_5)_4N^+$: $R = C_2H_5$.

The chloride analysis was approximately 1% low and the infrared spectrum showed a small C-O stretch, suggesting the presence of alkoxide. The compound was purified by recrystallization and possible alkoxide replacement by chloride ion in thionyl chloride.

Analysis: Calculated for $[(C_2H_5)_4N)](WCl_6)$:

W, 34.90; Cl, 40.38; C, 18.24; H, 3.83; N, 2.66.

Found: W, 34.78; Cl, 39.94; C, 18.49; H, 4.02; N, 2.72.

b. The preceding process applies with the following: For B = $(C_3H_7)_4N^+$ and $(C_4H_9)_4N^+$ a green precipitate was obtained but not characterized. If methanol or 1-propanol was used as the solvent, a similar green precipitate formed.

II. The Tetraalkylammonium pentachloroalkoxotungstates(V), $B[W(OR)Cl_5]$:

a. Procedure I was followed through the precipitation of the tetraalkylammonium hexachlorotungstate(V) complex. Considerable heat was evolved when HCl was bubbled through the suspension and it was converted into a yellow compound. The compound was washed with a 5:1 ethyl ether-alcohol solution and then ethyl ether and was dried under vacuum.

b. Procedure I was followed through the warming of the solution to 0^0. If the solution is further warmed to room temperature and stirred approximately for 45 minutes, the color changes to a very light green. Addition of the cation dissolved in the appropriate solvent caused precipitation of the yellow compound, $B[W(OR)Cl_5]$. Washing and drying instructions are given in part a.

1. B = $(C_2H_5)_4N^+$; R = CH_3.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][W(OCH_3)Cl_5]$: W, 35.19; Cl, 33.93. Found: W, 35.35; Cl, 33.49. The compound decomposed too rapidly to

obtain commerical C, H, and N analyses.

2. B = $(C_2H_5)_4N^+$; R = C_2H_5.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$: W, 34.27; Cl, 33.06; OC_2H_5, 8.40; C, 22.39; H, 4.70; N, 2.61. Found: W, 33.99; Cl, 32.93; OC_2H_5, 8.04; C, 22.15; H, 4.84; N, 2.67.

3. B = $(C_2H_5)_4N^+$; R = C_3H_7. This compound was obtained only by method IIb.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][W(n\text{-}OC_3H_7)Cl_5]$: W, 33.45; Cl, 32.18. Found: W, 33.21, Cl, 32.11.

4. B = $(C_3H_7)_4N^+$; R = C_2H_5.

<u>Analysis</u>: Calculated for $[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$: W, 31.03; Cl, 29.92; C, 28.38; H, 5.61; N, 2.36. Found: W, 30.72; Cl, 29.92; C, 28.15; H, 5.71; N, 2.36.

5. B = $(C_4H_9)_4N^+$; R = C_2H_5.

<u>Analysis</u>: Calculated for $[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$: W, 28.34; Cl, 27.33; C, 33.33; H, 6.37; N, 2.16. Found: W, 28.17; Cl, 27.76; C, 33.30; H, 6.45; N, 2.13.

III. The Tetraalkylammonium tetrachloroxotungstates(V), $B(WOCl_4)$:

The tetraalkylammonium salt of pentachloroalkoxotungstate(V) decomposed by elimination of RCl to give a blue compound, $B(WOCl_4)$. Some Cl_2 and HCl were also formed.

a. $B = (C_2H_5)_4N^+$; $R = C_2H_5$.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N](WOCl_4)$:

W, 38.96; Cl, 30.05; C, 20.36; H, 4.27; N, 2.97. Found: W, 38.39; Cl, 29.84; C, 20.39; H, 4.50; N, 2.84.

b. As the alkyl group of the cation and alkoxide group increased in size ($B = (C_3H_7)_4N^+$ and $(C_4H_9)_4N^+$; $R = n\text{-}OC_3H_7$) the concentration of gaseous Cl_2 and HCl impurities increased. Consequently, quantitative formation of the desired product did not occur and recrystallization from nitromethane did not resolve the mixture.

IV. Tetramethylammonium hexachloroethoxotungstate(V), $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$:

A 10.8g (0.03 mole) quantity of WCl_5 was added to 25 ml of ethanol (-78^0) which had been saturated with HCl at 0^0. The temperature was increased to 0^0. After 15 minutes a solution which contained 3.3g (0.03 mole) $[(CH_3)_4N]Cl$ in 35 ml of ethanol was rapidly added. Two hours later, a yellow precipitate which formed slowly was filtered, washed twice with a 5:2 ethyl ether-ethanol solution and finally with ethyl ether and then was dried under vacuum.

<u>Analysis</u>: Calculated for $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$:

W, 31.17; Cl, 36.06; OC_2H_5, 7.63; C, 20.36; H, 4.96; N, 4.75. Found: W, 31.01; Cl, 36.30; OC_2H_5, 8.16; C, 20.21; H, 4.95; N, 4.88.

V. The Tetraalkylammonium tetrachlorodialkoxotungstates(V), $B[W(OR)_2Cl_4]$:

a. A 10.8g (0.03 mole) sample of WCl_5 was added to 25 ml of ethanol at -78^0. After the temperature was increased to 0^0, a yellow-green solution was obtained. A solution which was prepared by dissolving 0.03 mole of BCl in 35 ml of ethanol was rapidly added to it. A yellow-green precipitate formed immediately. The compound was filtered, washed with 5:1 ethyl ether-ethanol and finally with ethyl ether, and was dried under vacuum. The resulting compound was a mixture of $BW(OR)Cl_5$ and $BW(OR)_2Cl_4$, as indicated by analyses, loss of ethyl chloride, and magnetic data.

A 50 ml portion of ethanol was added and the suspension was stirred for 18 hours and the mixture was thus converted to $B[W(OR)_2Cl_4]$. The green compound was filtered, washed with a 5:1 ethyl ether-ethanol solution and finally ethyl ether, and was dried under vacuum.

b. A 7.2g (0.02 mole) portion of WCl_5 was added to 35 ml of a cold (-78^0) ethanol solution, which contained 0.04 mole $Li(OC_2H_5)$. The heterogeneous mixture at -78^0 became a solution at 25^0. Addition of a solution which contained 0.02 mole BCl in 20 ml ethanol caused a green compound to precipitate. The product was washed with a 5:1 ethyl ether-ethanol solution and then with pure ethyl ether. It was dried under vacuum.

1. $B = C_2H_5N^+$; $R = C_2H_5$.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$: W, 33.10; Cl, 25.97; C, 26.40; H, 5.54; N, 2.57. Found: W, 33.73; Cl, 26.25; C, 26.46; H, 5.68; N, 2.57.

2. $B = (CH_3)_4N^+$; $R = C_2H_5$.

<u>Analysis</u>: Calculated for $[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$: W, 37.53; Cl, 28.95; C, 19.61; H, 4.53; N, 2.86. Found: W, 37.38; Cl, 29.41; C, 19.45; H, 4.48; N, 3.00.

3. $B = (CH_3)_4N^+$; $R = CH_3$.

<u>Analysis</u>: Calculated for $[(CH_3)_4N][W(OCH_3)_2Cl_4]$: W, 39.80; Cl, 30.70; C, 15.60; H, 3.93; N, 3.03. Found: W, 40.02; Cl, 30.74; C, 15.70; H, 4.09. N, 3.24.

VI. The Dimers of Dichlorotrialkoxotungsten(V), $W_2Cl_4(OR)_6$:

A 10.8g (0.03 mole) sample of WCl_5 was cooled to -78^0 before addition to 25 ml of ROH also at -78^0. The purple solution became green at room temperature. A red-brown solid remained upon vacuum evaporation of the solution. The product was purified by addition of 30 ml of ROH to the solid. A small amount of precipitate remained, was filtered, and discarded. The red-brown solution was concentrated to 10 ml by vacuum evaporation, cooled at -10^0 for two hours, filtered, washed with a small amount of ethyl ether, and dried under vacuum. The products were stable in water and inert to air.

a. $R = CH_3$:

<u>Analysis</u>: Calculated for $W_2Cl_4(OCH_3)_6$:

W, 52.85; Cl, 20.39. Found: W, 52.83; Cl, 20.43.

b. $R = C_2H_5$:

<u>Analysis</u>: Calculated for $W_2Cl_4(OC_2H_5)_6$:

W, 47.15; Cl, 18.18; C, 18.48; H, 3.88. Found:

W, 46.77; Cl, 18.65; C, 18.35; H, 3.65.

VII. The Dimer of Trichlorodimethoxotungsten(V), $W_2Cl_6(OCH_3)_4$

The compound was prepared after the manner of Funk and Naumann.[42] Tungsten pentachloride (10.7g) was added to 130 ml of chloroform. To this suspension, 2.4 ml of methanol was slowly added. At the ratio of 2:1 methanol-tungsten pentachloride, a vigorous reaction took place, the solution turned red, a red precipitate formed, and a large amount of HCl was evolved. The solid compound was filtered, washed with a small amount of ether, and dried under vacuum. It was then recrystallized from methanol and dried and washed as indicated previously. The compound turned blue in air and gave blue solutions in water.

<u>Analysis</u>: Calculated for $W_2Cl_6(OCH_3)_4$:

W, 52.19; Cl, 30.19; C, 6.82; H, 1.72. Found:

W, 52.06; Cl, 30.11; C, 6.73; H, 1.69.

Attempted Preparation of Tungsten(V) Compounds from WCl_6

Tungsten hexachloride reacts violently with alcohols at room temperature producing aldehyde, chlorine, and tungsten(V) according to Klejnot.[39] He also reported quantitative reduction of tungsten(VI) to tungsten(V) with formation of $W(OCH_3)_2Cl_3$ in methanol. A compound isolated by Klejnot's procedure was similar in color to his but contained an approximate tungsten to chlorine ratio of one to two. The infrared spectrum indicated that the compound also contained an oxy component as an impurity. This last observation was also noted in products which were prepared with WCl_6 substituted in place of WCl_5 under preparation procedure Va. Two compounds, a green one which approached $W(OCH_3)_2Cl_4^-$ by analyses and a white one which was isolated from the concentrated supernatant liquid of the green compound, were obtained. The white product had no electronic transitions which could be assigned to d-d absorptions. Thus, it was concluded that quantitative reduction of W(VI) to W(V) did not occur by this procedure.

Preparation of Tungsten(V) Compounds from WBr_5

I. Tetraethylammonium hexabromotungstate(V), $[(C_2H_5)_4N](WBr_6)$:

An 8.75g (0.015 mole) sample of WBr_5 was added to a solution (at -78^0) of 25 ml ethanol which had been presaturated with HBr at 0^0. The deep red solution which formed was warmed to 0^0 and filtered to remove any residual solids.

To the filtrate, a solution of 3.2g (0.015 mole) of $[(C_2H_5)_4N]Br$ in 25 ml ethanol was rapidly added. After the solution was allowed to warm to room temperature, a black precipitate formed, was washed with a 5:1 ether to ethanol mixture. This was followed by washing with ether alone and drying under vacuum. Spang Micro-analytical Laboratory, Ann Arbor, Michigan, reported difficulty in handling this compound so no C, H and N analyses were obtained.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4](WBr_6)$:
W, 23.17; Br, 60.42. Found: W, 22.71; Br, 59.78.

II. Tetraethylammonium tetrabromodimethoxotungstate(V), $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$:

Ten grams of $[(C_2H_5)_4N](WBr_6)$ was added to 25 ml of methanol. The suspension was gradually heated until the precipitate changed color from black to yellow-green. The precipitate was washed with a 5:1 ether to methanol solution and then with ethyl ether, and was dried under vacuum.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$:
W, 26.42; Cl, 45.94; C, 17.26; H, 3.77; N, 2.01.
Found: W, 25.91; Cl, 46.21; C, 17.17; H, 3.61; N, 2.06.

Preparation of Molybdenum(V) Compounds from $MoCl_5$

I. Tetraethylammonium tetrachlorodimethoxomolybdate(V), $[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$:

A 4.4g (0.015 mole) portion of $MoCl_5$ was added to a 20 ml methanol solution (-78^0) which had been presaturated with HCl at 0^0. A 2.5g sample of $[(C_2H_5)_4N]Cl$ which was dissolved in 20 ml of methanol was added to the above solution. As the solution warmed, the brown-orange suspension changed color to yellow. The precipitate was immediately filtered and was washed with a 5:1 ether to ethanol solution and then dried under vacuum. The compound was photosensitive and became brown after several days exposure to light. Infrared evidence points to methanol as one of the degradation products.

Analysis: Calculated for $[(C_2H_5)_4N](Mo(OCH_3)_2Cl_4]$: Mo, 22.30; Cl, 32.97; Found: Mo, 22.04; Cl, 33.34.

II. Tetraethylammonium tetrachlorodiethoxomolybdate(V), $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$:

A 4.4g (0.015 mole) sample of $MoCl_5$ was added to a solution (-78^0) of 20 ml of ethanol which was presaturated with HCl at 25^0. The solution was allowed to warm to 0^0. A solution of 2.5g tetraethylammonium chloride in 20 ml of ethanol was added to it. A yellow-green precipitate was obtained, washed with a 5:1 ether to ethanol solution and then with ether, and was dried under vacuum. The compound was photosensitive and became brown after several days exposure to light. Infrared evidence points to ethanol as one of the degradation products.

<u>Analysis</u>: Calculated for $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$: Mo, 20.94; Cl, 30.95. Found: Mo, 21.12; Cl, 31.32.

III. The Tetraalkylammonium tetrachloroxomolybdates(V), $B(MoOCl_4)$:

A 4.4g (0.015 mole) sample of $MoCl_5$ was added to a solution (-78^0) of 20 ml of ethanol which was presaturated with HCl at 0^0. A solution of 0.015 mole tetraalkylammonium chloride in 20 ml ethanol was slowly added. A brown-orange precipitate formed. It was filtered, washed with ethyl ether and dried under vacuum. All manipulations were carried out at -78^0. The compound was maintained under a vacuum and was then allowed to warm to room temperature. The initial compound changed color from brown-orange to light green.

a. $B = (C_3H_7)_4N^+$

<u>Analysis</u>: Calculated for $[(C_3H_7)_4N](MoOCl_4)$: Mo, 21.80; C., 32.22; C, 32.75; H, 6.56; N, 3.18. Found: Mo, 21.48; Cl, 32.38; C, 32.38; H, 6.70; N, 3.08.

b. $B = (C_4H_9)_4N^+$

<u>Analysis</u>: Calculated for $[(C_4H_9)_4N](MoOCl_4)$: Mo, 19.33; Cl, 28.58; C, 38.73; H, 7.31; N, 2.82. Found: Mo, 19.47; Cl, 28.83; C, 38.45; H, 7.26; N, 2.72.

Spectroscopic Measurements

Optical Spectra: - Molecular vibrations were recorded in the infrared and far infrared regions. The former were obtained by means of a Unicam SP-200 instrument and the latter with a Perkin-Elmer 301 spectrophotometer. All spectra were determined in Nujol mulls. Sodium chloride plates were used from 5000 cm^{-1} to 650 cm^{-1}, CsBr plates from 650 cm^{-1} to 320 cm^{-1}, and polyethylene disks from 320 cm^{-1} to 80 cm^{-1}. The low solubility and instability preclude a far infrared study in solution.

Electronic absorption spectra of solutions were determined with a Cary Model 14 and Unicam SP-800 spectrophotometer. Solution spectra were obtained by use of nitromethane, methylene chloride, and acidic alcohol solutions as solvents. Band positions in solutions were compared to those obtained from the solids whose spectra were recorded on the Cary Model 14 instrument and on a Bausch and Lomb Spectronic 600 with a reflectance attachment. The former instrument required the use of Nujol mulls which were squashed between glass plates. In order to obtain spectra on the latter machine, an air tight tube with a special flat-windowed adapter was constructed.

Nuclear Magnetic Resonance Spectra: - Nuclear magnetic resonance (nmr) spectra were recorded with a Varian A-60 spectrophotometer.

Electron Spin Resonance Spectra: - X-Band esr spectra were recorded at 298^{0} and 78^{0}K with a Varian V-4502-04 spectrophotometer. First derivative absorptions were recorded on an X-Y recorder with the X-axis proportional to the magnetic field strength. A Hall probe was used as field sensor. Markings, which were placed on recorded spectra by means of a Hewlett-Packard 524C frequency counter, allowed calibration of the magnetic field. These data enable calculation of hyperfine splittings. The g values were calculated from the measured magnetic field and the Klystron frequency.

Magnetic Moment Measurements: - The Gouy method was used to measure magnetic susceptibilities. Apparatus and techniques similar to those of Vander Vennen[55] were used for low temperature work.

Magnetic Moments

Calculations were made by a comparative method. The equation used to determine the susceptibility was:

$$10^{6}\ \chi = \frac{\alpha + \gamma F'}{w} .$$

The volume constant, α, was zero because the tube was filled with nitrogen rather than air. Thus, the equation reduced to:

$$10^{6}\ \chi = \frac{\gamma F'}{w} .$$

In this equation, γ equals the tube calibration constant, w is the weight of the sample, and F' is the force on the sample, i.e. $F' = (F - \delta)$ where F is the measured force on the specimen and δ is the measured force on the tube.

The tube constant, γ, was found by use of a known substance, $CuSO_4 \cdot 5H_2O$, which has a susceptibility of 5.92×10^{-6} c.g.s units at 25°.

The molar magnetic susceptibility, χ_m, was then found by multiplying by the molecular weight of the specimen. χ_m must be corrected for the diamagnetism of the ligands and cation. These were obtained from Pascal's constants,[55] which are additive entities. The new value, χ_m', is the susceptibility of the metal ion.

A plot of $1/\chi_m'$ versus T gives a straight line whose intercept on the T axis is, θ, the Weiss constant.

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

C is the slope and T is the absolute temperature in the equation.

The value of χ_m' is proportional to the square of the effective magnetic moment.

$$\mu_{eff} = \left(\frac{N\beta}{3k}\right)^{-1/2} (\chi_m' T)^{1/2} \text{ B.M.}$$

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

N is Avogadro's number, β is the Bohr magneton, and k is Boltzman's constant.

The moment can also be derived quantum-mechanically.

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

The Lande splitting factor, g, is a function of the amount of orbital and spin angular momentum which a state possesses.

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

The sum of the spin quantum numbers is denoted by S; the quantum number, L, is obtained by adding the m_1 values of all electrons in incomplete subshells; J is found by: $|L + S|$, $|L + S - 1|$, -----, $|L - S|$. The quantum number, J, describes the total angular momentum of the system.

The condition of L equal to zero gives rise to moments with "spin only" values. The equation becomes:

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

Two basic conditions give rise to quenching of orbital angular momentum ($L = 0$). It may be quenched by the ligand field or by an electron with the same spin as the electron in the other degenerate orbital. However, the degeneracy of the d orbitals may not be completely removed by the ligand field. For example, in an octahedral field, two dedenerate sets remain, the e_g and t_{2g}. The e_g set can not give rise to orbital angular momentum since no rotation can turn the d_{z^2} into the $d_{x^2-y^2}$ orbital. However, for the t_{2g} set, rotation about the Z-axis turns d_{xz} into d_{yz} or rotation about the X- or Y-axis turns the d_{xy} orbital into the d_{xz} and d_{yz} respectively. Thus, there is spin orbit coupling associated with the t_{2g} set.

Figgis[57] has reported methods by which it is possible to compare results of measured magnetic susceptibilities over a wide temperature range with theory. His method applies to complexes in which the t_{2g} term has been removed by a ligand field component of axial symmetry or spin orbit coupling. Figgis defines Δ as the separation of the t_{2g} set into an orbital singlet and doublet by an axial ligand component. Δ is positive if the orbital singlet lies lowest. Another term, ν, is defined as Δ/λ where λ is the spin orbit coupling constant. Plots of μ_{eff} vs. kT/λ are presented for assumed values of ν and k. The quantity, k, is the spin delocalization factor. Thus, a proper fit of an experimental curve over a wide temperature range to a theoretical curve leads to values of Δ, λ, ν, and k. The method works best for the intermediate dependence of μ_{eff} on the temperature. Too little or too great a dependence creates ambiguity and allows only qualitative predictions.

Electron Spin Resonance

The degeneracy of an electron spin state in the simplest case, $(m_s = \pm 1/2)$ can be removed by the application of a magnetic field. A transition occurs from $m_s = -1/2$ to $m_s = +1/2$ upon absorption of microwave radiation. The energy of the transition is given by:

$$E = h\nu = g\beta H_0$$

where h is Plank's constant, ν the radiation frequency, β

the Bohr magenton, g the spectroscopic splitting factor, and H_0 the field strength.

The interaction between the electron spin and nuclear spin of a metal atom results in the splitting of the single absorption into $2I + 1$ components, where I is the nuclear spin of the central metal atom. There are as many hyperfine splittings as there are allowed orientations of the magnetic moments of the nucleus, $m_I = (-I, -I + 1, -----, I - 1, I)$. The energy due to interaction of the nuclear magnetic moment with the electron magnetic moment for the hydrogen atom is given by:

$$E(m_s m_I) = g\beta H_0 + a m_s m_I .$$

The hyperfine coupling constant is a.

The preceding phenomena become modified in transition metal complexes. The free ion now is surrounded by a ligand environment which exerts a strong electrical field on the unpaired electron. An understanding of paramagnetic resonance spectra of complex ions is made possible through the ligand field concept and group theoretical properties. The ligand field gives rise to various possible symmetries which may be either isotropic or anisotropic. The degree of electron interaction with the external magnetic field will vary with the orientation of the complex. This effect gives rise to more than one g value. The spin Hamiltonian which accounts for an electron spin resonance spectrum of a compound with axial symmetry in a liquid glass is:[58]

$$H = g_{||}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y)$$

Where $S = 1/2$, $I(^{95}Mo, 15.8\%; ^{97}Mo, 9.6\%) = 5/2$, $I(^{183}W, 14.2\%) = 1/2$.

At room temperature the anisotropies add to zero and the Hamiltonian becomes:

$$H = \langle g \rangle \beta H \bullet S + \langle a \rangle I \cdot S$$

$$\langle g \rangle = 1/3 \; (g_{||} + g_{\perp})$$

$$\langle g \rangle = 1/3 \; (A + 2B)$$

The eigenvalues which lead to correction of $h\nu = g\beta H_0$ are:[59] for isotropic g

$$H_0 = H_m + \langle a \rangle m_I + \frac{\langle a \rangle^2}{2H_m} \; [I(I + 1) - m_I^2]$$

for $g_{||}$

$$H_0 = H_m + Am_I + \frac{B^2 \; [I(I + 1) - m_I^2]}{2H_m}$$

for $g_{\perp}$

$$H_0 = H_m + Bm_I + \frac{(A^2 + B^2)}{4 \; H_m} \; [I(I + 1) - m_I^2]$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the klystron frequency, and A and B are the nuclear hyperfine splitting constants. These corrections were reiterative and were performed with a program designed for this purpose and were carried out on the M.S.U. Control Data

3600 computer. Five iterations were carried through. The program also contained a plot routine. The simulated spectrum was changed by altering magnetic tensor values until a match was obtained between the computed and experimental spectra.

The program was written by T. Krigas and P. T. Manoharan.

RESULTS AND DISCUSSION

The reactions of WCl_5 in the alcohols which were studied are summarized in Figure 1. Tungsten pentachloride reacted with alkoxide ion in neutral alcohol solutions and produced a mixture of $W(OR)Cl_5^-$ and $W(OR)_2Cl_4^-$. By evaporation of the solution to dryness, dimeric compounds, $[W(OR)_3Cl_2]_2$, were isolated, whereas both anions were precipitated upon the addition of a tetraalkylammonium cation, B^+. The mixture could be converted into a single component, $B[W(OR)_2Cl_4]$, by stirring a suspension of the precipitate in ROH for a long time.

Solutions were made basic with RO^- by reaction of metallic lithium or sodium with the appropriate alcohol. At ratios of 2:1 RO^- to WCl_5, $W(OR)_2Cl_4^-$ complexes were precipitated. Dimers[60] formed at ratios greater than 2:1. If an equilibrium process such as $2\ W(OR)_3Cl_3^- \rightleftharpoons [W(OR)_3Cl_2]_2 + 2Cl^-$ were involved in basic alkoxide solution, one might expect to precipitate $B[W(OR)_3Cl_3]$. However, addition of tetraalkylammonium chloride produced no precipitate.

Tungsten pentachloride reacted with alkoxide and/or chloride ion in acidic HCl alcohol solutions. The compound, $[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$, formed with the $(CH_3)_4N^+$ cation.

