THE PREPARATION OF SOME TETRACHLORODIALKOXOMOLYBDENUM (V) COMPLEXES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
David A. McClung
1966

ABSTRACT

THE PREPARATION OF SOME TETRACHLORODIALKOXOMOLYBDENUM(V) COMPLEXES

by David A. McClung

Four compounds, all having the general composition $BH[Mo(OR)_2Cl_4]$, have been prepared and characterized. BH^+ was pyridinium, quinolinium, or tetramethylammonium ion. The alkoxo group was either methoxo or ethoxo.

The tetrachlorodimethoxomolybdate(V) compounds were prepared by reacting molybdenum pentachloride with dry methanol, followed by the addition of a mixture containing the organic base or $(CH_3)_4NCl$ in alcohol. All attempts to prepare the analogous ethoxo compounds by this method resulted in the formation of mixed products.

The pyridinium tetrachlorodiethoxomolybdate(V) complex was prepared by alkoxo exchange between the methoxo complex and ethanol.

The infrared spectra of the compounds show intense absorption in the region 1040-1050 cm^{-1}, which is typical of the C-O stretching vibration in alkoxides. The O-H vibrational mode was not found in the infrared spectra of any of the compounds. The compounds are paramagnetic and have magnetic moments corresponding to the spin-only value of 1.73 B.M., which is characteristic of the $4d^1$ configuration of molybdenum(V).

Each of the compounds exhibit two bands in the visible region. The bands are assumed due to the reduction of symmetry from octahedral

to tetragonal. A third band is apparently masked by a charge transfer peak.

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By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1966

ACKNOWLEDGMENT

The author wishes to express his appreciation to Professor Carl H. Brubaker, Jr., for his guidance and inspiration during this investigation.

Sincere thanks are extended to my wife, Marcella, for her patience, understanding, and talent which helped to make this work possible.

Appreciation is also extended to the National Science Foundation for financial assistance.

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INTRODUCTION

Molybdenum, the congener of chromium, has a variety of oxidation states which range from +2 to +6. However, the higher oxidation states are more common and more stable with the most common one being the +6 state. One of the common compounds containing molybdenum in the hexavalent state is the trioxide, MoO_3.

Molybdenum pentachloride, a compound in which molybdenum has a $4d^1$ configuration, has a spin-only moment of 1.73 B.M. Compounds of molybdenum in the di-, tri-, and tetravalent states are not very numerous.

Alkoxides of a few transition metals have been reported, with those of Groups IV B and V B the most extensively studied. Bradley has published review articles on a number of metal alkoxides (1,2,3).

Titanium tetraalkoxides of Group IV B were first synthesized by Demarcay (4). The first results of structural significance of these titanium complexes were given by Claughan, who found that the degree of polymerization was concentration dependent, increasing from unity at low concentration to a maximum of three (5). On the other hand, Bradley found that the degree of polymerization was constant at 2.4 over a reasonable concentration range in boiling benzene (6). Recently, Ibers has reported preliminary details of the crystal structure of $Ti(OC_2H_5)_4$ as determined by X-ray diffraction and concluded that the substance is tetrameric in the solid state (7).

Bradley observed that there was an increase in volatility of the zirconium tetraalkoxides as the alkyl group was changed from primary to secondary to tertiary (8) and that the volatility was directly related to the molecular complexity (9). The molecular complexities of the zirconium tetraalkoxides were the same as those of the analogous hafnium derivatives (10). The mechanism for the reaction involved in the preparation of the zirconium and hafnium tetraalkoxides has been studied (11).

A number of alkoxides of the Group V B have been prepared. The syntheses of vanadium trialkoxides (12) and tetraalkoxides (13) has been reported. Vanadium tetraethoxide was found to have a value of 2.04 for the degree of polymerization, suggesting that it is predominantly in the dimeric form (14). The value of 2.04 for vanadium tetraethoxide is slightly lower than for the corresponding titanium alkoxide. The lower value is attributed to a difference in steric effects (15). Thus, in the case of a given alkoxide group, shielding of the central atom and consequent opposition to polymerization will depend on the size of the central atom, if other factors are equal.

Pentaalkoxides of niobium were prepared and found to be dimeric in boiling benzene (16). Wentworth and Brubaker reported a number of complexes of niobium, including $(C_5H_6N)_2[Nb(OR)Cl_5]$ ($R = CH_3$, C_2H_5, or i-C_3H_7), $[NbCl(OC_2H_5)_2(C_5H_5N)]_2$, and $Nb(OC_2H_5)_4$ (17,18,19). The pyridinium pentachloroalkoxoniobate compound was prepared by electrolytic reduction of niobium pentachloride in HCl-saturated alcohols, followed by addition of alcoholic pyridinium salts and showed normal, spin-only paramagnetism. The other two compounds, $Nb(OC_2H_5)_4$ and $[NbCl(OC_2H_5)_2(C_5H_5N)]_2$, were diamagnetic and the dimer consisted of two octahedra joined by bridging chloride ligands.