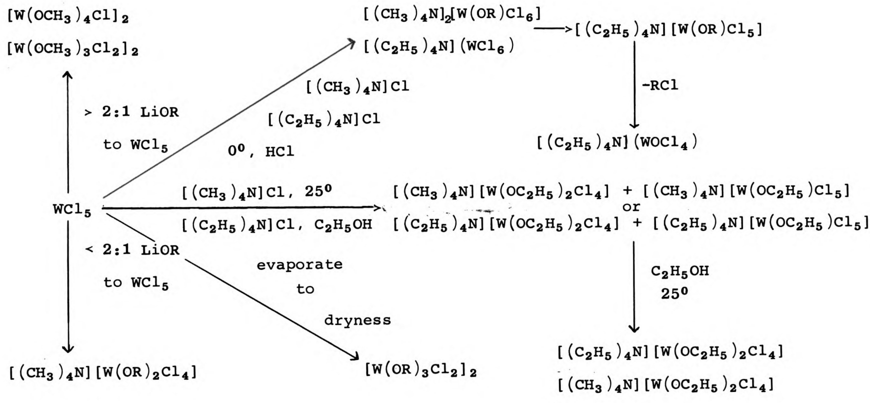


Figure 1. Reactions of WCl_5 in alcohols.

Larger tetraalkylammonium cations precipitated WCl_6^-. Heating the reaction suspension transformed $B(WCl_6)$ into $B[W(OR)Cl_5]$. This product lost alkyl halide and formed $B(WOCl_4)$.

In contrast to $B(WCl_6)$, heating a reaction suspension of $B(WBr_6)$ in alcohol resulted in the formation of $B[W(OR)_2Br_4]$. The $B(WBr_6)$ compound was prepared from the reaction of WBr_5 in acidic HBr solutions.

The loss of alkyl halide from $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$ prompted further investigations in molybdenum pentachloride chemistry. Figure 2 summarizes the results. A modified preparation of $Mo(OCH_3)_2Cl_4^-$ was used and a direct preparation of $Mo(OC_2H_5)_2Cl_4^-$ was found. Furthermore, an attempt was made to prepare the analogous molybdenum monoalkoxide complex. Two compounds, which were prepared and isolated at -78^0, changed color from brown-orange to green and evolved ethyl chloride at room temperature. The green end products were $[(C_4H_9)_4N](MoOCl_4)$ and $[(C_3H_7)_4N](MoOCl_4)$. Thus, the elimination of alkyl halide also occurred with $Mo(OC_2H_5)Cl_5^-$, but in contrast to the tungsten monoalkoxide complexes, the molybdenum complexes evolved the alkyl halide rapidly.

The alkyl halide evolution was demonstrated by infrared spectroscopy. Figure 3A illustrates that the molybdenum monoalkoxide species had a C–O absorption at 1020 cm^{-1} and Figure 3B shows that the green product had a molybdenum-oxygen double bond stretch at 990 cm^{-1}. Similarly,

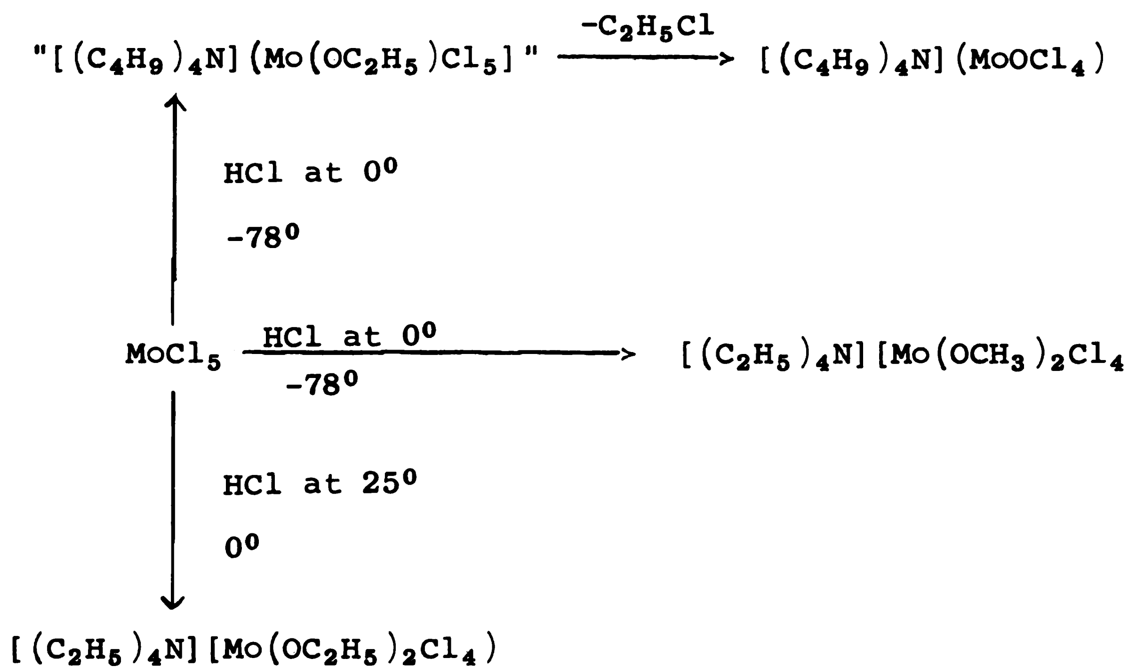


Figure 2. Reactions of $MoCl_5$ in alcohols

Figure 3: Infrared spectra

A: "$[(C_4H_9)_4N][Mo(OC_2H_5)Cl_5]$"

B: $[(C_4H_9)_4N](MoOCl_4)$

C: $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$

D: $[(C_2H_5)_4N](WOCl_4)$

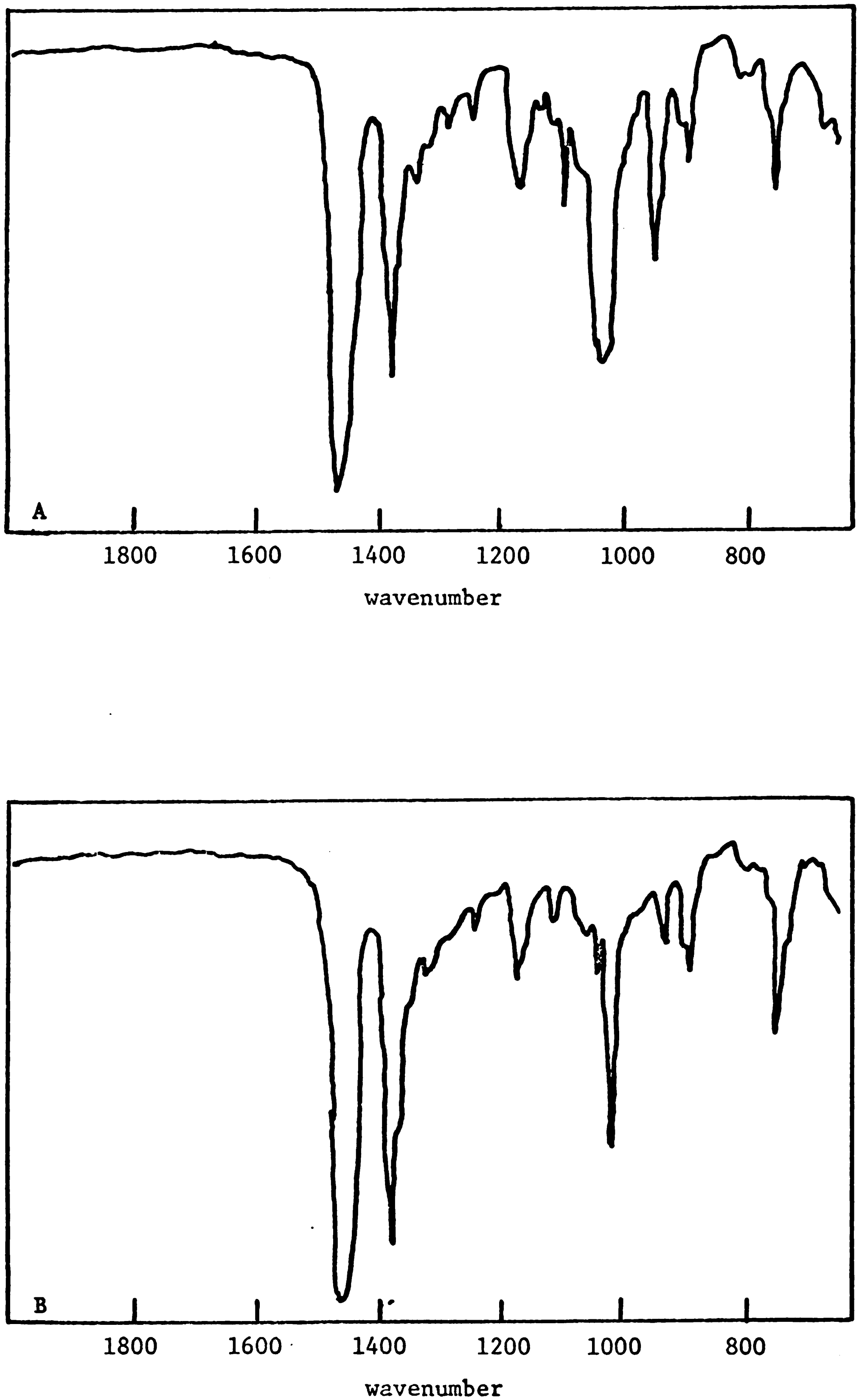
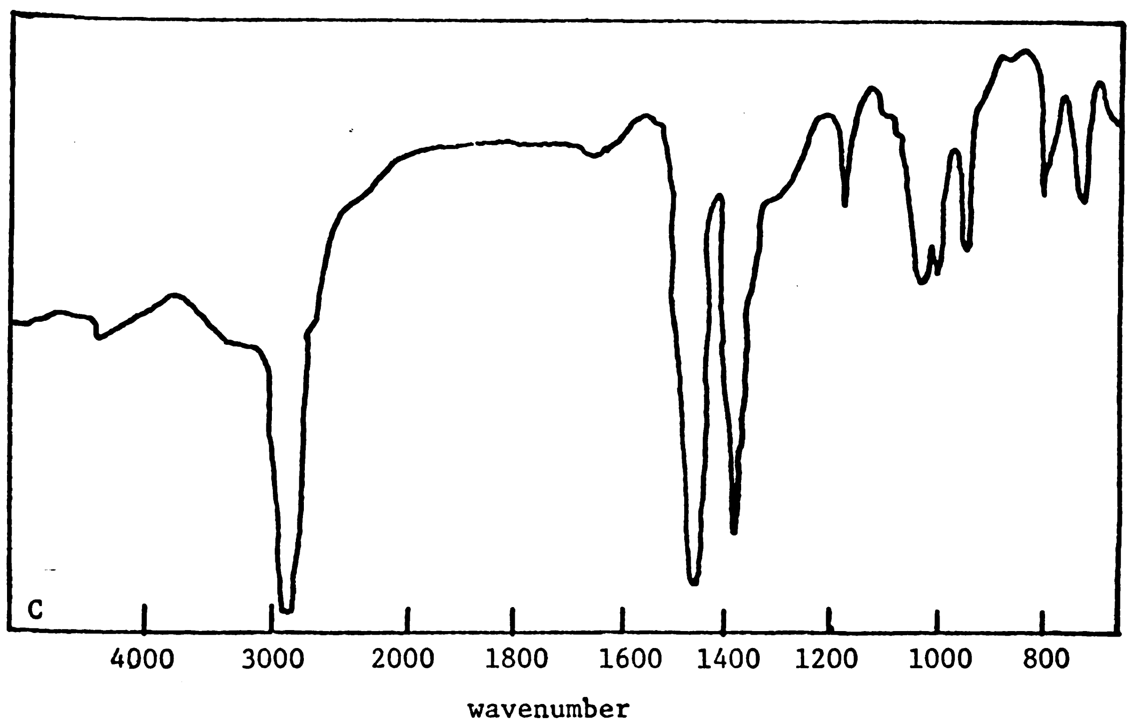

A
1800
1600
1400
1200
1000
800
wavenumber
B
1800
1600
1400
1200
1000
800
wavenumber

Figure 3.


C
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

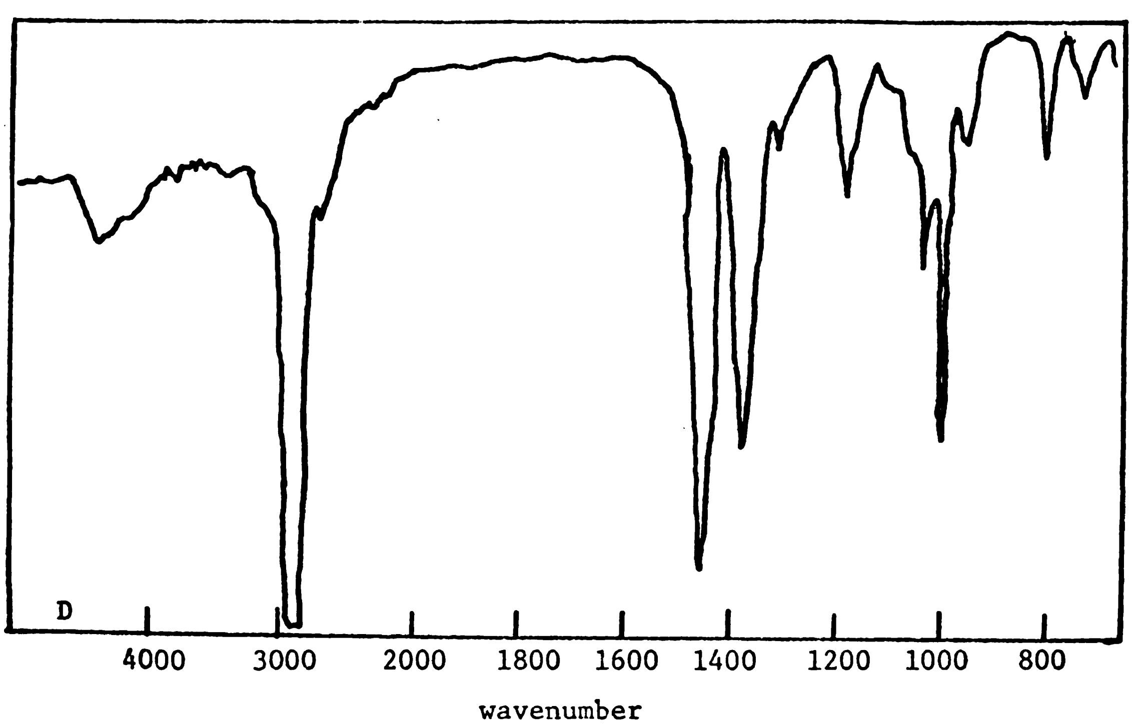

D
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

Figure 3.

Figures 3C and 3D demonstrate that the original C-O stretch at 1029 cm^{-1} was lost and a tungsten-oxygen double bond stretch appeared at 990 cm^{-1} after alkyl halide evolution from $B[W(OC_2H_5)Cl_5]$.

In the decomposition of $[(C_2H_5)_4N][W(OCH_3)Cl_5]$, the vapors released were collected in a vacuum trap. The identity of methyl chloride obtained in the gases was verified by vapor pressure measurements on the trapped liquids. The infrared spectra of methyl chloride and ethyl chloride, which were obtained by the elimination reaction, are given in Figure 4A and 4B respectively. These compare well with known spectra except additional absorptions are located at 1150 cm^{-1} and 2380 cm^{-1}. The one at 2380 cm^{-1} is a Cl_2 absorption; the other's identity is unknown. Presence of HCl is also probable since a solution of the trapped materials in water was acidic and formed a white precipitate upon the addition of $AgNO_3$.

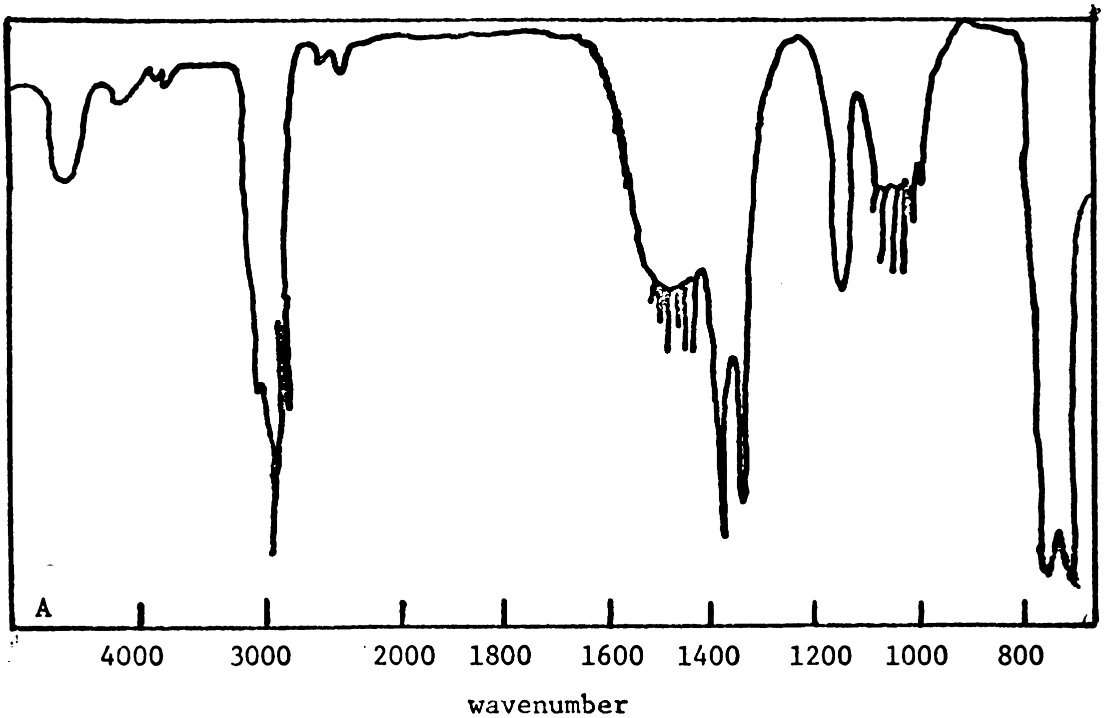
The relative heterogeneous rates of alkyl chloride evolution were determined qualitatively by use of a constant volume Warburg apparatus. With tetraethylammonium as the cation, the appearance rate of alkyl chloride was CH_3Cl > C_2H_5Cl > C_3H_7Cl. The rate of ethyl chloride evolution was found to decrease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

Under constant volume conditions, the reaction yields about one mole RCl per mole of reactant. However, the solid which was under continuous vacuum lost more weight

Figure 4: Infrared spectra

A: CH_3Cl from $[(C_2H_5)_4N][W(OCH_3)Cl_5]$

B: C_2H_5Cl from $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$


A
4000
3000
2000
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1600
1400
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1000
800
wavenumber

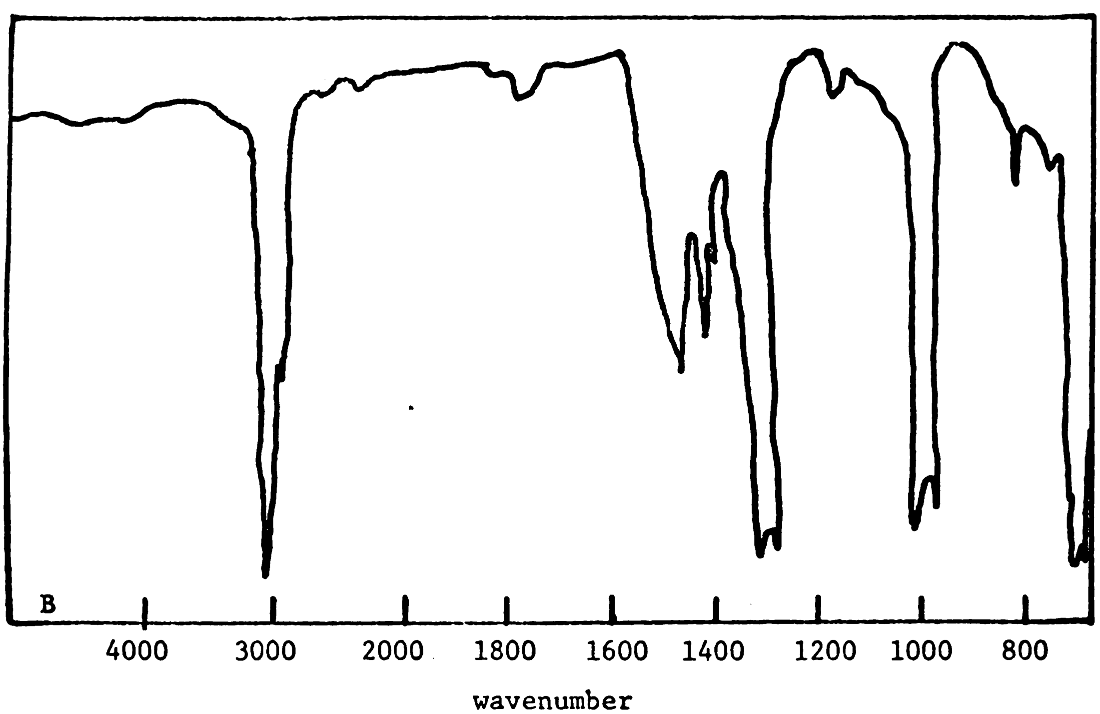

B
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

Figure 4.

than necessary to produce one mole of RCl. Quantitative rate features of weight loss experiments were similar to constant volume results except the rate of decomposition of the alkoxocomplexes appeared to be tetraethyl > tetrabutyl > tetrapropyl. The complications of excess weight loss were due to evolution of other gases. Thus, the solid product which remained was not pure, and the impurities could not be removed.

The results of infrared studies permit speculation into the nature of the processes which take place in alkyl halide elimination and will be considered after some remarks about spectra are made.

In a complex, such as $W(OCH_3)Cl_5^-$ which has C_{4v} symmetry, there should be $4A_1$ and $4E$ modes as described in the introduction. In addition, ligand and cation vibrations were investigated. The C-O stretch ($\sim$1030 cm^{-1}) occurred in a region characteristic of bound alkoxide groups.[61] The C-H vibrations were masked by Nujol. There were no O-H bands at 3600 cm^{-1}. Thus, alcoholates or hydrolysis products were discounted. The spectra illustrate these facts in Figure 5.

The infrared spectra of dialkoxide complexes are shown in Figure 6. There were vibrations of the cation and the typical C-O stretch of the alkoxide ligand at $\sim$1060 cm^{-1} and $\sim$1100 cm^{-1}. However, the framework vibrations were different than for monoalkoxide complexes because the symmetry of the complex changed. The dialkoxide complexes have axial

Figure 5: Infrared Spectra

A: $[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

B: $[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

C: $[(C_2H_5)_4N][W(OCH_3)Cl_5]$

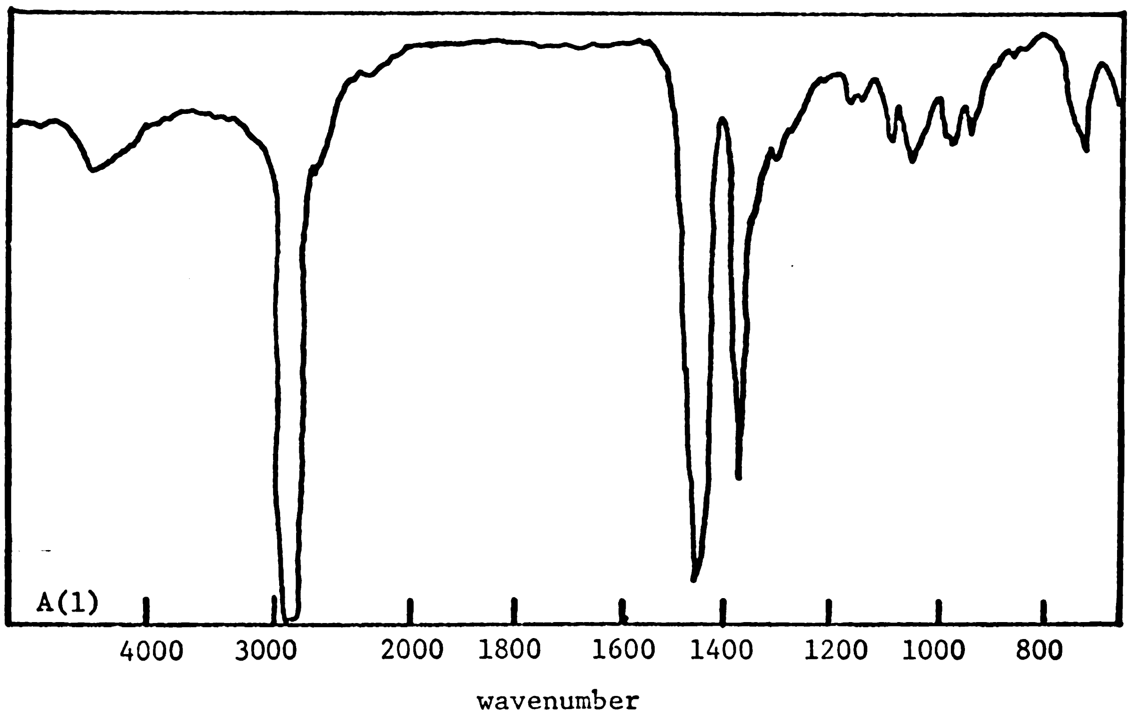
(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

D: $[(C_2H_5)_4N][W(n\text{-}OC_3H_7)Cl_5]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}


A(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

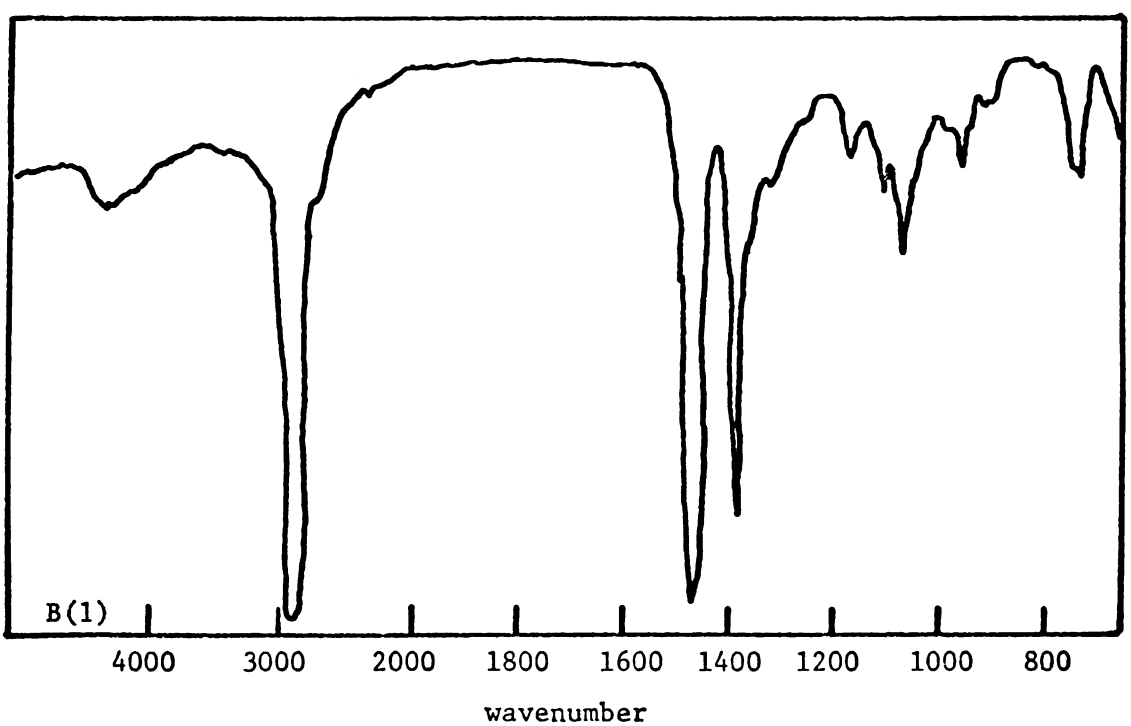
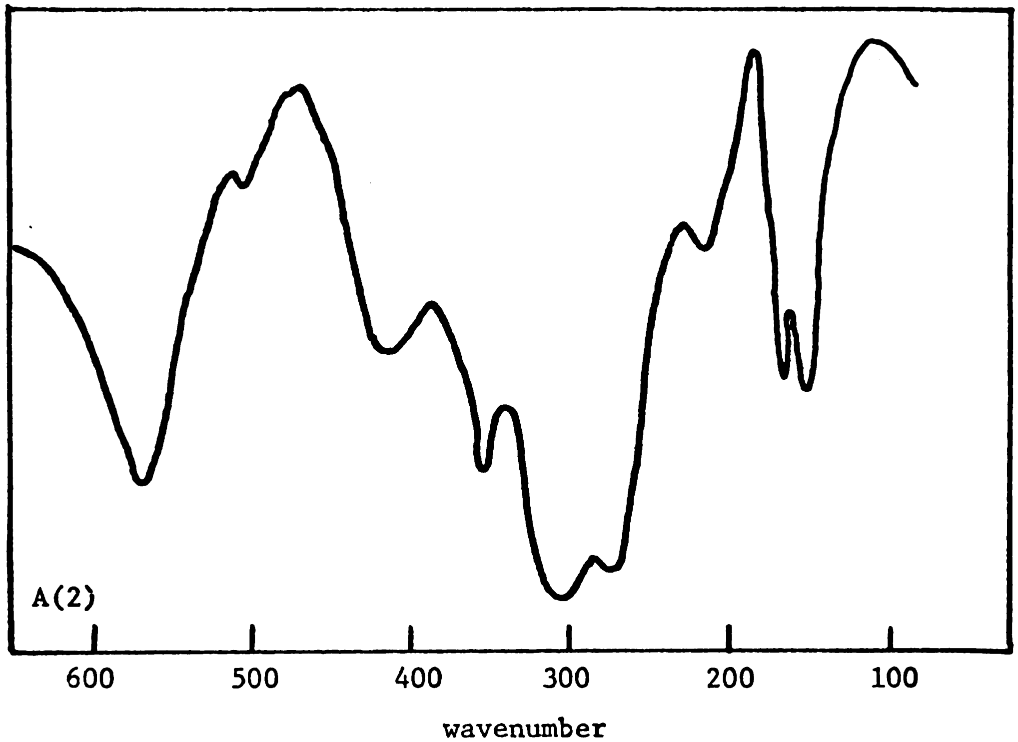

B(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

Figure 5.


A(2)
600
500
400
300
200
100
wavenumber

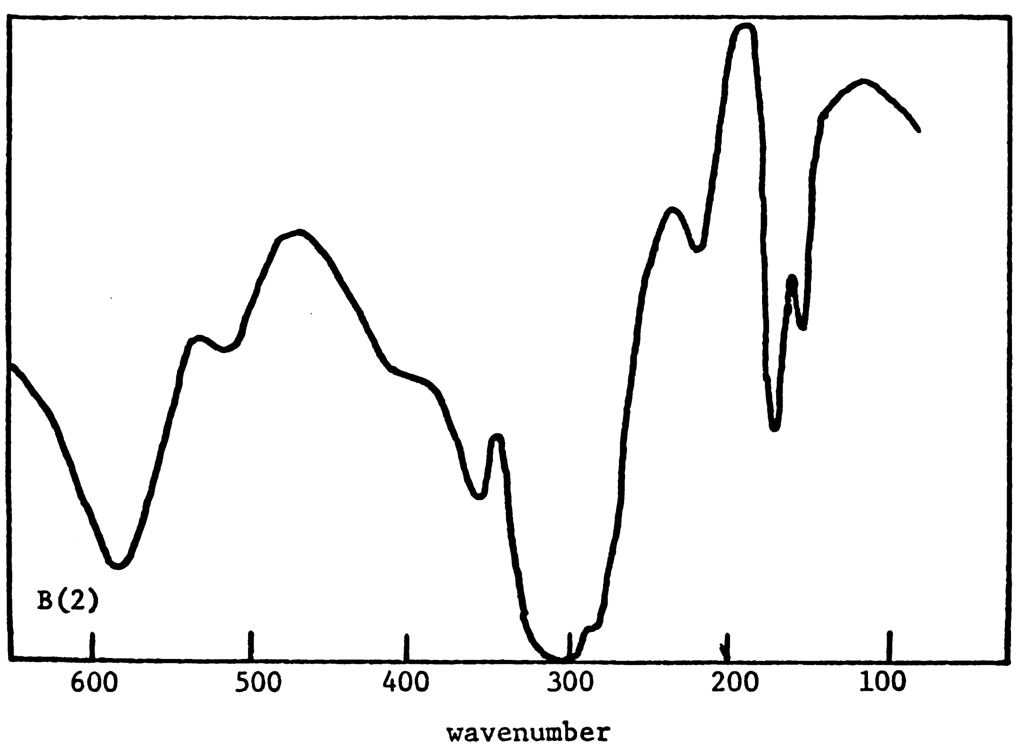
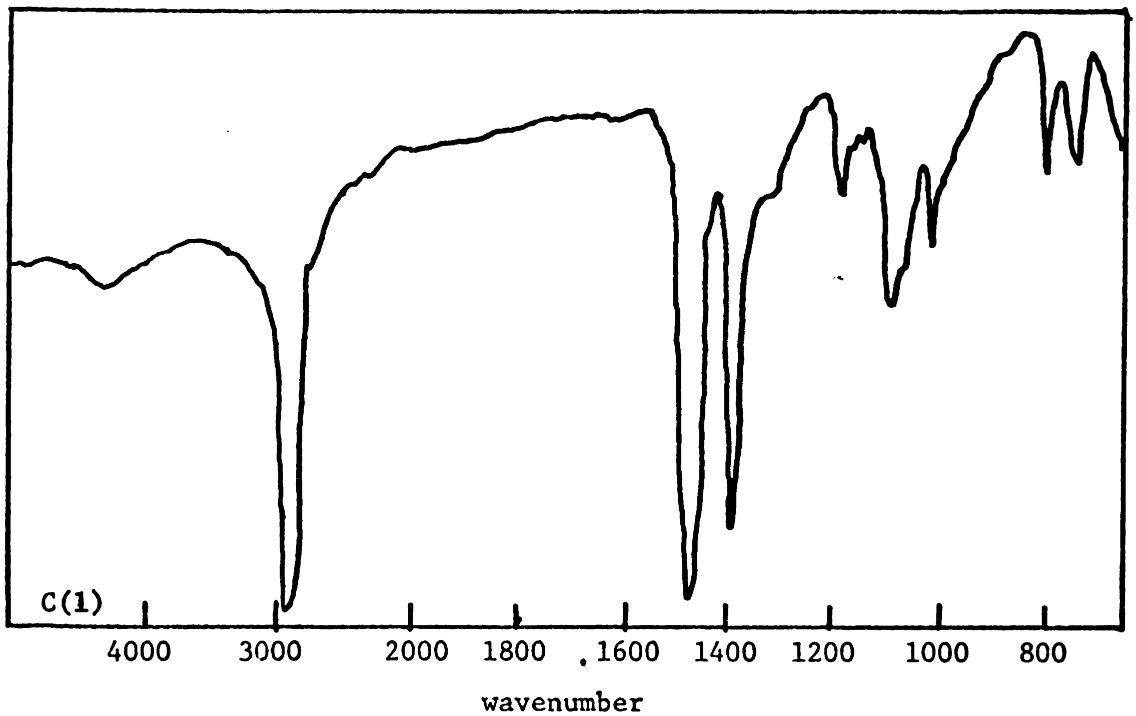

B(2)
600
500
400
300
200
100
wavenumber

Figure 5.


C(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

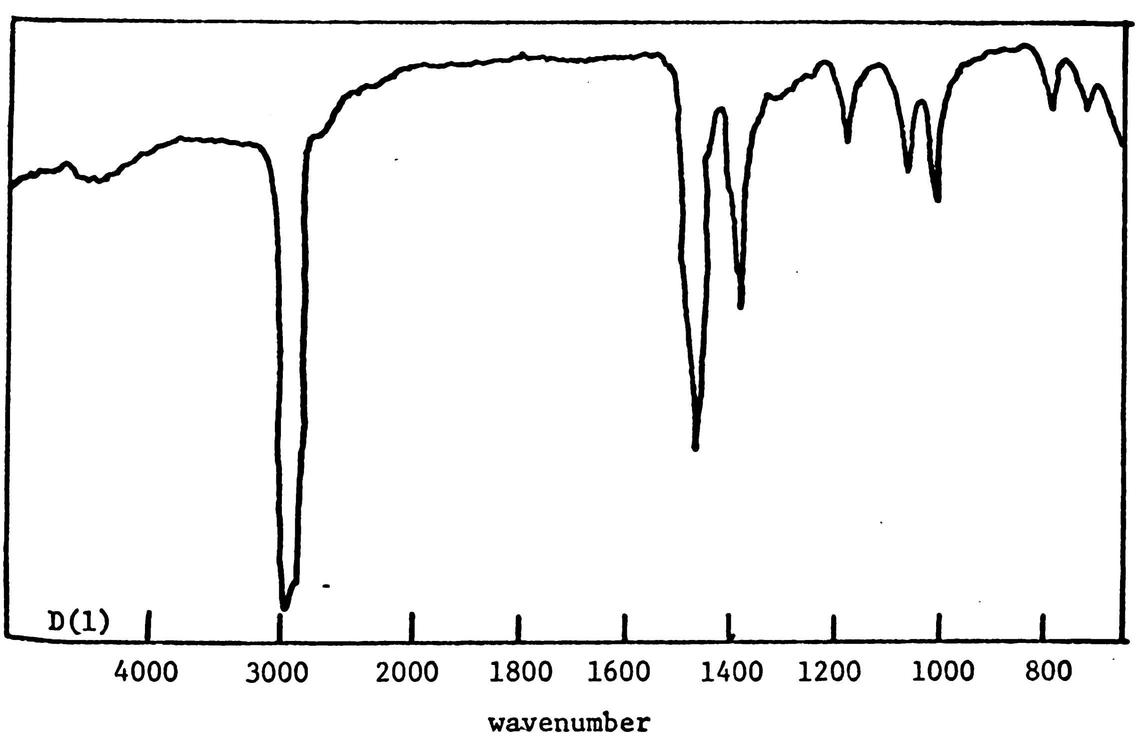
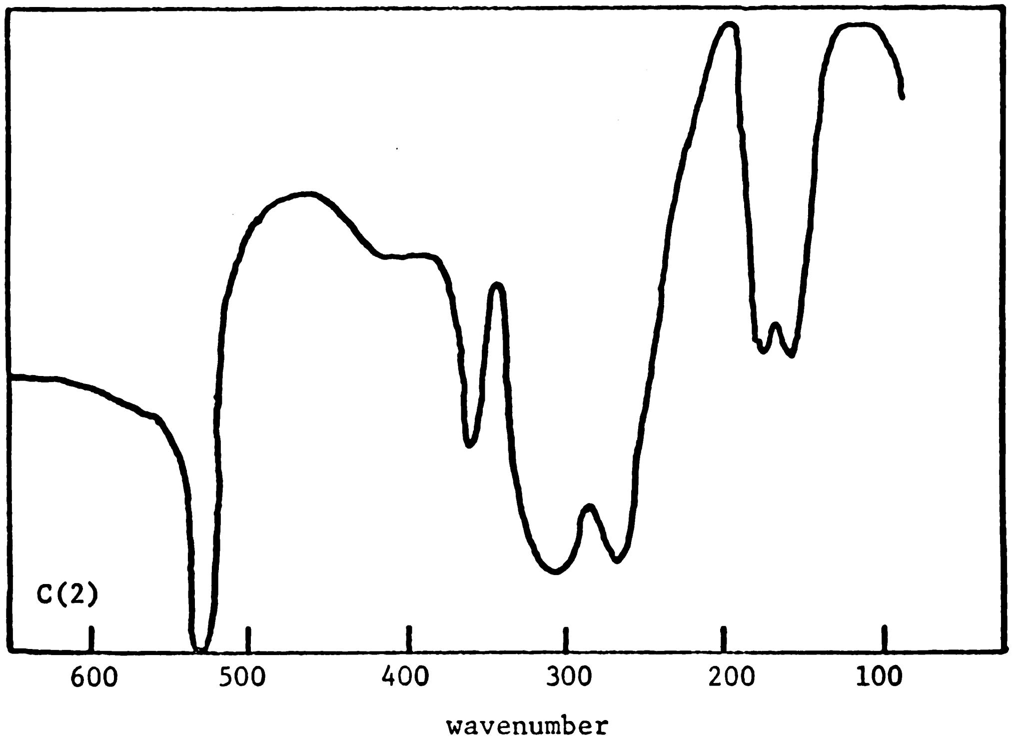

D(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber

Figure 5.


C(2)
600
500
400
300
200
100
wavenumber

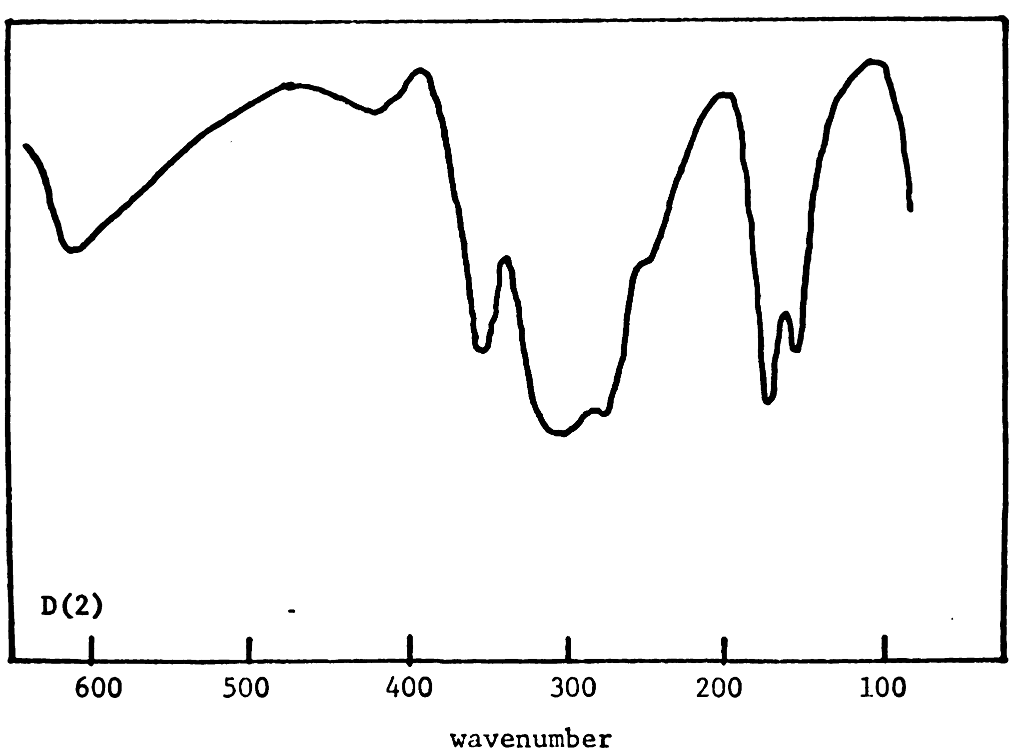

D(2)
600
500
400
300
200
100
wavenumber

Figure 5.

Figure 6: Infrared spectra:

A: $[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

B: $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

C: $[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

D: $[(CH_3)_4N][W(OCH_3)_2Cl_4]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

E: $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$

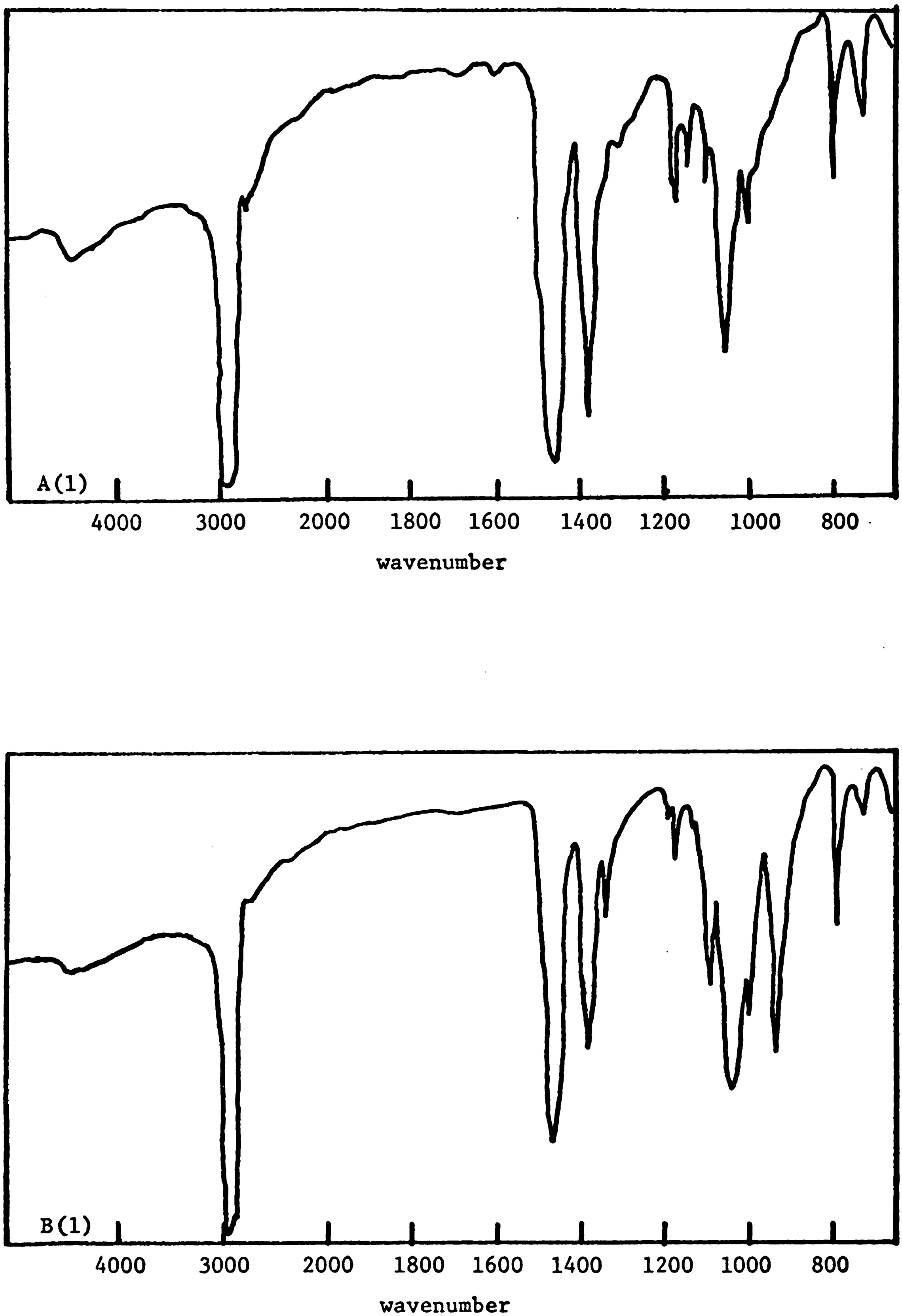
(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}

F: $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$

(1) 5000 - 650 cm^{-1}

(2) 650 - 80 cm^{-1}


A(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber
B(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber
Figure 6.