Tantalum pentaalkoxides were investigated by Bradley and were found to exist as dimers in benzene (20).

Chromium triethoxide was one of the first alkoxides of the Group VI B metals to be prepared. This compound was obtained by the reaction of chromium trichloride with sodium ethoxide (21).

A few molybdenum alkoxides have been reported, all of which contain molybdenum in the +5 oxidation state. The compound $Mo(OCH_3)_2Cl_3 \cdot 3CH_3OH$ was reportedly prepared by reaction of molybdenum pentachloride with methanol at -78°C. The compound precipitated in large green crystals after standing in a stoppered vessel for several days (22). Upon treatment of this compound with an excess of a methanol-pyridinium chloride solution, light green needle-shaped crystals of $C_5H_6N[Mo(OCH_3)_2Cl_4]$ were reportedly formed (23). According to Funk (24), reaction of molybdenum pentachloride with methanol followed by addition of a pyridinium chloride solution resulted in a mixed product if the intermediate compound was not isolated. The compound $Mo(OCH_3)_3Cl_2$ supposedly resulted from the addition of an excess of methanol and pyridine to pyridinium tetrachlorodimethoxomolybdate(V) (25). Funk (26) also obtained black crystals of $Mo(OCH_3)_4Cl$ when an excess of pyridine was added to a solution of molybdenum pentachloride in methanol. Unfortunately, no properties or characterization other than elemental analyses were reported for any of these compounds.

Chloride alkoxides of tungsten have been reported (27,28). Compounds of the composition $WCl_3(OR)_2$ ($R = CH_3$, C_2H_5) were obtained by reaction of tungsten hexachloride with the corresponding alcohol.

From a solution of $WCl_3(OC_2H_5)_2$ the diamagnetic dimer, $W_2Cl_4(OC_2H_5)_6$, was obtained. A bi-octahedral structure with two bridging chloride ligands has been proposed for the structure of the dimer (29). Recently compounds of the type $WO(OR)_4$ have been synthesized by the reaction of $WOCl_4$ with ammonia in alcohol (30).

Alkoxides and chloroalkoxides of copper (II) were reported by Brubaker and Wicholas (31). These complexes were found to have magnetic moments lower than the spin-only moment of 1.73 B.M. Other known alkoxides of transition elements include $Mn(OC_2H_5)_2$ (32) and $Fe(OC_2H_5)_3$ (33,34).

Also of interest are the vanadyl (VO^{+2}) derivatives, where vanadium exists as V^{+4}, with the electronic structure [Argon]$3d^1$. The most significant feature of the electronic structure seems to be the existence of considerable oxygen to vanadium π-bonding. In general, the magnetic moments of powdered samples and aqueous solutions of vanadyl complexes are all approximately equal to the spin-only value of 1.73 B.M. for one unpaired electron (35).

The chromyl and molybdenyl ions, CrO^{+3} and MoO^{+3}, are electronically equivalent to VO^{+2}, since they can be formulated as containing Cr^{+5} ($3d^1$) and Mo^{+5} ($4d^1$). Compounds containing these ions are rare, and the only well characterized complexes containing CrO^{+3} and MoO^{+3} are of the types $M'_2[MOCl_5]$, where M' is NH_4^+, Na^+, K^+, Rb^+, or Cs^+ and M is Cr(V) or Mo(V) (36). These complexes are assumed to have a tetragonal structure, with a short M-O bond. The electronic transitions observed for compounds containing the $[MoOCl_5]^{-2}$ ion showed bands at 14,050 and 22,500 cm^{-1}, corresponding to the transitions $b_2 \longrightarrow e$ and $b_2 \longrightarrow b_1$ respectively (37). The $b_2 \longrightarrow a_1$ transition is apparently masked by the charge transfer band. Charge transfer bands were found at 32,200 and 41,700 cm^{-1}. The electron spin resonance spectra and magnetic susceptibilities of $(NH_4)_2[MoOCl_5]$ and $Rb_2[CrOCl_5]$ were obtained and reported by Hare (38). The average effective moment for $(NH_4)_2[MoOCl_5]$ after correction for temperature independent paramagnetism was 1.67 B.M.

Although there is a slight difference in the symmetry of compounds containing the $[MoOCl_5]^{-2}$ ion and the tetrachlorodialkoxomolybdate complexes, the spectra of the compounds containing the $[MoOCl_5]^{-2}$ ion can be used qualitatively in interpreting the spectra of the tetrachlorodialkoxomolybdates.