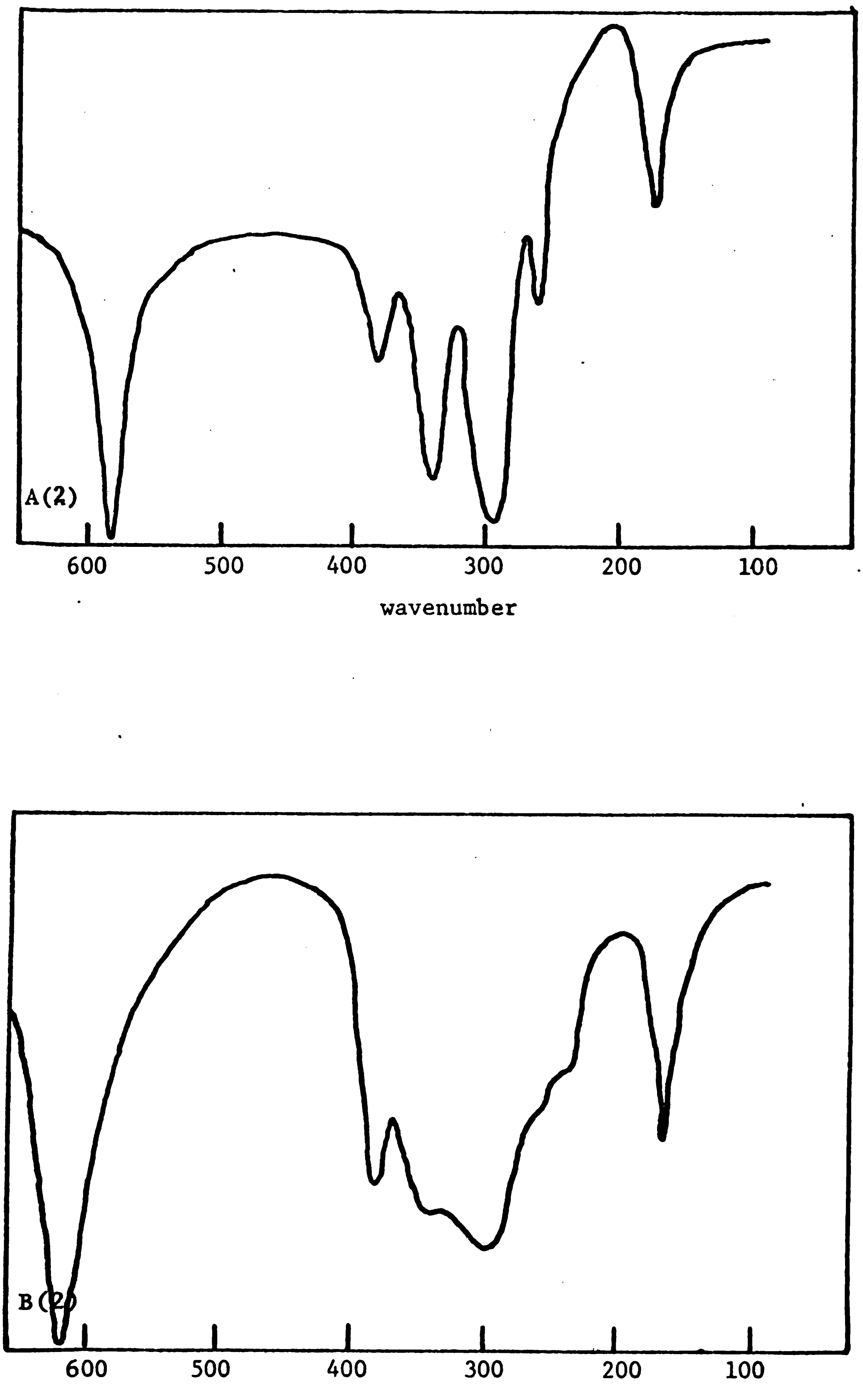
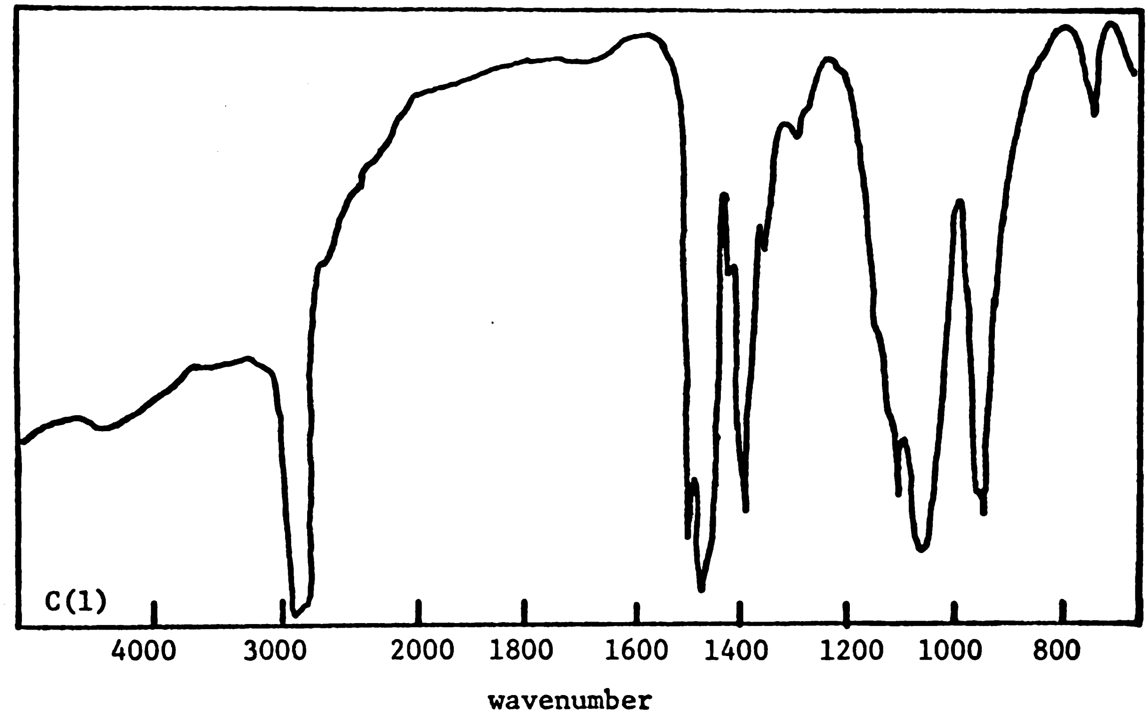
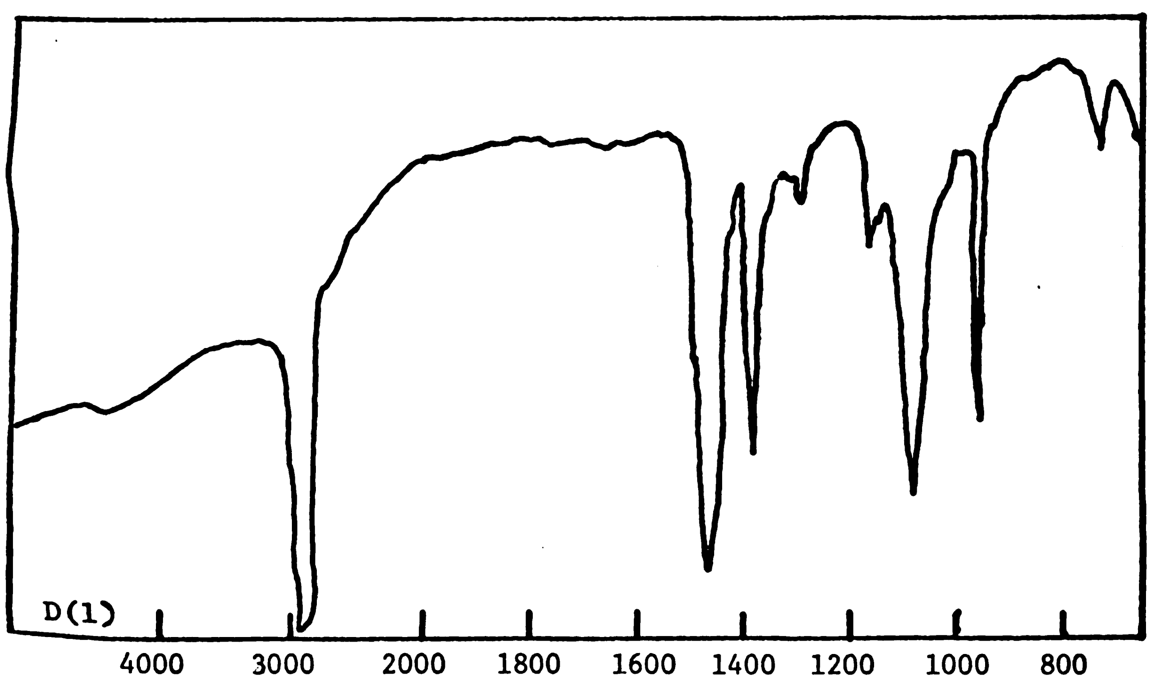

A(2)
600
500
400
300
200
100
wavenumber
B(2)
600
500
400
300
200
100
wavenumber

Figure 6.


C(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber


D(1)
4000
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1600
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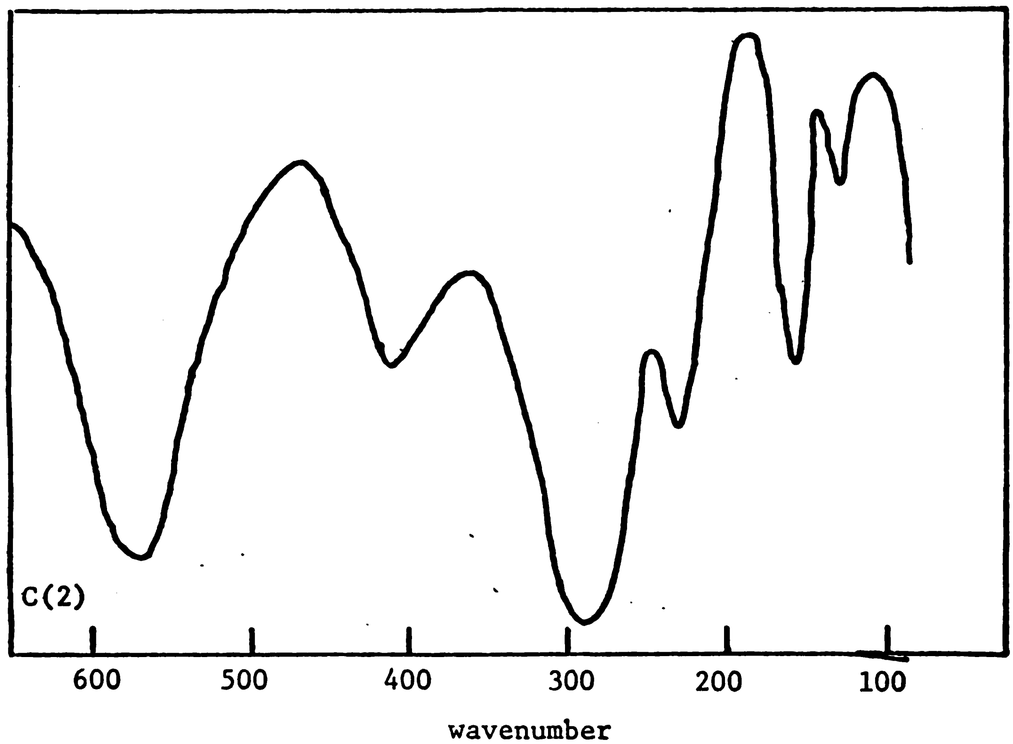
1200
1000
800
wavenumber

Figure 6.


C(2)
600
500
400
300
200
100
wavenumber

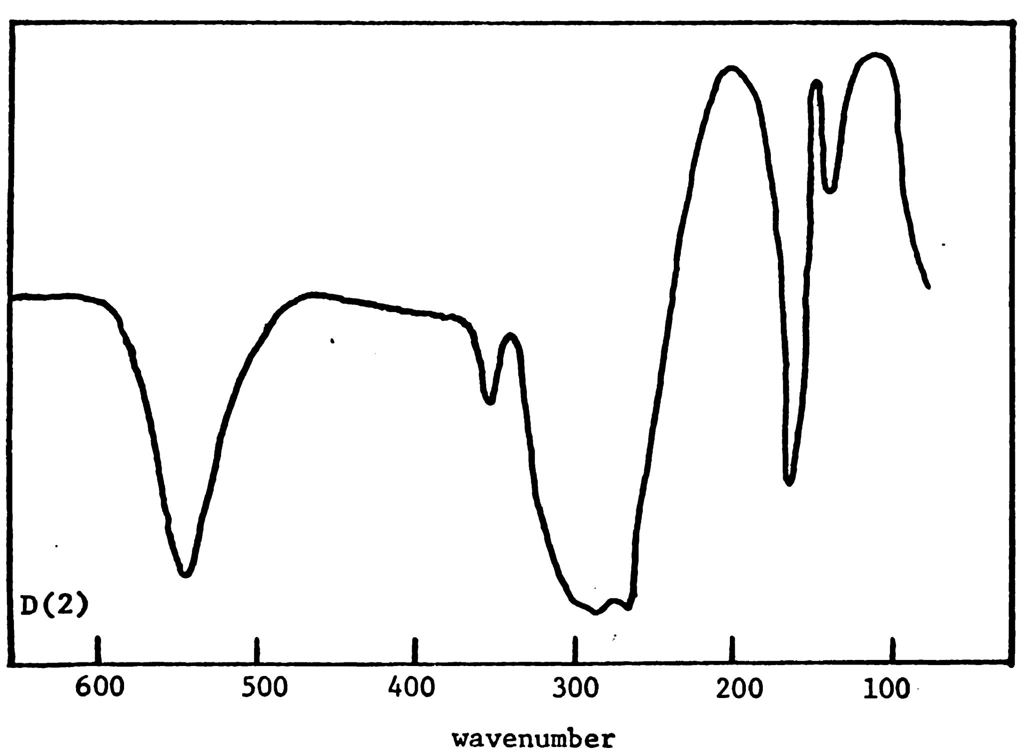
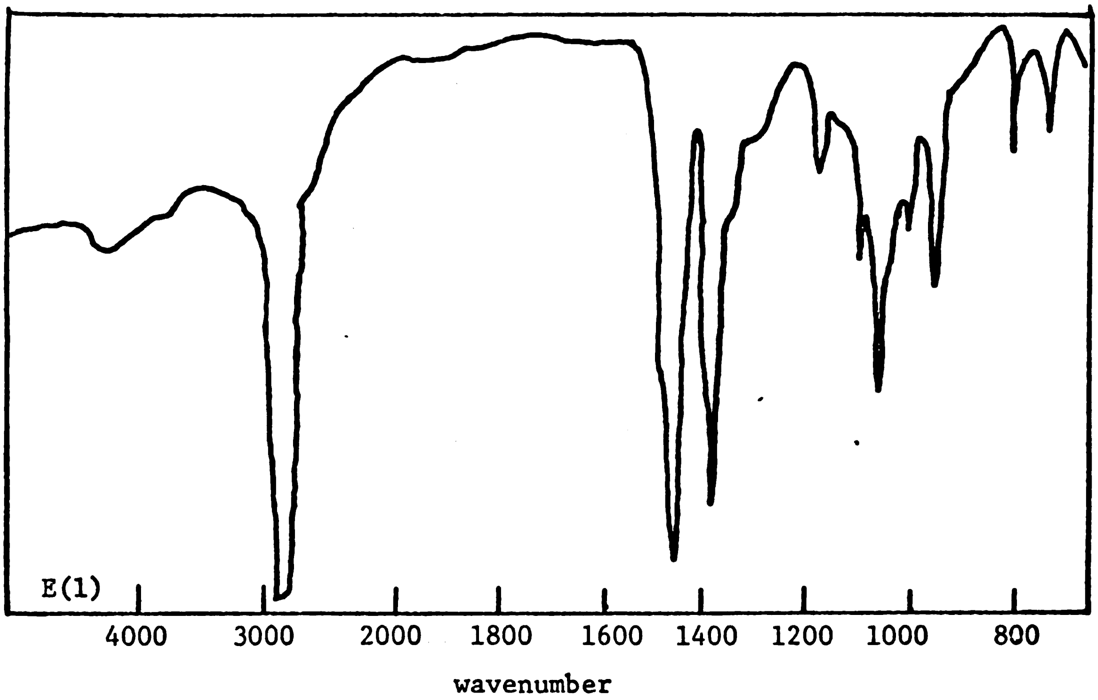
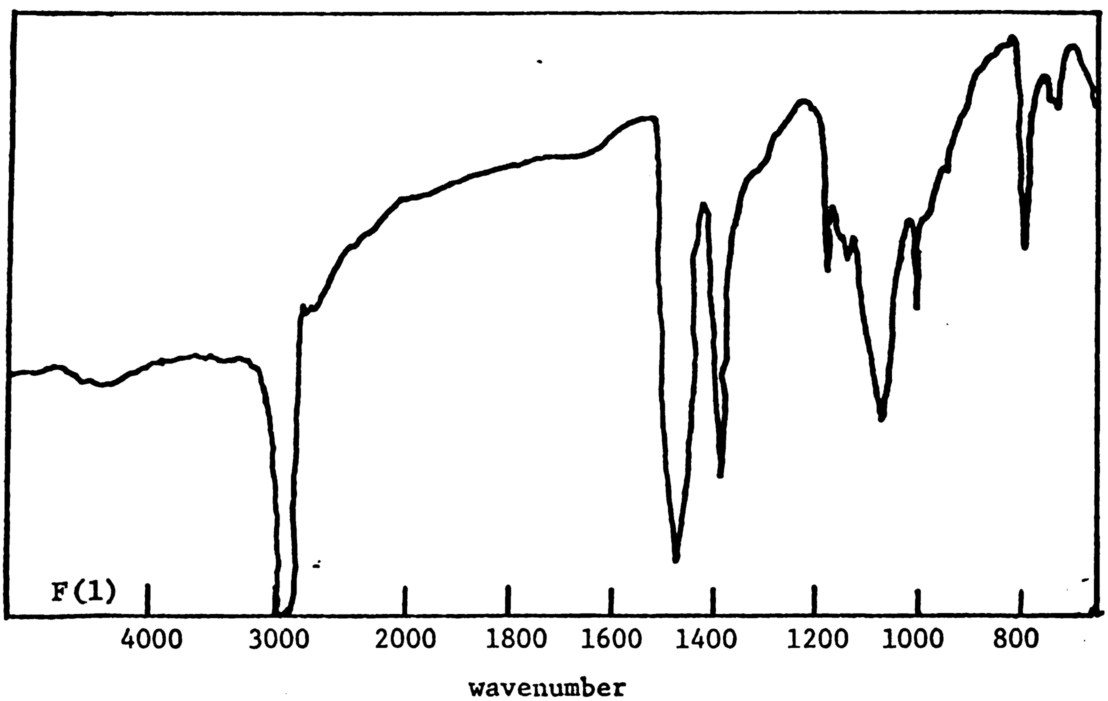

D(2)
600
500
400
300
200
100
wavenumber

Figure 6.


E(1)
4000
3000
2000
1800
1600
1400
1200
1000
800
wavenumber


F(1)
4000
3000
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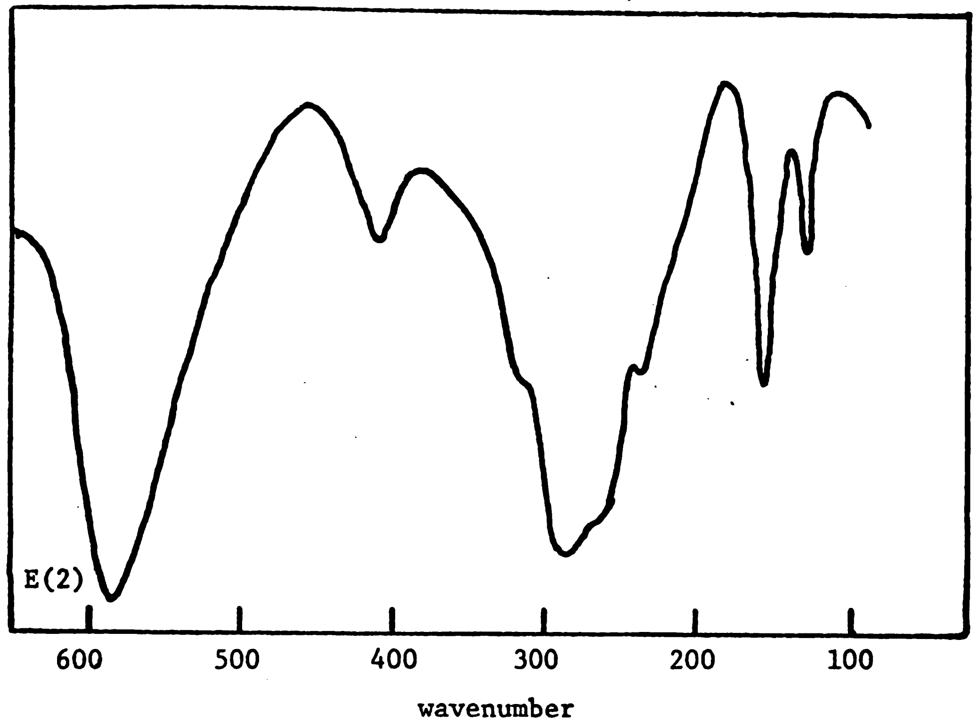
1600
1400
1200
1000
800
wavenumber

Figure 6.


E(2)
600
500
400
300
200
100
wavenumber

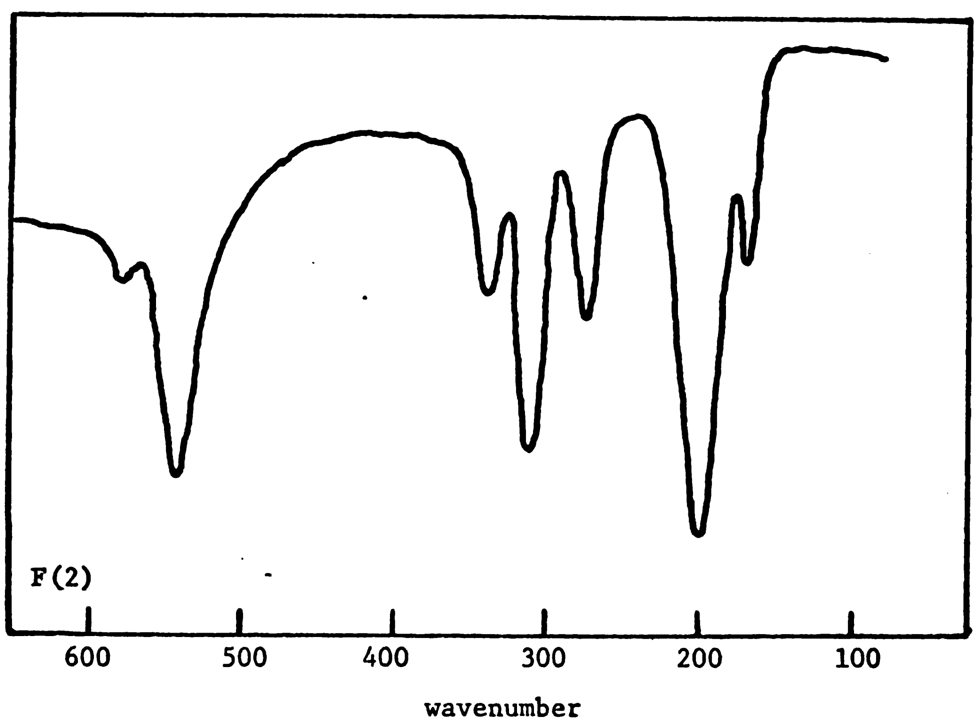

F(2)
600
500
400
300
200
100
wavenumber

Figure 6.

symmetry, according to esr measurements, and so should possess D_{4h} symmetry. Of the eleven normal modes, only five, the A_{2u} and E_u are infrared active. The A_{2u} species are an M-O stretching vibration and an O-M-X bending mode. The E_u representations are M-X, X-M-X and X-M-O bending modes.

Tables 3 and 4 contain infrared absorptions for the monoalkoxo and dialkoxo complexes respectively.

In polymeric chromium alkoxides,[62] M-O was considered to appear at 500 cm^{-1}. The bridging frequency of Co-Cl in the polymer lies about 70 cm^{-1} lower than the terminal frequency of Co-Cl.[63] Therefore, it seems reasonable that the absorption in the 600 cm^{-1} region be assigned as a M-O stretching vibration.

The metal-halogen stretching frequencies are approximately the same in monoalkoxo complexes as the hexachloro compound.[30] Two of three metal-halogen stretching frequencies were found near 300 cm^{-1} and 275 cm^{-1} for monoalkoxide complexes. The third probably lies under the other two. In the dialkoxide species, the stretching frequency is almost 20 cm^{-1} lower. The $MoOCl_4^-$ ion gave the highest absorption, ~360 cm^{-1} (Table 5). Comparison of the M-X stretch, of the complexes studied, with the results of Sabatini and Bertini,[24] leads one to conclude that the following is the order of metal-halogen bond strength; $WOCl_4^- > WOCl_5^= > WCl_6^- \sim W(OR)Cl_5^- > W(OR)_2Cl_4^-$ and $MoOCl_4^- > MoOCl_5^= \sim MoCl_6^- \sim Mo(OR)Cl_5^- > Mo(OR)_2Cl_4^-$ ($R = CH_3$, C_2H_5, or C_3H_5).

Table 3. Infrared absorption frequencies (cm^{-1}) of $M(OR)Cl_5^-$ ions (with possible assignment)[a]

Assignment	$[(C_2H_5)_4N][W(OCH_3)Cl_5]$	$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$	$[(C_2H_5)_4N][W(OC_3H_7)Cl_5]$
ν (M-O)	551 m	606 m	613 m
ν (C-C-O)	416 wk	412 wk	414 wk
ν (O-M-X)	354 sh	330 sh	352 sh
ν (M-X)	306 vstr	304 vstr	306 vstr
ν (M-X)	265 vstr	283 vstr	275 vstr
ν (O-M-X)	219 sh	238 sh	250 sh
ν (X-M-X)	174 m	175 m	170 m
ν (X-M-X)	153 m	155 m	155 m
ν (C-O)	1080 s	1029 s	1060 s

Assignment	$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$	$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$
ν (M-O)	567 m	584 m
	509 wk	522 wk
ν (C-C-O)	420 m	411 wk
ν (O-M-X)	354 sh	354 sh
ν (M-X)	306 vstr	306 vstr
ν (M-X)	274 vstr	281 vstr
ν (O-M-X)	214 sh	220 sh
ν (X-M-X)	167 m	169 m
ν (X-M-X)	154 m	152 m
ν (C-O)	1050 s, 1088 m	1063 s, 1099 m

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

Table 4. Infrared absorption frequencies (cm^{-1}) of $M(OR)_2Cl_4^-$ ions (with possible assignment)[a]

Assignment	$[(CH_3)_4N][W(OCH_3)_2Cl_4]$	$[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$	$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$
ν (M–O)	544 s	573 s	584 s
ν (C–C–O)		412 wk	412 wk
ν (O–M–X)	351 sh	337 sh	
ν (M–X)	290 vstr	289 vstr	286 vstr
ν (O–M–X)	267 sh	233 sh	239 sh
ν (X–M–X)	162 m	160 m	159 m
ν (X–M–X)	139 wk	129 wk	131 wk
ν (C–O)	1080 s, 1160 wk	1052 s, 1093 wk	1060 s, 1095 wk

Assignment	$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$
	625 wk		580 wk
ν (M–O)	582 s	617 s	542 s
ν (O–M–X)	337 sh, 381 m	331 m, 379 m	311 m, 338 m
ν (M–X)	300 vstr	306 vstr	198 vstr
ν (O–M–X)	262 m	288 vstr	373 m
ν (X–M–X)	175 m	164 m	167 sh
ν (C–O)	1060 s, 1102 wk	1078 s	1066 s, 1115 wk

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

Table 5. Infrared absorption frequencies (cm^{-1}) of $MOCl_4^-$ ions and dimeric tungsten species (with possible assignment)[a]

Assignment	$[W(OCH_3)_2Cl_3]_2$	$[W(OCH_3)_3Cl_2]_2$	$[W(OC_2H_5)_3Cl_2]_2$
ν(M-O)	567 s	566 s	623 s
ν(M-O)	542 s	520 m	519, 501 m
ν(O-M-O)		455 m	397 m
ν(O-M-X)	357 s	339 wk	
ν(M-X)	328 s	318 s	305 s
ν(M-X)	291 s	305 s	288 s
ν(O-M-X)		279 s	247 sh
ν(O-M-X), (M-X)	255 s	252 m	218 m
ν(X-M-X)	177 s		
ν(X-M-X)	91 m		
ν(C-O)	990 sh, 1080 s, 1110 sh	990 s, 1080 s, 1110 m	995 s, 1050 s, 1105 wk

Assignment	$[(C_3H_7)_4N](MoOCl_4)$	$[(C_4H_9)_4N](MoOCl_4)$
ν(M-O)	990 wk	980 wk
ν(M-X)	358 s	354 s
ν(X-M-X)	162 m	161 m
ν(X-M-X)	154 m	155 m

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

The metal-oxygen stretch is also interesting. As the alkoxide increased in size, the metal-oxygen stretch increased in frequency, $OC_3H_7 > OC_2H_5 > OCH_3$. The metal-oxygen stretching frequencies are higher for monoalkoxide than the analogous dialkoxide complex, $[(C_2H_5)_4N][W(OC_2H_5)Cl_5] > [(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$. The stretch occurs at 613 cm^{-1} for $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$ compared to 584 cm^{-1} for the tungsten case. The absorption was lowered slightly on changing from chloride to bromide.