EXPERIMENTAL

Preparation and Standardization of Reagents

Silver Nitrate.-- The 0.1 N solution of silver nitrate was prepared by dissolving 8.5 g of "Baker Analyzed" reagent grade silver nitrate in 500 ml of demineralized distilled water. The concentration of this solution was determined by titration with a standard sodium chloride solution to the potassium chromate end point (39).

Ammonium Thiocyanate.--To prepare a solution of 0.1 N ammonium thiocyanate, 7.6 g of Mallinckrodt reagent grade ammonium thiocyanate was dissolved in distilled water to give one liter of solution. The concentration was determined by titrating with standard silver nitrate solution to the ferric alum end point (40).

Cerium(IV) Sulfate.--A 0.1 N ceric sulfate solution in sulfuric acid was prepared by dissolving 40 g of cerium(IV) sulfate in 56 ml of a 1:1 sulfuric acid solution. After the addition of 400 ml of distilled water, the solution was warmed until the material had dissolved completely. After filtering, the solution was diluted to one liter (41). The concentration of the solution was determined by titration with a standard As_2O_3 solution (42).

Materials

Molybdenum Pentachloride.--Molybdenum pentachloride was obtained from

K & K Laboratories and was used without further purification. The manufacturers claim that the purity of the compound was 99.8%.

Pyridine and Quinoline.--These were purchased from Matheson, Coleman, and Bell. Both were dried by refluxing over barium oxide and distilling.

Tetramethylammonium Chloride.--Tetramethylammonium chloride was Eastman White Label grade. It was dried for eight hours at 100°C before use.

Nitrogen and Hydrogen Chloride.--Both the anhydrous hydrogen chloride and nitrogen were in cylinders and obtained from the Matheson Co. The hydrogen chloride was bubbled through concentrated sulfuric acid before use. Nitrogen was used without further purification.

Methanol.--Methanol was dried by reacting it with magnesium turnings. It was then refuxed and distilled.

Ethanol.--"Absolute" ethanol was dried by reacting it with sodium and subsequent distillation.

Solvents.--Other solvents were used for washing and purification. Pentane was distilled over phosphorus pentoxide. Chloroform was Fischer reagent grade and was used without further purification.

Analytical Methods

Molybdenum Analyses.--Molybdenum analyses were done according to the procedure given by Kolthoff (43) and Busev (44). Enough hydrochloric acid was added to the sample in water to make the acidity about 3 N. The solution was then titrated with 0.1 N cerium(IV) sulfate.

Chloride Analyses.--Chlorides were determined by the Indirect Volhard Method with excess standard silver nitrate and back titration with ammonium thiocyanate (45).

Carbon, Hydrogen, and Nitrogen Analyses.--These analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Apparatus

The reaction vessel consisted of a 3-necked round bottom flask. Inserted into the middle neck was a ground glass mechanical stirrer. In another neck of the flask was an adaptor with a vacuum outlet into which was inserted a dropping funnel, and in the third neck was a 90° connecting tube with a standard taper joint and stopcock, through which nitrogen, or hydrogen chloride, entered the flask. The nitrogen served to exclude air and moisture from the system.

Preparation of Compounds

Pyridinium tetrachlorodimethoxomolybdate(V).

A complete description of the preparation of this compound will be given and this procedure applies to the preparation of all similar tetrachlorodimethoxo complexes. In the dry box 2.75 g (0.01 mole) of molybdenum pentachloride was weighed and put into the 3-necked round bottom flask. The flask was stoppered and brought out of the dry box where nitrogen was passed through it. From a dropping funnel 8.1 ml (0.2 mole) of dried methanol was added slowly, the flask being cooled in an acetone-dry ice bath. A vigorous reaction occurred with HCl gas being evolved. A dark green solution resulted after all of the greenish-black molybdenum pentachloride had dissolved in the methanol. Anhydrous

HCl gas was passed through the flask and 8.1 ml of a mixture containing 10 ml of pyridine and 90 ml of methanol (0.01 mole pyridine) was added slowly. A lime-green precipitate formed immediately. Nitrogen gas was again passed through the flask to remove the excess HCl gas. The flask was stoppered and taken into the dry box where filtration was carried out under a nitrogen atmosphere. The lime-green crystals were washed with three 20 ml portions of anhydrous ether and dried under nitrogen for approximately three hours.

$$C_5H_5N + 2\ CH_3OH + MoCl_5 \longrightarrow C_5H_6N[Mo(OCH_3)_2Cl_4] + HCl$$

Analysis: Calculated for $C_5H_6N[Mo(OCH_3)_2Cl_4]$: C, 22.13%; Cl, 37.33%; H, 3.18%; Mo, 25.25%; N, 3.69%. Found: C, 21.12%; Cl, 37.33%; H, 2.88%; Mo, 24.87%; N, 3.66%.