The X-M-X modes for monoalkoxo complexes were considered to be at ~170 cm^{-1} and ~150 cm^{-1} by comparison with WCl_6^{2-} and $MoCl_6^{2-}$ spectra.[64] A broad band began near 90 cm^{-1} but had no maximum above 80 cm^{-1}. Sabatini and Bertini assign a band in this region to an X-M-X vibration.[24] For dialkoxo and tetrachloroxo complexes, the X-M-X vibrations should be those at ~160 and ~130 cm^{-1}. The degeneracy of the E_u modes is apparently removed in the solid state.

The O-M-X vibrations were assigned by comparison with $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$. Three vibrations are observed in the 300 cm^{-1} region and are probably O-W-Br vibrations. Since X-M-X vibrations are slightly lower (~40 cm^{-1}) for X = Br than Cl,[24] one would expect a similar behavior for O-M-X modes. An M-O rocking vibration rather than any of the O-M-X modes is observed[24] in oxyhalide compounds and can be rationalized if one considers relative masses and bond strengths of the degenerate modes. However, none was observed for $MoOCl_4^-$.

In addition, a C-C-O bending mode at 370 cm^{-1} was observed for chromium ethoxide complexes.[62] A band found near 400 cm^{-1} is believed to be this vibration in the molybdenum and tungsten complexes.

The release of an alkyl group by monoalkoxide complexes indicates the greater stability of a complete π bond for oxygen in M-OR. The far infrared data (Table 3) further probably indicate that the bond trans to the metal-oxygen is weakened. The low frequency M-X band is thought to be the M-X stretch trans to the alkoxide group. The greater instability of the molybdenum compound compared to the tungsten complex ought to be due to better overlap of the oxygen p orbitals with the t_{2g} orbitals of the molybdenum in forming a molybdenum-oxygen multiple bond. Thus, a weaker metal-halide bond trans to the alkoxide group is the result. Although the frequency of the metal-oxygen bond trans to the halide increases as the size of the alkyl group increases, the rate of alkyl halide evolution decreases.[60] It is conceivable that the rearrangement in the solid state is hampered by the larger alkyl group.

The elimination is viewed as a concerted process that involves an axial chloride from one ion with the alkyl group from a neighbor. Evidence points to an intermolecular process since the rate of alkyl halide evolution decreased as the size of the cation increased. The driving force is the formation of the more stable metal oxygen double bond.

The most stable arrangement for dialkoxo complexes would be trans alkoxides where there is competition for the same t_{2g} orbitals. Further evidence for this structure is found in a shift of 16-20 cm^{-1} to lower energy for M-Cl stretches in dialkoxo compared to the similar hexachloro compound and also it is supported by the number of observed vibrations. Five normal modes are required in D_{4h} symmetry whereas thirteen are possible in C_{2v} symmetry. The number of absorptions found for the tetrachloroxo anion indicate D_{4h} symmetry as was postulated previously.[65] Only trans dialkoxides have been prepared (as confirmed by esr studies discussed below).

The infrared absorptions of dimeric compounds are given in Table 5. The structure of the dimeric compounds is thought to be two edge-to-edge octahedra.[39] The proton nmr absorption spectrum of $[W(OCH_3)_2Cl_3]_2$ in chloroform, Figure 7, gave a line absorption at $\tau = 5.6 \pm .1$. This indicates the equivalence of the methyl groups and, thus, only chloride bridges are possible. Two similar alkoxide groups could either lie in the equatorial plane or trans to one another in axial positions, if one assumes an octahedral structure around each metal atom. The latter of the two is preferred because the vibrations are similar to the dialkoxide monomeric species but shifted to slightly higher wavelength.

The above observation is noted for absorptions of $[W(OCH_3)_2Cl_3]_2$ and $[W(OCH_3)_3Cl_2]_2$. The nmr studies of $[W(OC_2H_5)_3Cl_2]_2$ indicate the non equivalence of the alkoxide

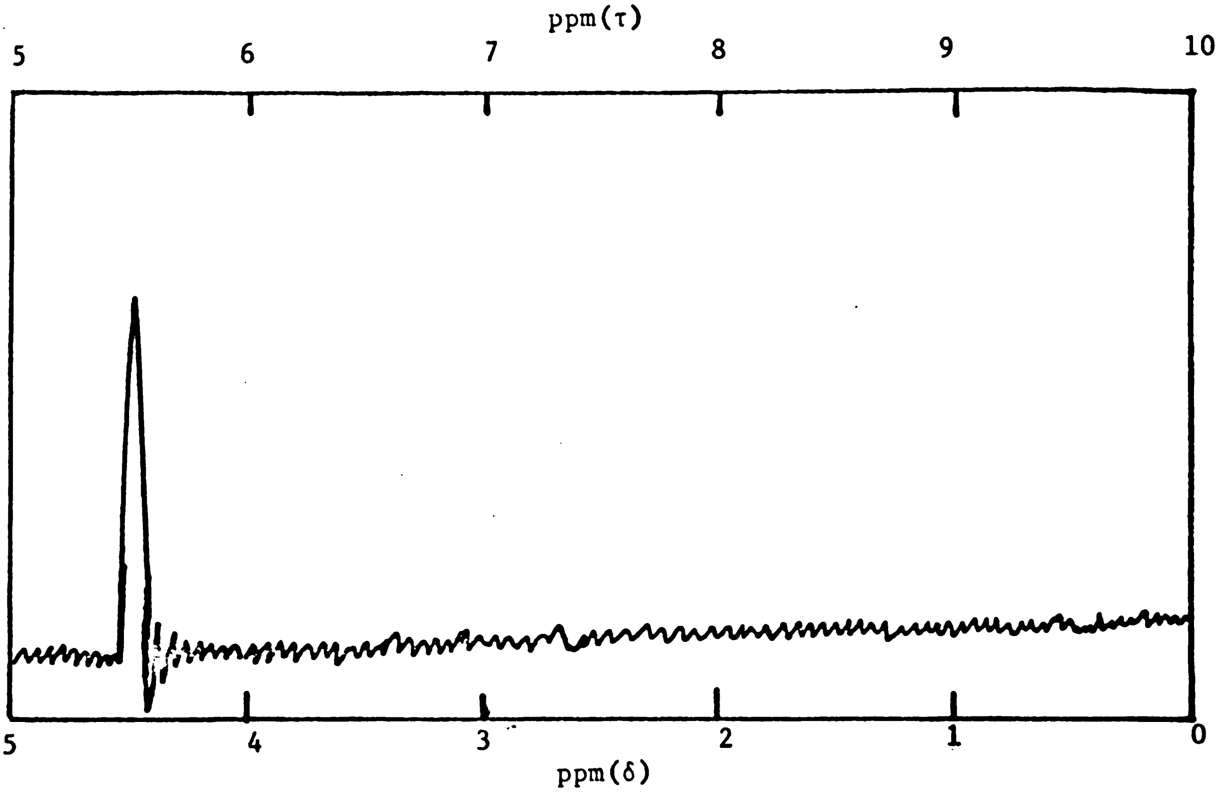


Figure 7. Proton nmr spectrum of $[W(OCH_3)_2Cl_3]_2$.

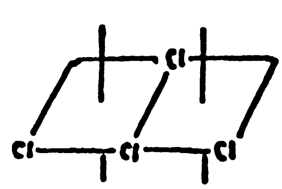


Figure 8. Structure proposed for $[W(OC_2H_5)_3Cl_2]_2$.

groups. Klejnot found a ratio of 2:1 for the proton nmr absorption spectrum of the dimer and he also found the molecule had a dipole moment. Figure 8 shows the structure he proposed.[39]

Since there are no observed X-M-X vibrations and the molecule has a dipole moment, one must assume the proposed structure is correct. The band at 218 cm^{-1} for $[W(OCH_3)_3Cl_2]_2$ is attributed to the M-X bridging vibration. This band is probably that at 255 cm^{-1} for $[W(OCH_3)_2Cl_3]_2$ and 252 cm^{-1} for $[W(OCH_3)_3Cl_2]_2$. For the latter two species the band probably contains some O-M-X character. The dimeric species also exhibit vibrations at ~520 cm^{-1} which are probably M-O stretches of terminal alkoxide groups in the equatorial plane. The O-M-O vibrations are probably found in the 400 cm^{-1} region by analogy with the other results.[62] The other assignments were made in comparison with the other compounds studied.

The number of possible vibrations was determined by a knowledge of the molecular symmetry. The interpretation of the electronic spectra is also based upon the structure of the complex ion.

Compounds of O_h symmetry, WBr_6^- and WCl_6^-, gave electronic spectra similar to ones previously reported.[27-30] Values for 10 Dq were WBr_6^- = 18,900 cm^{-1} and WCl_6^- = 21,700 cm^{-1}.

The paramagnetic alkoxide complexes demonstrated D_{4h} or C_{4v} symmetry. Both point groups give the same splitting pattern of d energy levels. The splittings from lowest to highest energy are a singlet $B_2(d_{xy})$ state, a doublet $E(d_{xz}$ and $d_{yz})$ state, and a singlet $A_1(d_z2)$ state. Three d-d transitions are Laporte forbidden but spin allowed. These transitions have absorption coefficients from 10-20 $\underline{M}^{-1}$ cm^{-1}.

Illustrative spectra of dialkoxide complexes both in solid and solution are given in Figures 9 and 10. Transitions for molybdenum compounds are believed to be $B_2 \rightarrow E$ and ~12,000 cm^{-1} and $B_2 \rightarrow B_1$ at ~21,500 cm^{-1}. For tungsten it seems that the degeneracy of the E state is removed. Thus two transitions are observed at ~11,000 and ~14,000 cm^{-1}. The $B_2 \rightarrow B_1$ transition is thought to occur at ~25,000 cm^{-1}. For both molybdenum and tungsten, the $B_2 \rightarrow A_1$ transition is masked by the charge transfer band.

Dilute solutions of $W(OR)_2Cl_4^-$ in ROH were stable during measurement of the electronic spectrum, but slowly changed thereafter. The $M(OR)_2Cl_4^-$ anions were most stable in anhydrous nitromethane which contained no HCl. It was possible to measure electronic transitions of $Mo(OR)_2Cl_4^-$ in acidic alcohol solutions at 0^0. If the alcohol solution is not saturated with HCl or warmed to 25^0, spectra change with time and suggest that reactions occur and the species is no longer $Mo(OR)_2Cl_4^-$. The spectra reported previously[44,45] were more like the tetrachloroxomolybdate(V) species in alcohol than the absorptions found here. Furthermore, the

Figure 9. Electronic spectra of:

A: Solution-nitromethane

B: Reflectance-solid

C: Reflectance-mull.

Key:	$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	———————
	$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	— — — — —
	$[(C_3H_7)_4N](MoOCl_4)$	- · - · - ·
	$[(C_4H_9)_4N](MoOCl_4)$	- x - x - x

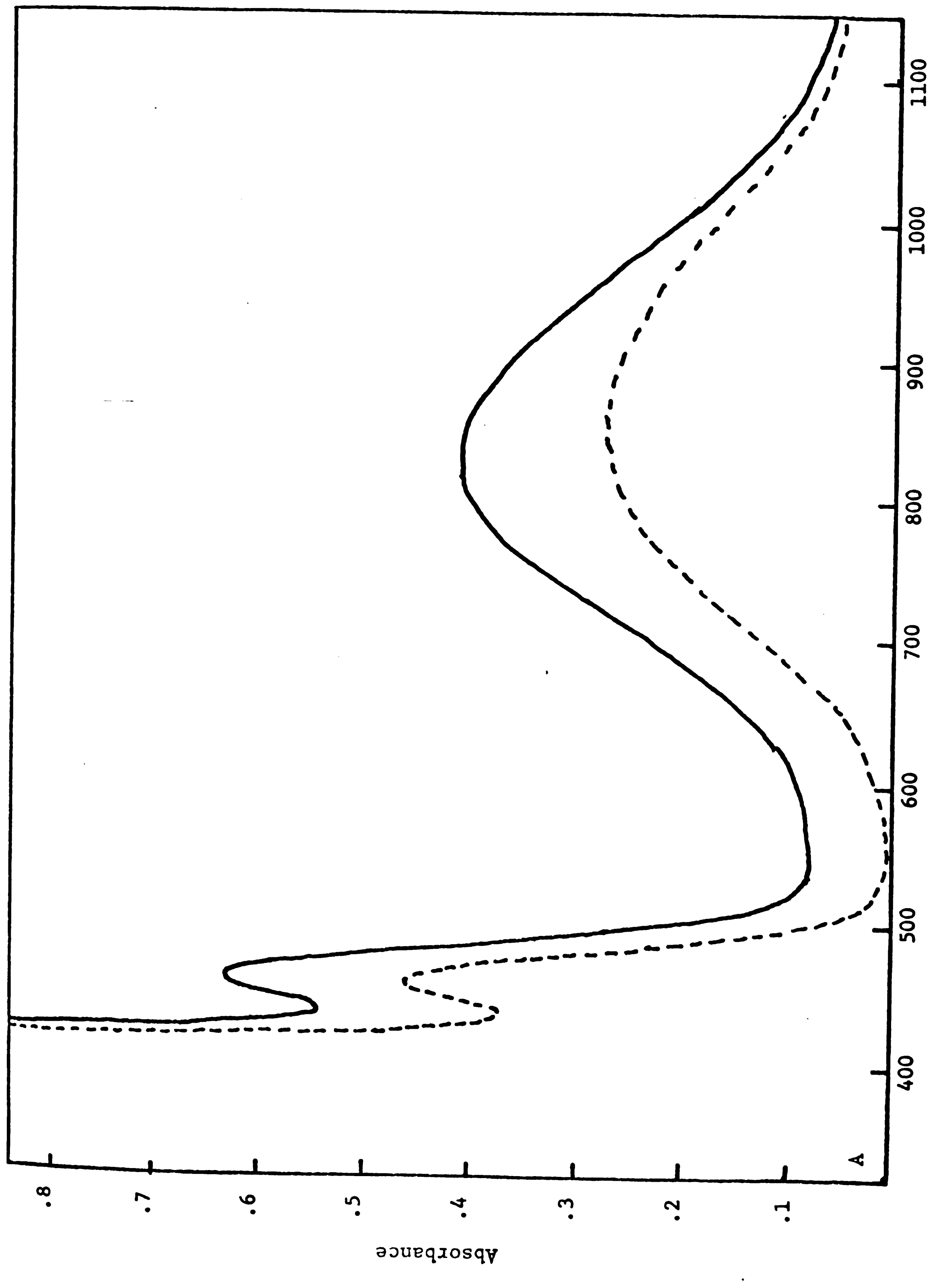

Absorbance
.8
.7
.6
.5
.4
.3
.2
.1
A
400
500
600
700
800
900
1000
1100
millimicrons

Figure 9.

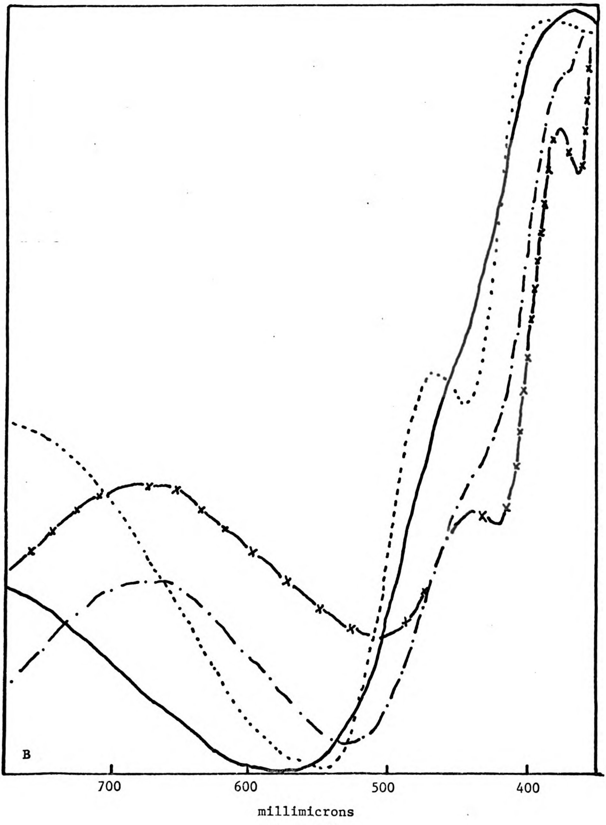


Figure 9.

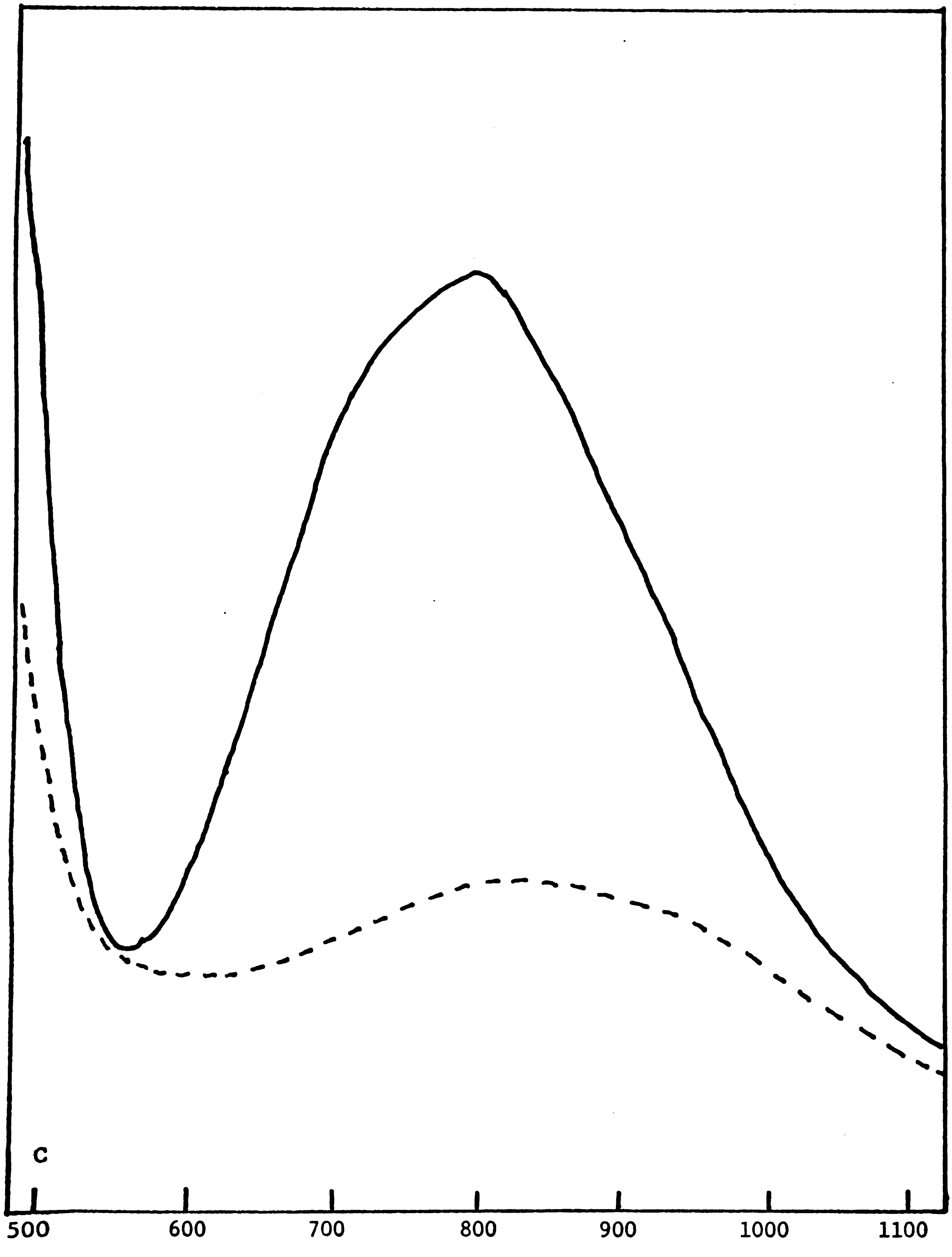


Figure 9.

Figure 10. Electronic spectra of

A: Solution-nitromethane

B: Reflectance-solid

C: Reflectance-mull.

Key: $[(CH_3)_4N][W(OCH_3)_2Cl_4]$ ——————

$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$ – – – – – –

$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$ - · - · - · -

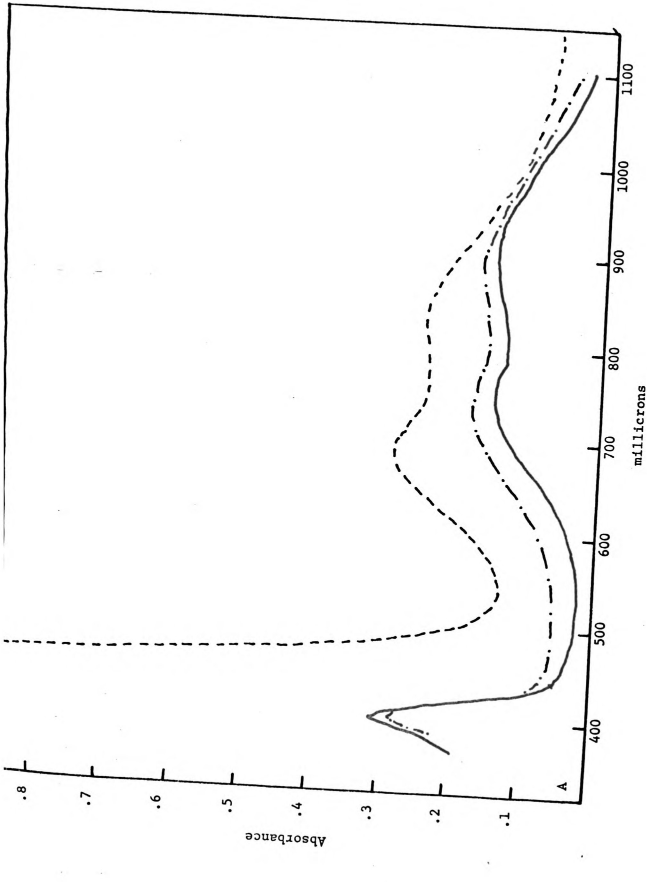

Absorbance
.1
.2
.3
.4
.5
.6
.7
.8
A
400
500
600
700
800
900
1000
1100
millicrons

Figure 10.


B

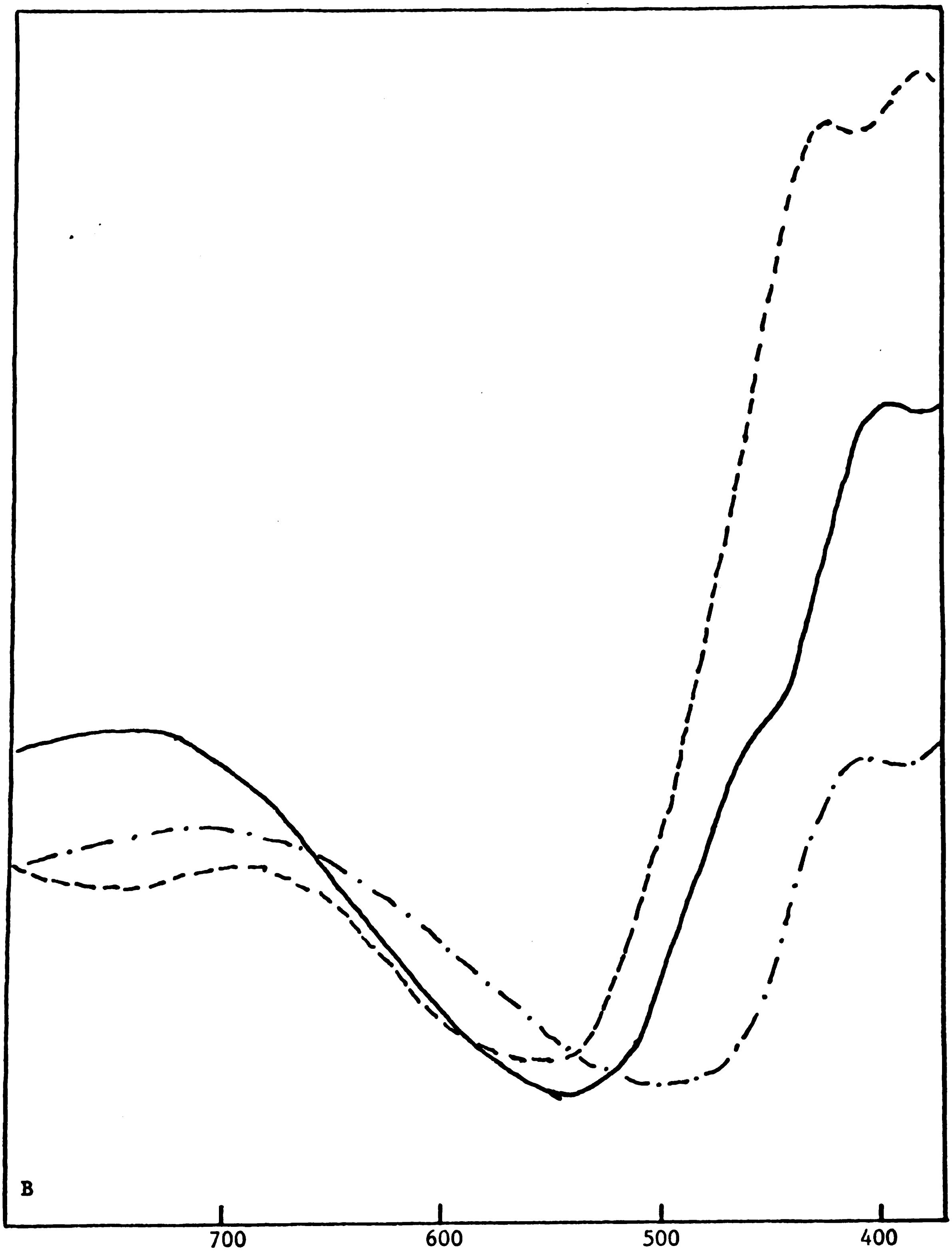


Figure 10.

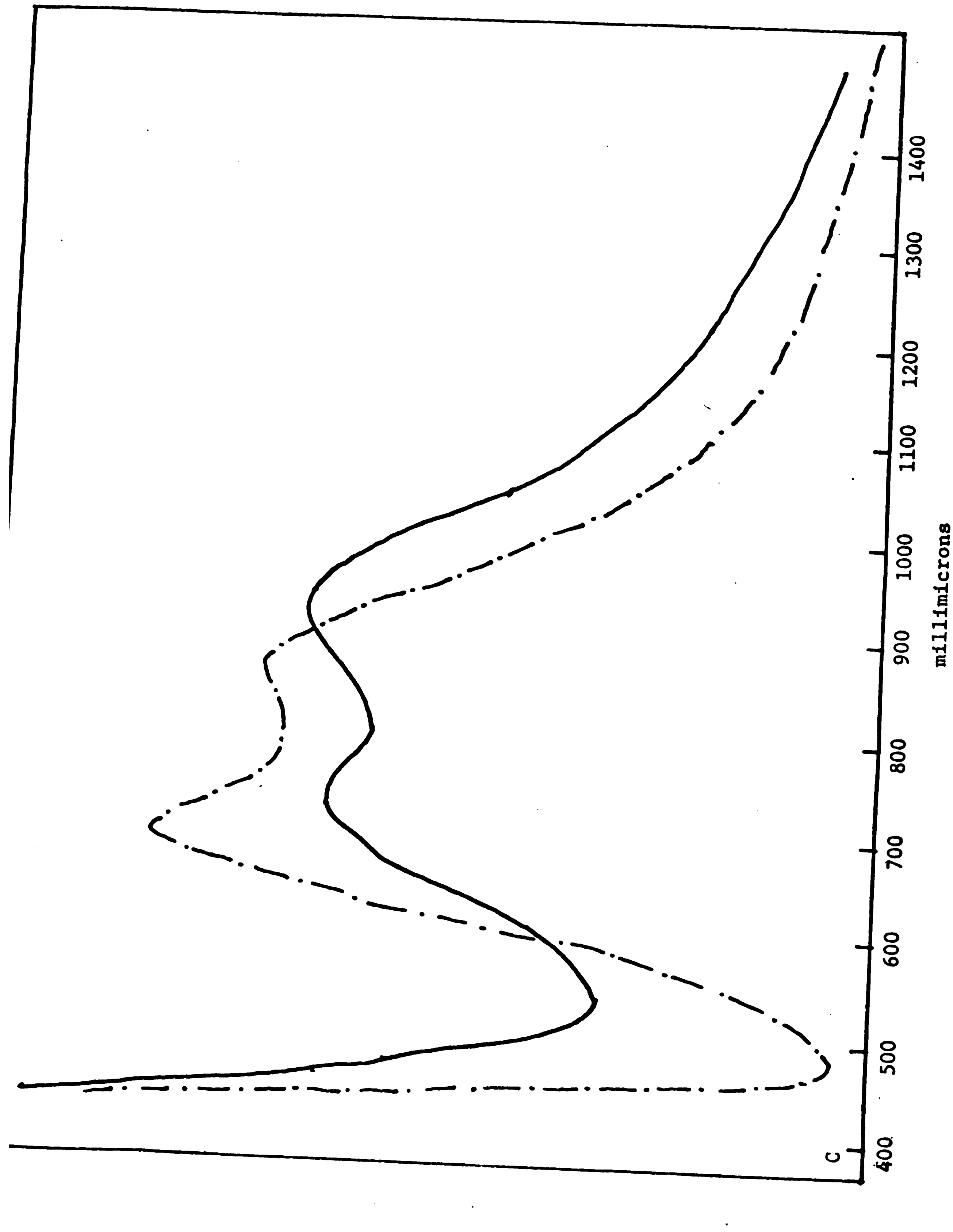

C
400
500
600
700
800
900
1000
1100
1200
1300
1400
millimicrons

Figure 10.

spectrum of the tetrachloroxomolybdate(V) anion changes slightly with time.

The $W(OR)Cl_5^-$ anion in nitromethane shows two absorptions. A broad absorption at 5,800 cm^{-1} is probably an infrared overtone or multiple vibration. The transition at ~8,500 cm^{-1} is thought to be the $B_2 \rightarrow E$ transition. Nitromethane absorbs in the ultraviolet, but the solid reflectance spectrum shows the $B_2 \rightarrow B_1$ transition at ~22,500 cm^{-1}. The $B_2 \rightarrow A_1$ absorption is again masked by the charge transfer band. Several solid and solution spectra are given in Figure 11.

Special precautions were taken to match qualitatively the electronic spectrum of the solid to that in solution. This adds insurance that the species in solution and the solid are the same and, hence, facilitates the interpretation of electron spin resonance spectra. Table 6 gives both solution and solid data for the electronic absorptions of the compounds studied.

The measured magnetic susceptibilities at 77°, 195°, and 298°K are given in Table 7. The weak temperature dependence of the magnetic susceptibilities is reflected in the small values of the Weiss constant (θ = -2°K) and near constant values of the magnetic moments. Thus, the conclusion which can be drawn from the Figgis calculations is qualitative. For tungsten dialkoxide complexes, ν is greater than 10, Δ probably ranges from 8,000 to 11,000 cm^{-1}, and λ is approximately 500 cm^{-1} This value agrees with that found for λ in tungsten(V) oxyhalide compounds.[27]

Figure 11. Electronic spectra of

A: Solution-nitromethane

B: Reflectance-solid

C: Reflectance-mull.

Key:	$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$	———————
	$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$	- - - - - - -
	$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$	- · - · - · -

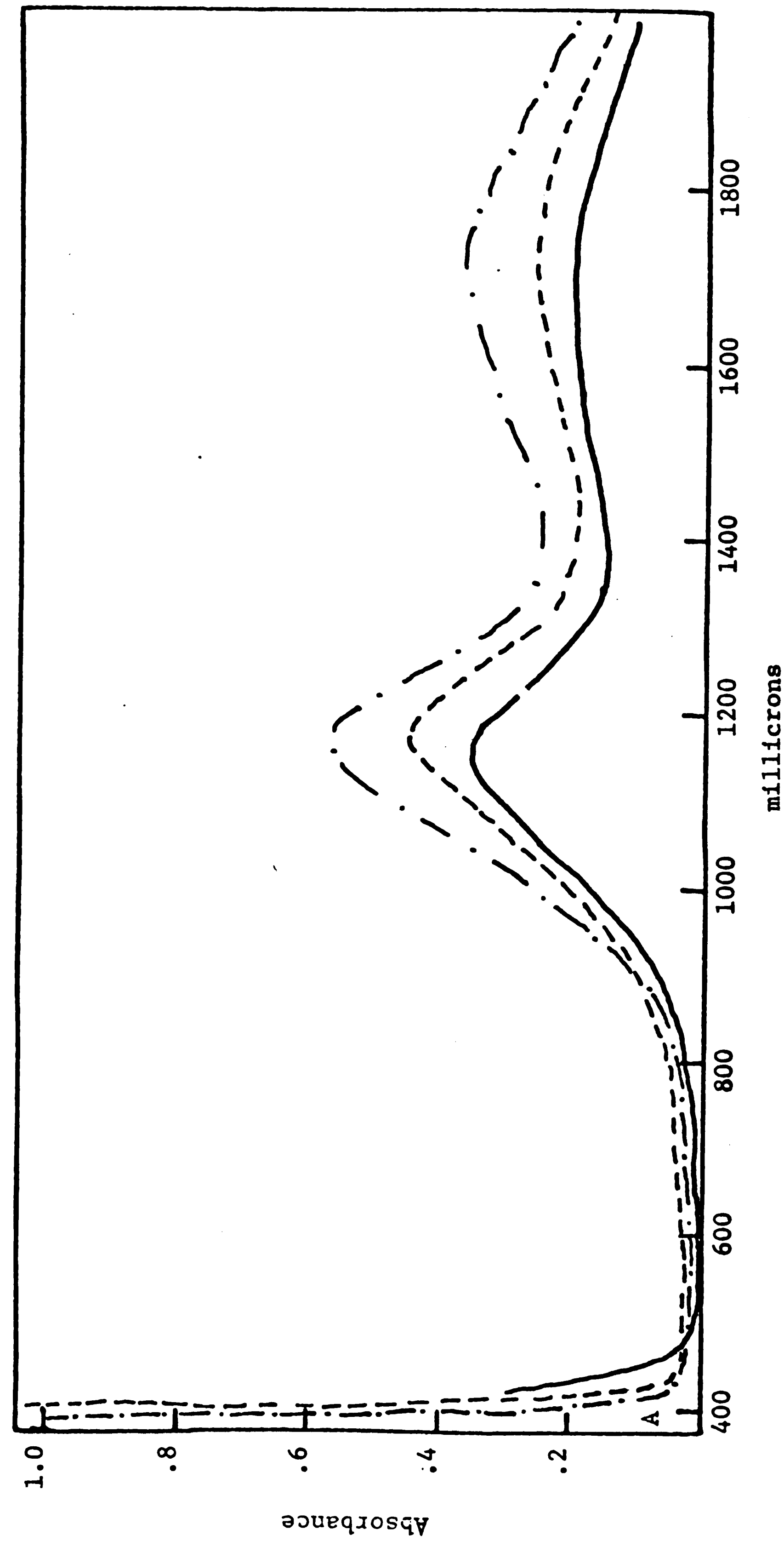

1.0
.8
.6
.4
.2
Absorbance
A
400
600
800
1000
1200
1400
1600
1800
millicrons

Figure 11.

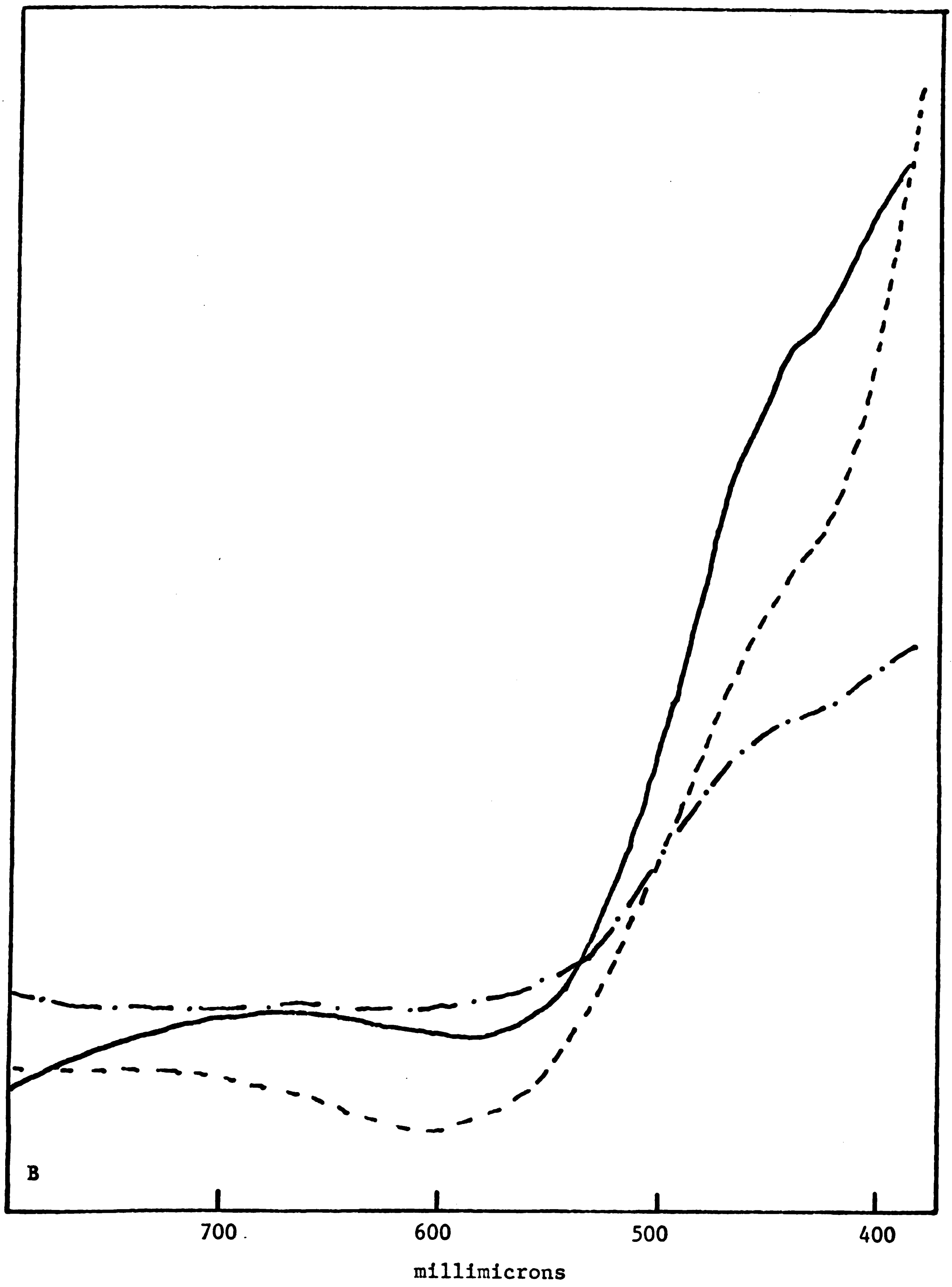


Figure 11.

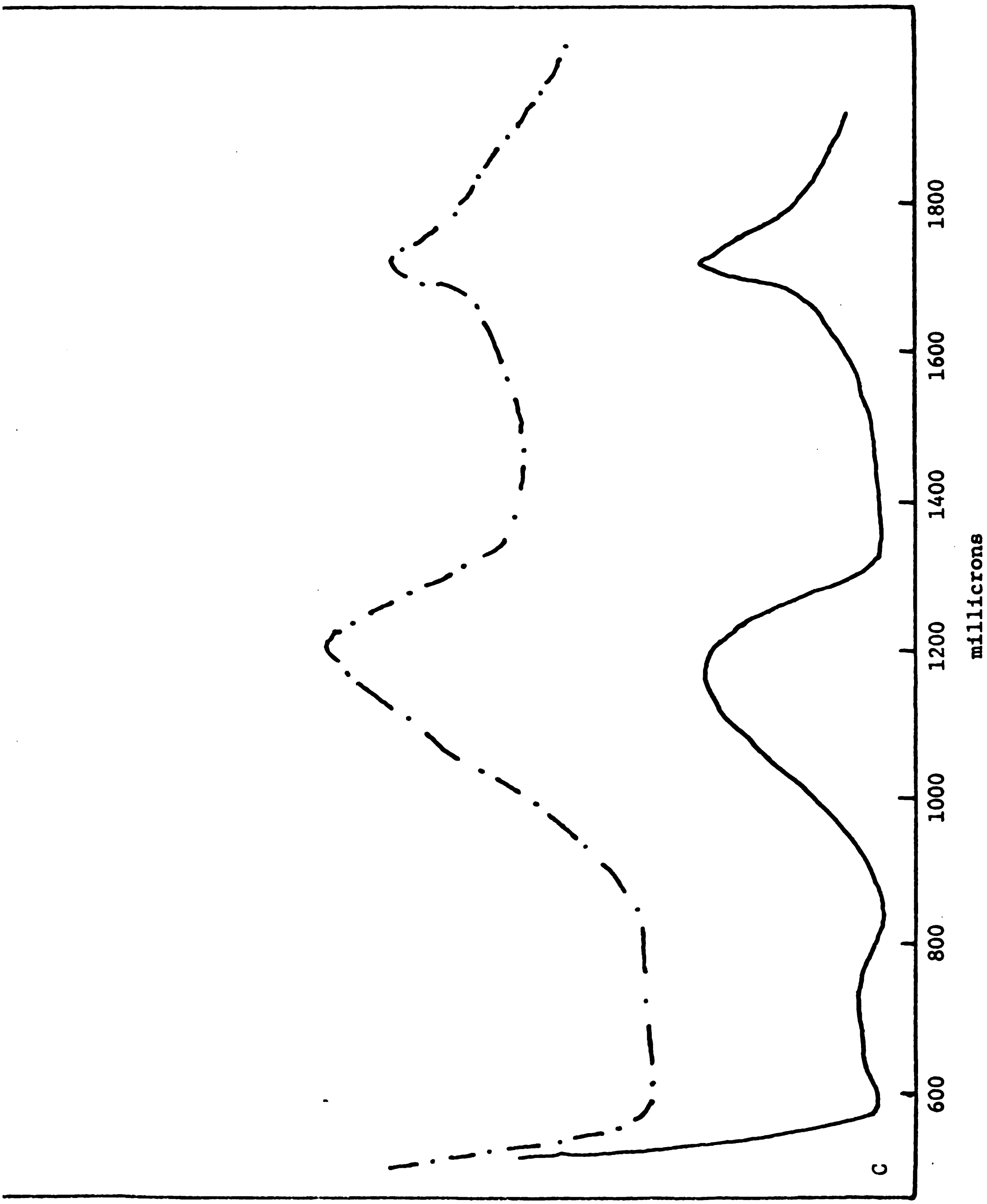


Figure 11.

Table 6. Electronic absorption spectra of compounds[a]

Compound	Medium	Absorption $cm^{-1} \times 10^{-3}$ (ε max in parenthesis)
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	Solid	11.9, 21.8, 27.4
	Nitromethane	11.7(16), 21.8(27)
	CH_3OH-HCl	11.7(16), 21.8(27)
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	Solid	12.7, 21.3, 26.0
	Nitromethane	12.1(19), 21.5(29)
	C_2H_5OH-HCl	12.1(19), 21.5(29)
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$	Solid	11.9, 14.6, 23.5
	Nitromethane	11.9(17), 14.7(19)
	Methylene Chloride	11.9(17), 17.7(19), 23.6(630), 26.0(5.0 x 10^3), 35.0(3.0 x 10^3), 31.7(3.8 x 10^3), 29.0(5.9 x 10^3)
$[(C_4H_9)_4N](MoOCl_4)$	Solid	14.8, 22.7(sh), 26.3(sh)
	Nitromethane	13.6(18), 22.5(17)
	Methylene Chloride	14.6(23), 22.7(19), 26.4(240), 31.3(5.1 x 10^3)
$[(C_3H_7)_4N](MoOCl_4)$	Solid	14.8, 22.7(sh), 26.7(sh)
	Nitromethane	13.6(14), 22.5(23)
	Methylene Chloride	14.6(23), 22.6(30), 26.4(280), 31.3(5.1 x 10^3)
	Methanol (initially)	14.1(25), 23.2(200), 30.8(2.0 x 10^3), 37.7(sh)
	(after 2 hrs)	14.1(25), 23.0(241), 32.5(1.7 x 10^3), 37.7(sh)

Table 6. (Continued)

Compound	Medium	Absorption $cm^{-1} \times 10^{-3}$ (ε max in parenthesis)
$[(CH_3)_4N][W(OCH_3)_2Cl_4]$	Solid	10.9, 13.5, 21.7(sh), 25.3
	Nitromethane	10.6(10.9), 13.7(12.6), 25.0(26.1)
	Methanol	10.6(10.9), 13.7(12.6), 21.1(~13.5)(sh), 25.0(~26)(sh), 30.8(~775)(sh), 34.6(~4,670)(sh)
$[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$	Solid	11.1, 14.1, 24.7(sh)
	Nitromethane	10.8(12.5), 14.0(13.6), 24.7(25.1)
	Ethanol	10.8(12.5), 14.0(13.6), 24.7(~20)(sh), 30.8(~750)(sh), 35.5(~5188)(sh)
$[(CH_3)_4N]_2[W(OC_2H_5)Cl_6]$	Solid	5.8, 7.5, 8.2, 15.4, 24.7(sh)
$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$	Solid	11.6, 14.1, 24.5(sh)
	Nitromethane	10.9(12.7), 13.9(13.4), 24.3(22.7)
	Ethanol	10.9(12.7), 13.9(13.4), 24.3(~20)(sh), 30.8(~750)(sh), 35.5(~5188)(sh)
$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$	Solid	5.8, 8.6, 13.7, 23.3(sh)
	Nitromethane	5.7(4.6), 8.7(7.2), 23.3(7.2)
$[(C_2H_5)_4N][W(OCH_3)Cl_5]$	Solid	5.8, 8.4, 15.1, 22.6(sh)
	Nitromethane	5.7(4.8), 8.4(6.8), 22.5(7.6)
$[(C_2H_5)_4N][W(n\text{-}OC_3H_7)Cl_5]$	Solid	5.8, 8.5
	Nitromethane	5.8(5.2), 8.7(8.2)

Table 6. (Continued)

Compound	Medium	Absorption $cm^{-1} \times 10^{-3}$ (ε max in parenthesis)
$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$	Solid	5.8, 8.5, 22.9
	Nitromethane	5.8(4.7), 8.6(7.3)
$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$	Solid	5.8, 8.4, 23.3
	Nitromethane	5.8(5.1), 8.6(7.1)
$[(C_2H_5)_4N](WOCl_4)$	Solid	5.8, 9.6, 12.3, 17.5, 25.0
	Nitromethane	11.2(11.6), 14.2(18.4), 26.0(14.4)

[a] sh = shoulder.

Table 7. Magnetic properties of compounds

Compound	Temp.	$\chi_m' \times 10^6$ cgs units	μB.M.	θ^0K
$[(CH_3)_4N][W(OCH_3)_2Cl_4]$	297	973	1.53	-2
	195	1465	1.52	
	77	3679	1.51	
$[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$	297	1002	1.55	-2
	195	1503	1.54	
	77	3769	1.53	
$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$	297	977	1.53	-2
	195	1486	1.53	
	77	3743	1.52	
$[(C_2H_5)_4N][W(OCH_3)Cl_5]$	297	745	1.34	-3
	195	1195	1.33	
	77	1117	1.33	
$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$	297	777	1.36	-2
	195	1175	1.36	
	77	2966	1.36	
$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$	297	831	1.41	-4
	195	1246	1.40	
	77	3127	1.39	
$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$	297	803	1.39	-2
	195	1223	1.39	
	77	3012	1.39	
$[(C_2H_5)_4N][W(OC_3H_7)Cl_5]$	297	797	1.38	-2
	195	1219	1.38	
	77	3075	1.38	
$[(CH_3)_4N][W(OC_2H_5)Cl_6]$	297	873	1.45	-81
	195	1143	1.34	
	77	1986	1.11	
$[(C_2H_5)_4N](WOCl_4)$	297	863	1.44	12
	195	1226	1.39	
	77	3204	1.41	

Table 7. (Continued)

Compound	Temp.	$\chi_m' \times 10^6$ cgs units	μB.M.	θ^0K
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	297	1226	1.71	2
	195	1885	1.72	
	77	4747	1.72	
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	297	1252	1.73	4
	195	1915	1.74	
	77	4956	1.75	
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$	297	1067	1.60	-1
	195	1605	1.59	
	77	4080	1.60	
$[(C_3H_7)_4N](MoOCl_4)$	297	1216	1.71	2
	195	1837	1.70	
	77	4628	1.70	
$[(C_4H_9)_4N](MoOCl_4)$	297	1224	1.72	4
	195	1912	1.73	
	77	4841	1.73	

The magnetic moments of molybdenum(V) compounds were near the spin only values.

The magnetic moments increase as the number of alkoxide groups increases and suggest the formation of a strong tungsten oxygen multiple bond which increases the spacings between the e and b_2 orbitals. As a result, the spin orbit contribution to the magnetic moment is lowered. Consequently, a large difference in g values was anticipated between $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$ and $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$.

Electron spin resonance spectra were obtained on powdered samples and on various solutions at 78° and 297°K. The ^{95}Mo-^{97}Mo hyperfine spectrum was observed.

An absorption in an experimental spectrum of tungsten was thought to be the hyperfine component from ^{183}W. Since no hyperfine structure could be duplicated by the computer, the absorption may have been due to a rhombic distortion or an impurity. The ^{183}W hyperfine structure was probably masked by the broad absorption of the isotopes with $I = 0$ because the half width is approximately 100 gauss.

Illustrative spectra of mono and dialkoxo complexes are given in Figures 12 and 13 respectively. In comparing the g values of mono and dialkoxo tungsten complexes as listed in Table 8, $g_{\perp}$ is found to change more than $g_{||}$. However, changing from Cl^- to Br^- in $[(C_2H_5)_4N][W(OCH_3)_2X_4]$ caused a greater alteration in the $g_{||}$ value than $g_{\perp}$. A similar observation is reported[11] in complexes of the type $WOX_5^{=}$. Thus in compounds of C_{4v} symmetry, it seems

Figure 12. Electron spin resonance spectra of

A: $[(C_2H_5)_4N][W(1\text{-}OC_3H_7)Cl_5]$ in frozen nitromethane

B: $[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$ in the powder

Key: Experimental ————————————

Computed -----------------

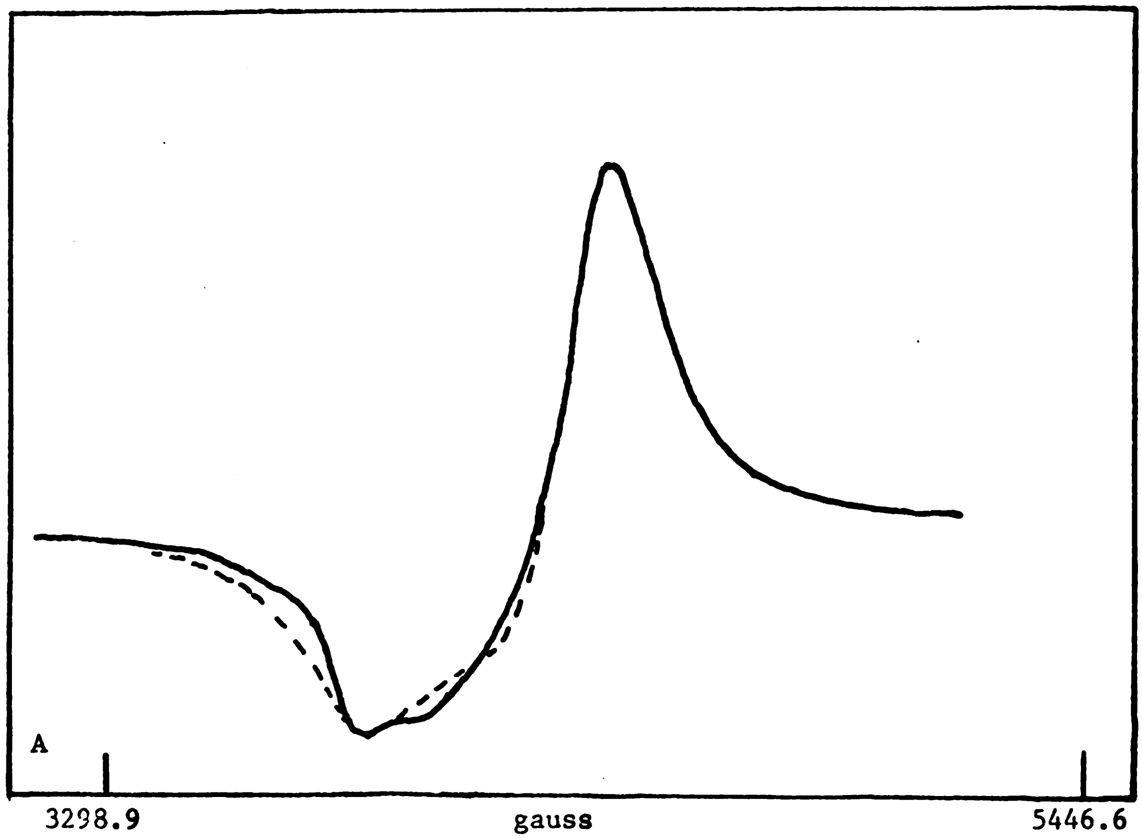


Figure 12.

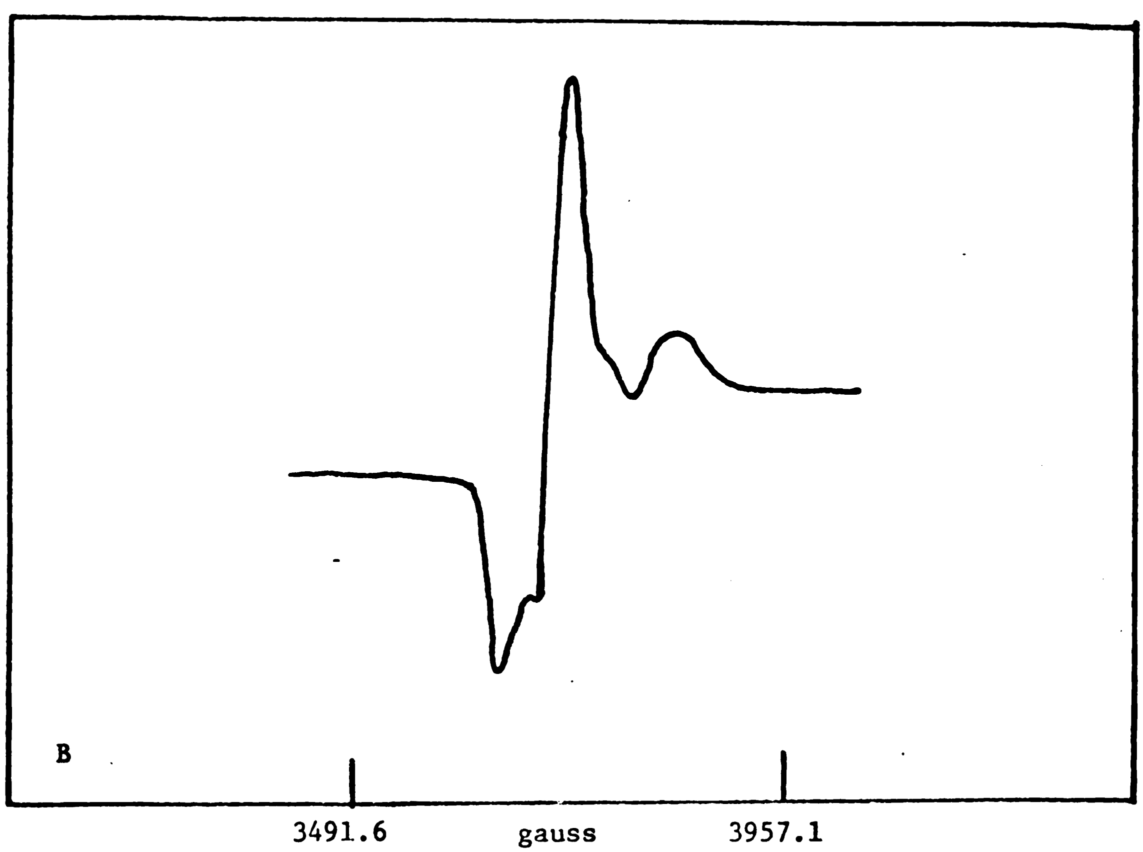


Figure 13. Electron spin resonance spectra of

A: $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$ in the powder

B: $[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$ in frozen nitromethane

Key: Experimental ————————————

Computed - - - - - - - - - - - - - - - - -

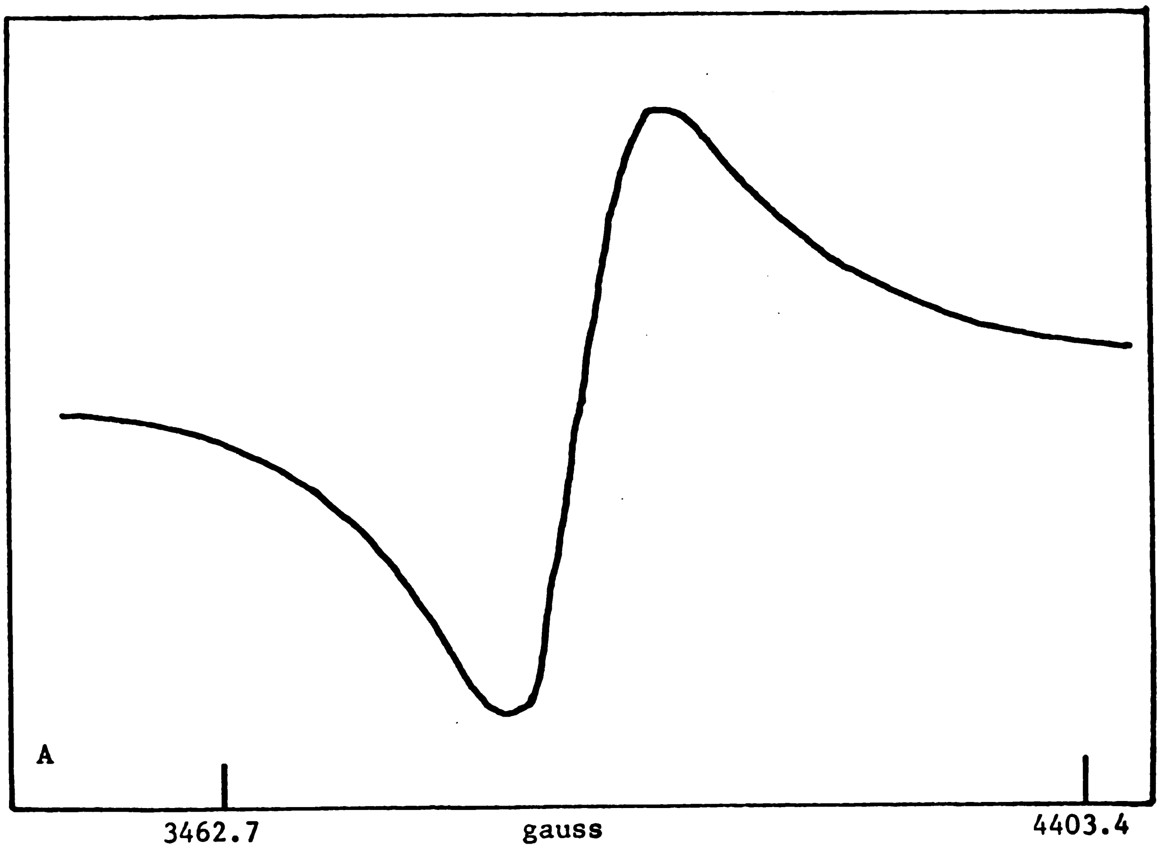


Figure 13.

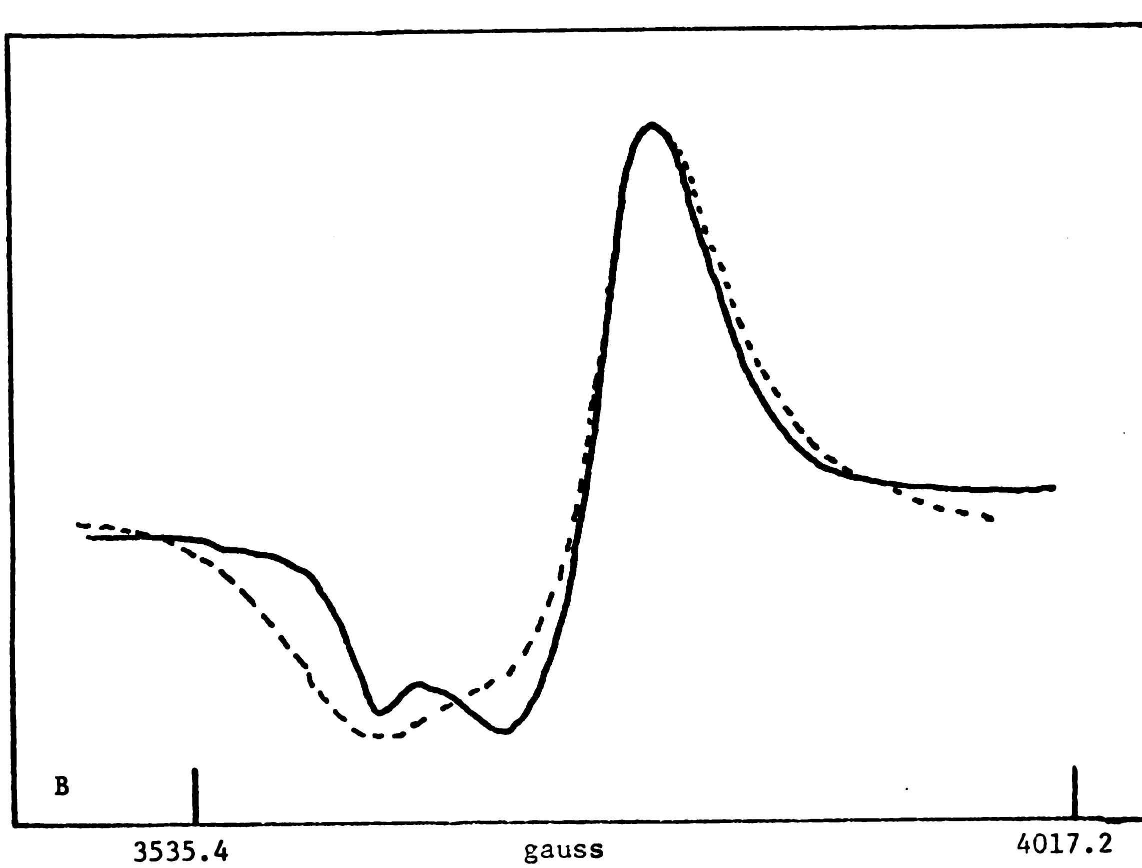


Table 8. Magnetic tensor values for tungsten(V) complexes[a]

Compound	Temp ^0K	$\langle g \rangle$	$g_{\perp}$	$g_{\parallel}$
$[(C_2H_5)_4N][W(OCH_3)_2Br_4]$				
CH_3NO_2	297	1.80		
	78		1.94	1.79
Powder	297		1.85	1.75
$[(C_2H_5)_4N][W(OC_2H_5)_2Cl_4]$				
CH_3NO_2	297	1.74		
	78		1.79	1.72
CH_2Cl_2	297	1.73		
Powder	297	1.76		
$[(CH_3)_4N][W(OC_2H_5)_2Cl_4]$				
CH_3NO_2	78	(1.75)	1.80	1.73
Powder	297	1.75		
$[(CH_3)_4N][W(OCH_3)_2Cl_4]$				
CH_3NO_2	78	(1.75)	1.80	1.73
Powder	297	1.74		
$[(C_2H_5)_4N][W(OCH_3)Cl_5]$				
CH_3NO_2	78	(1.56)	1.70	1.49
$[(C_2H_5)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2	78	(1.57)	1.71	1.50
$[(C_2H_5)_4N][W(1\text{-}OC_3H_7)Cl_5]$				
CH_3NO_2	78	(1.58)	1.71	1.51
$[(C_4H_9)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2	78	(1.57)	1.70	1.50
$[(C_3H_7)_4N][W(OC_2H_5)Cl_5]$				
CH_3NO_2	78	(1.57)	1.70	1.50

[a]( ) = Calculated values.

that axial ligands cause the greatest change in $g_{\perp}$ whereas equatorial ligands alter the $g_{||}$ value to the greatest extent.

Further evidence for this phenomenon was obtained from a comparison of molybdenum complexes. Powder, solution, and frozen solution esr spectra for $Mo(OC_2H_5)_2Cl_4^-$ and $MoOCl_4^-$ are shown in Figures 14 and 15. Table 9 contains measured magnetic tensor values. The value for $g_{||}$ is nearly the same for $MoOCl_4^-$, $MoOCl_5^=$, and $Mo(OCH_3)_2Cl_4^-$ and $g_{\perp}$ values are quite similar[11] for $MoOCl_4^-$ and $MoOCl_5^=$. However, $g_{\perp}$ values are lower for $Mo(OCH_3)_2Cl_4^-$.

In an attempted ligand exchange experiment between $Mo(OC_2H_5)_2Cl_4^-$ and SCN^-, the g values essentially remained constant and probably indicate little exchange of either ethoxide or chloride took place with SCN^-.

If $MoOCl_4^-$ is dissolved in methanol, the spectrum changes with time. Two lines were obtained as illustrated in Figure 16A. Figure 16B shows the spectrum of $Mo(OC_2H_5)_2Cl_4^-$ in ethanol. Again two species are present. Since molybdenum(V) compounds are very susceptible to oxygen abstraction[1-5] and Funk et al.[40-42] found that oxymethoxy compounds could be isolated from methanol, the species present (in addition to parent compounds) are probably mixed alkoxooxo complexes.

It is also interesting to note $\langle g \rangle$ values for $MoOCl_4^-$ in methylene chloride and nitromethane. The $\langle g \rangle$ is 1.956 in CH_2Cl_2 and 1.949 in CH_3NO_2. Electronic absorptions

Figure 14. Electron spin resonance spectra of $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$ in:

A: The powder

B: Nitromethane solution

C: Frozen nitromethane solution.

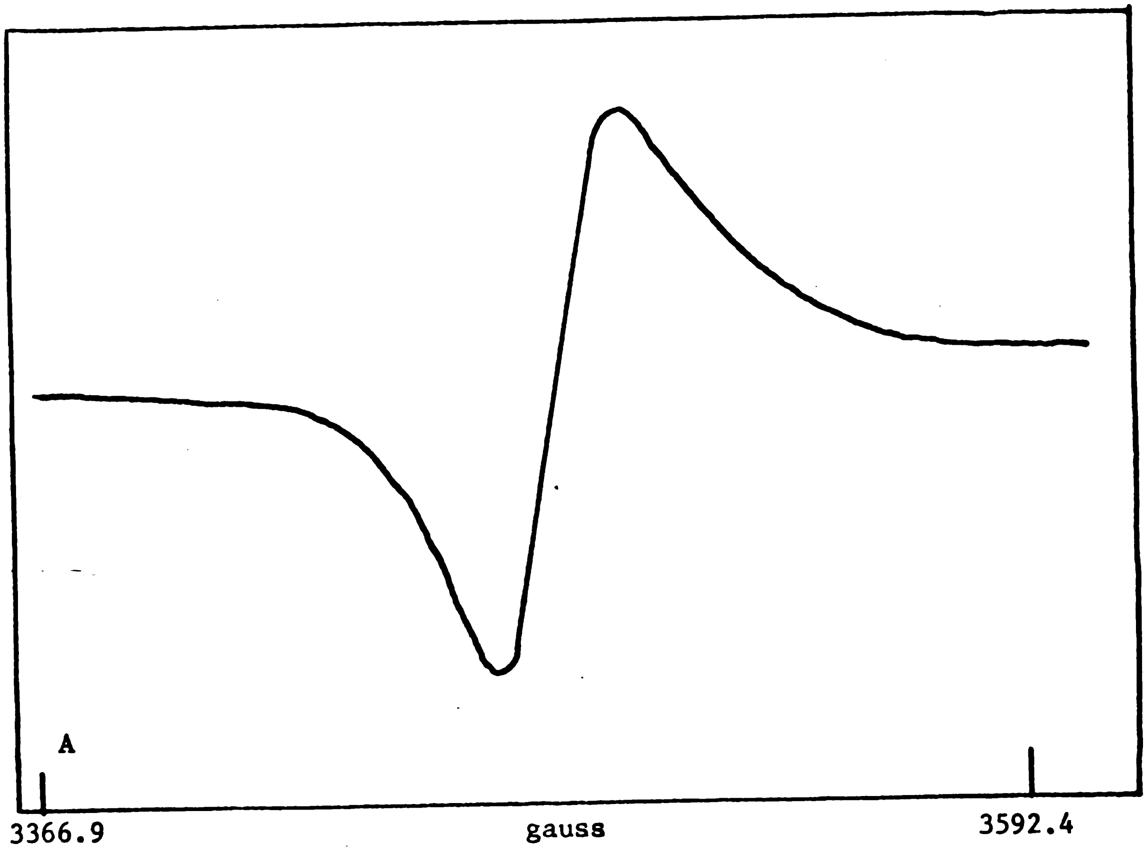
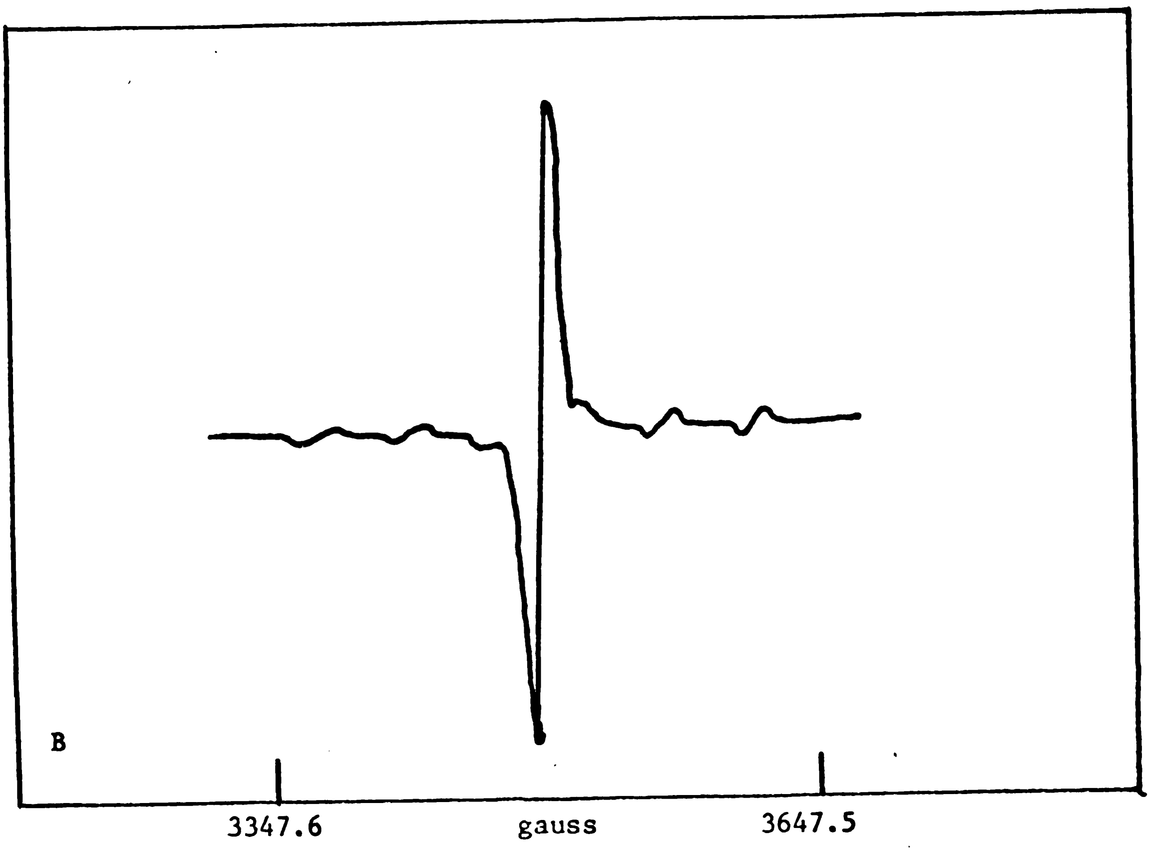


Figure 14.



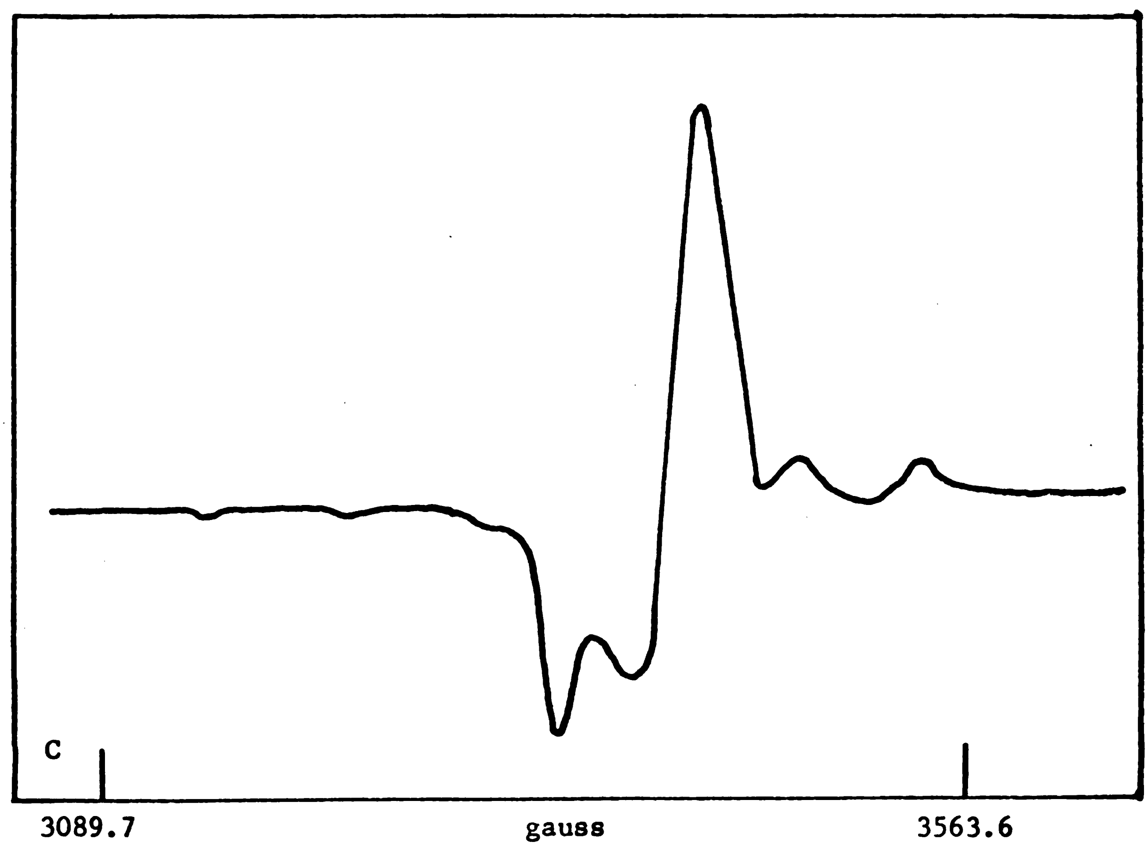


Figure 14.

Figure 15. Electron spin resonance spectra of $[(C_3H_7)_4N](MoOCl_4)$

A: The powder

B: Nitromethane solution

C: Frozen nitromethane solution.

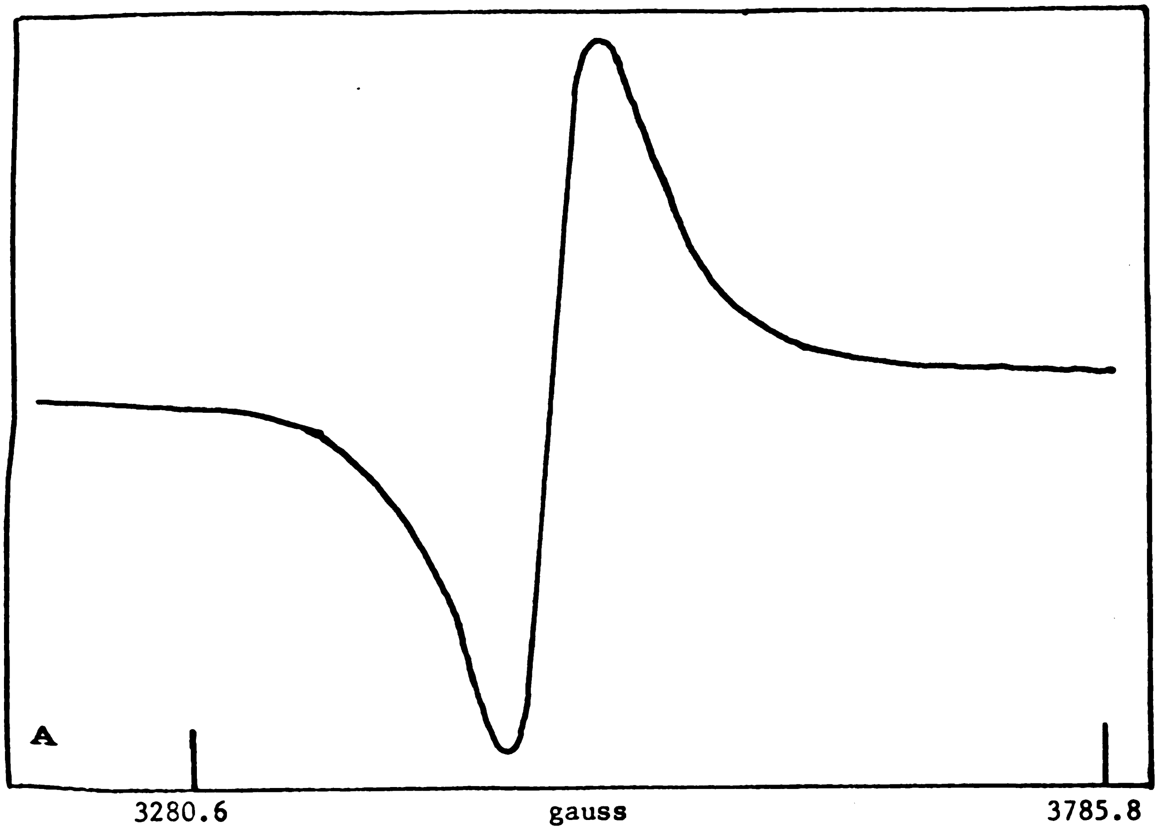
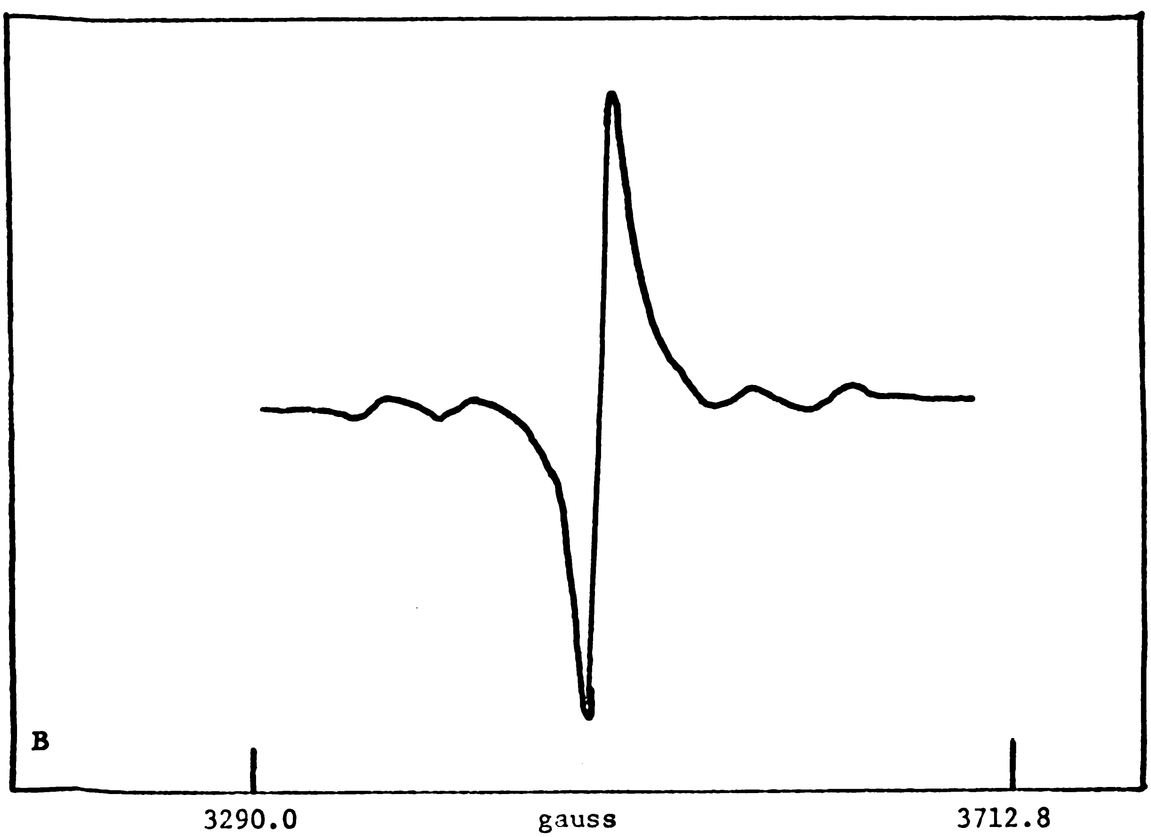


Figure 15.



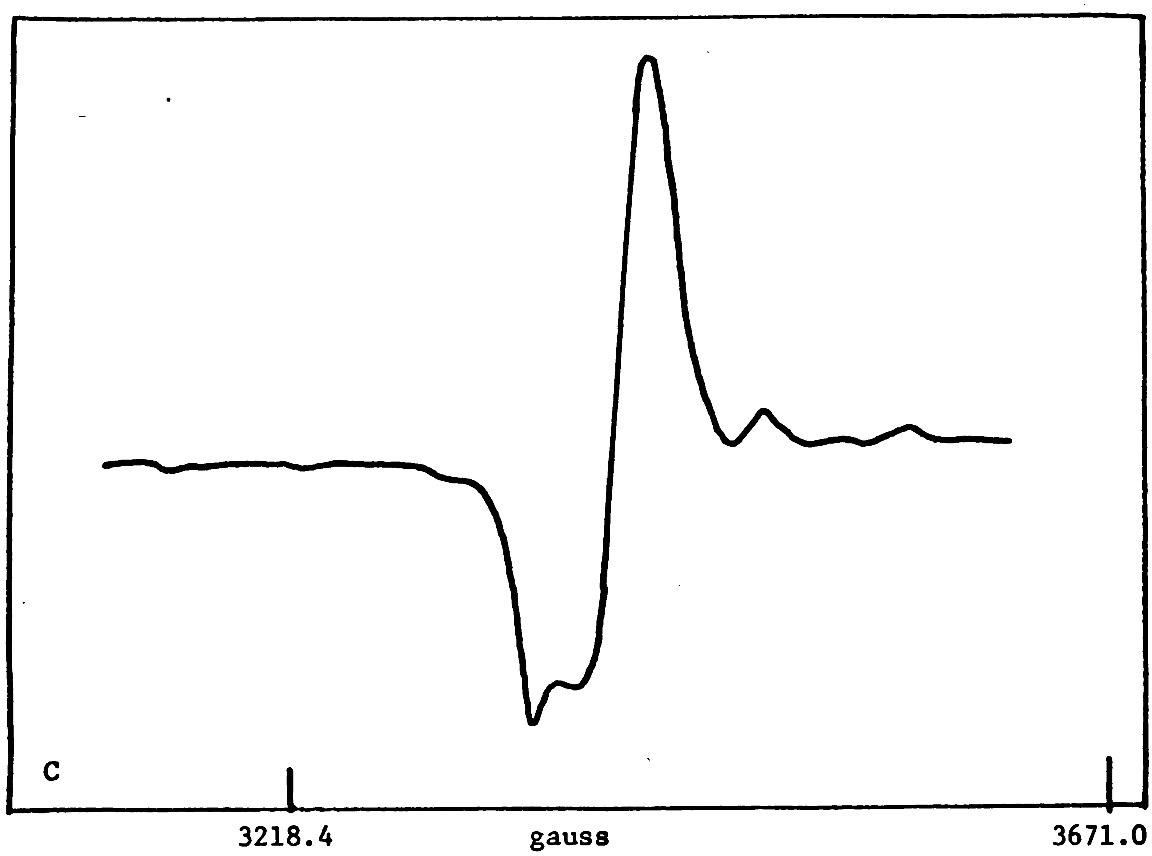


Figure 15.

Table 9. Magnetic tensor values for molybdenum(V) complexes.

Compound	Temp ^0K	$\langle g \rangle$	$g_{\parallel}$	$g_{\perp}$	$\langle a \rangle^a$	A^a	B^a
$[(C_2H_5)_4N](Mo(OCH_3)_2Cl_4]$							
CH_3NO_2	297	1.939			43.3		
	78		1.970	1.923		70.8	31.0
CH_3OH-HCl	297	1.938			43.5		
	78		1.971	1.923		70.9	29.2
Powder	297		1.970	1.920			
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$							
CH_3NO_2	297	1.939			43.2		
	78		1.970	1.923		71.7	28.7
C_2H_5OH-HCl	297	1.939					
	78		1.975	1.923		77.5	31.0
Powder	297	1.944					
CH_3NO_2 + Sat. NH_4SCN	78		1.970	1.923		71.7	28.3

Table 9. (Continued)

Compound	Temp ^0K	$\langle g \rangle$	$g_{\|\|}$	$g_{\perp}$	$\langle a \rangle^a$	A^a	B^a
$[(C_3H_7)_4N](MoOCl_4)$							
CH_3NO_2	297	1.949			47.1		
	78		1.970	1.934		74.7	36.1
Powder	297	1.951					
$[(C_4H_9)_4N](MoOCl_4)$							
CH_3NO_2	297	1.949			46.1		
	78		1.968	1.930		75.5	36.9
CH_2Cl_2	197	1.956			47.1		
Powder	297	1.949					

[a] $cm^{-1} \times 10^{-4}$.

attributed to the $B_2 \rightarrow E$ are at 14,600 cm^{-1} and 13,600 cm^{-1}. Thus, the larger difference between the ground and excited state, the less spin orbit coupling occurs, and the greater is the g-value.

Most powder samples gave a one line esr absorption spectrum except $[(C_2H_5)_4N](Mo(OCH_3)_2Cl_4]$ and $[(C_2H_5)_4N][W(OCH_3)_2Br_4]$, in whose spectra $g_{||}$ and $g_{\perp}$ could be resolved. Electron spin resonance spectra of pentachloroalkoxotungstate(V) could not be obtained at room temperature. A spectrum which is believed to be that of $WOCl_4^-$, the decomposition product of $W(OC_2H_5)Cl_5^-$, is observed at 78^0K. The broad hump in the spectrum in Figure 12B probably arises from $W(OC_2H_5)Cl_5^-$. The g values of the presumed $WOCl_4^-$ are $g_{||}$ and $g_{\perp}$ equal to 1.80 and 1.77 respectively. These compare well[11] to those g values of $WOCl_5^=$.

The powdered complex, $[(C_2H_5)_4N](WCl_6)$, gave a one line absorption spectrum at room temperature with g = 1.79. One line was also observed for $[(C_2H_5)_2N](WCl_6)$ doped into $[(C_2H_5)_4N](TaCl_6)$, but the author[66] only reported that the g value was less than 2. Dowsing and Gibson[17] report that $[(C_2H_5)_4N](MoCl_6)$ gave a room temperature spectrum with $g_{||} = 1.977$ and $g_{\perp} = 1.935$. Distortion of the lattice is believed to remove the degeneracy of the ground state and an esr signal is then observed in these hexachlorocomplexes.[17]

Figure 16. Electron spin resonance spectra of

A: $[(C_3H_7)_4N](MoOCl_4)$ in CH_3OH

B: $[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$ in C_2H_5OH.

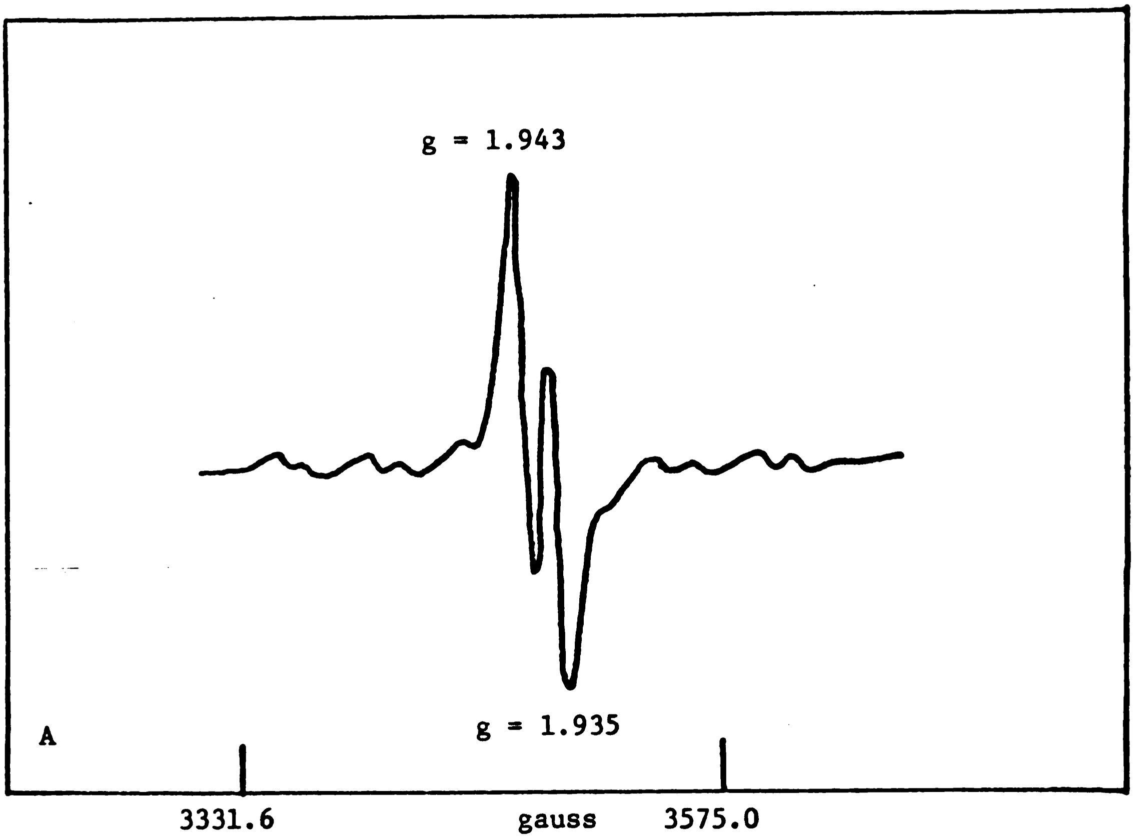
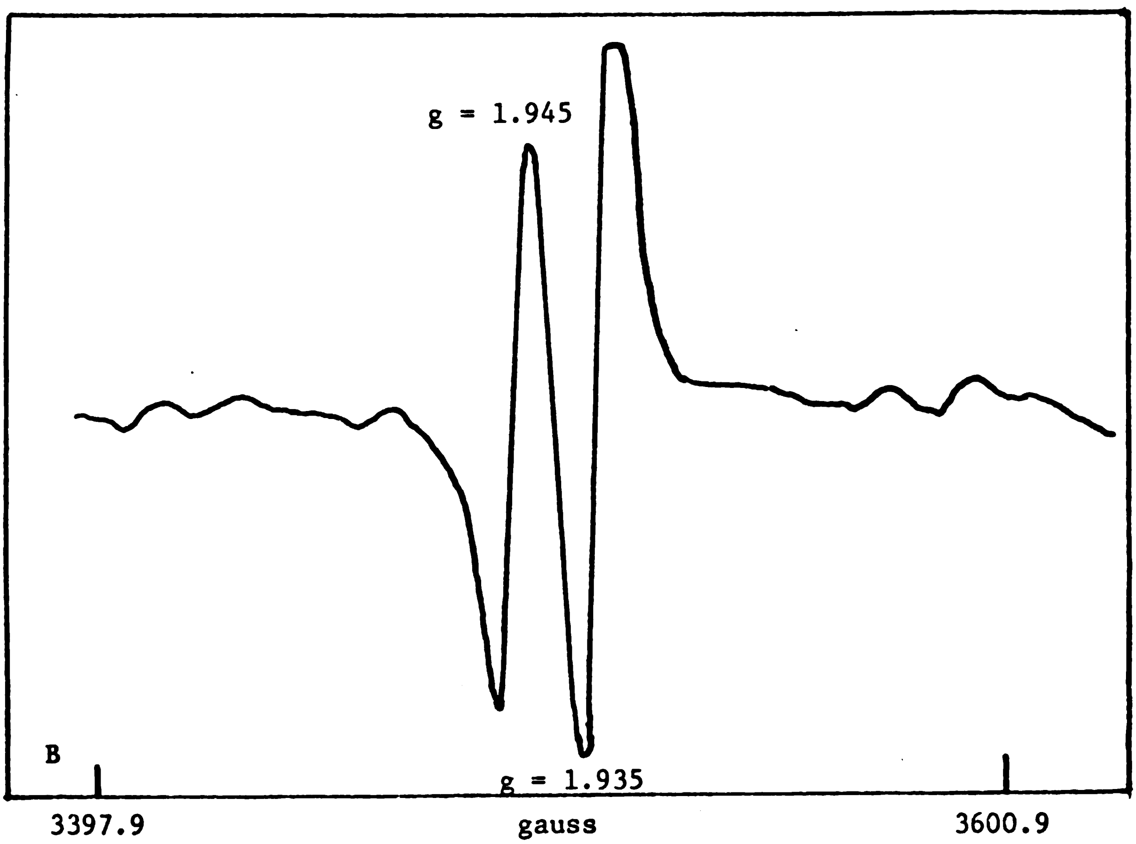

g = 1.943
g = 1.935
A
3331.6
gauss
3575.0

Figure 16.


g = 1.945
B
g = 1.935
3397.9
gauss
3600.9

Certain values of theoretical interest can be calculated for molybdenum(V) compounds. If it is assumed that the d^1 electron is in the $b_2(d_{xy})$ orbital, the isotopic contact term, K, and the fraction of time the electron spends in the d_{xy} orbital, β^2, can be calculated from the equations:[67]

$$A = -K - 4/7\beta^2 P + (g_{||} - 2.0023)P + 3/7(g_{\perp} - 2.0023)P$$

$$B = -K + 2/7\beta^2 P + 11/14(g_{\perp} - 2.0023)P.$$

If P, which is defined at $2.0023 g_n \beta_e \beta_n (r^{-3})_{av}$, is taken for the "free ion" (-55.0 x 10^{-4} cm^{-1} for Mo^{3+}, i.e., the average for the two isotopes and a net charge of +3 for the $Mo(OCH_3)_2{}^{3+}$ or MoO^{3+} unit[67]), then one may solve for $\beta^2 P$ and thus determine β^2. To determine g_n, an average was employed for the two isotopes:

$$g_n = \frac{1/2(-0.9099 - 0.9290)}{5/2}$$

The quantity, χ, which results from a polarization of the inner filled S orbital by the unpaired d electrons, is determined by the equation:

$$\chi = -3/2 \frac{[hca_0{}^3]}{[2.0023 g_n \beta_n \beta_e]} K$$

The values of K, χ, β^2, and P complex (= $\beta^2 P$) are listed in Table 10. The β^2 values indicate that the electron is a b_2 electron and spends more time in the

Table 10. Isotopic contact terms, K, and χ, β^2, and P for molybdenum(V) complexes in glasses at 78^{0}K

Compound	$-K^a$	$-\chi^b$	$-P^a$	β^2
$[(C_2H_5)_4N][Mo(OCH_3)_2Cl_4]$	46.5	5.95	48.8	.887
$[(C_2H_5)_4N][Mo(OC_2H_5)_2Cl_4]$	46.5	5.95	50.4	.917
$[(C_3H_7)_4N](MoOCl_4)$	52.2	6.68	45.9	.834
$[(C_4H_9)_4N](MoOCl_4)$	53.0	6.78	45.4	.826

^{a}cm^{-1} x 10^{-4}

^{b}a.u.

d_{xy} orbital in dialkoxo than oxo complexes. The other values, $-K$, $-\chi$, and β^2P are comparable to those obtained for other molybdenum(V) complexes.[10-12,23]

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