Quinolinium tetrachlorodimethoxomolybdate(V).--Yellow crystals formed immediately.

Analysis: Calculated for $C_9H_8N[Mo(OCH_3)_2Cl_4]$: C, 19.27%; Cl, 32.98%; H, 4.79%; Mo, 22.31%; N, 3.75%. Found: C, 18.26%; Cl, 32.90%; H, 4.74%; Mo, 22.01%; N, 3.63%.

Tetramethylammonium tetrachlorodimethoxomolybdate(V).--Yellow-green crystals were formed immediately.

Analysis: Calculated for $(CH_3)_4N[Mo(OCH_3)_2Cl_4]$: Cl, 37.93%; Mo, 25.66%. Found: Cl, 37.68%; Mo, 25.64%.

Physical Properties of the Tetrachlorodimethoxomolybdates.--The compounds are all somewhat sensitive to air, turning brown after being exposed for a short period of time. They are soluble in water producing reddish-brown solutions. The pyridinium compound is very soluble in methanol and the quinolinium and tetramethylammonium compounds are moderately soluble. All complexes give green solutions. All three compounds are moderately soluble in acetone but insoluble in ether.

Attempted Preparation of Analogous Ethoxo Compounds.

Attempts to prepare the analogous ethoxo complexes by the procedure given above resulted in the isolation of what appeared to be mixed products. A number of solvents and mixtures of solvents were used for purification without success.

Preparation of Pyridinium Tetrachlorodiethoxomolybdate(V).--This compound was prepared by alcohol exchange with pyridinium tetrachlorodimethoxomolybdate(V). A small amount of pyridinium tetrachlorodimethoxomolybdate(V) was put into a vial and enough ethanol was added so that the compound dissolved upon heating. A dark green solution was produced when all of the complex dissolved. Light-green needle shaped crystals formed when the solution was cooled. The resulting pyridinium tetrachlorodiethoxomolybdate(V) compound was filtered, washed with ether, and dried under a nitrogen atmosphere.

Analysis: Calculated for $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$: C, 26.49%; Cl, 34.76%; H, 3.95%; Mo, 23.52%; N, 3.43%. Found: C, 26.45%; Cl, 34.35%; H, 3.86%; Mo, 23.52%; N, 3.56%.

The low carbon and hydrogen values obtained for the pyridinium and quinolinium tetrachlorodimethoxomolybdate(V) compounds were apparently due to their air sensitivity. Partial hydrolysis evidently occurred during shipment of the samples to Spang Laboratory which resulted in the low values. Extra precautions were taken for shipment of the pyridinium tetrachlorodiethoxomolybdate(V) complex. The results obtained for the carbon and hydrogen analyses of the ethoxo complex were in good agreement with the theoretical values.

Attempted Preparation of the Monochloropentamethoxomolybdates.

Numerous attempts were made to prepare compounds containing the $[Mo(OCH_3)_5Cl]^-$ ion. A large excess (0.5 mole) of methanol was reacted with molybdenum pentachloride (.01 mole), followed by the addition of .01 mole of pyridine in methanol. A sodium methoxide solution was used instead of methanol in further attempts to obtain the monochloropentamethoxomolybdate compounds. In all cases only the pyridinium tetrachlorodimethoxomolybdate(V) compound was obtained.

Spectroscopic Measurements

The infrared spectra of the compounds were obtained in Nujol mulls with the use of a Unicam SP-200 spectrophotometer. The mulls were prepared in the dry box under a nitrogen atmosphere.

The visible solution spectra were obtained with a Cary Model 14 recording spectrophotometer and methanol, ethanol, or a methanol-acetone mixture as the solvent.

Magnetic Moment Measurements

Magnetic susceptibilities were measured by the Gouy method.

The calculations were made by use of the equation:

$$10^6\chi = \frac{\alpha + \beta F'}{\omega} \quad (46)$$

where χ is the gram-susceptibility of the sample, α is a constant allowing for the displaced air and is equal to 0.029 (specimen volume), β is the tube calibration constant, ω is the weight of the specimen, and F' is the force on the specimen, i.e., $(F-\delta)$, with F being the observed force and δ the force produced by the Gouy tube.

The constant α must be determined for the specimen tube by use of a material of known susceptibility. For these measurements, $Hg[Co(SCN)_4]$, with a susceptibility of 16.44×10^{-6} c.g.s. units at 20° C. was used.

To calculate the gram-susceptibility of the calibrant at any given temperature, the following equation is used:

$$\chi = 1/M \left[\frac{(\mu/2.84)^2}{T + \theta} - C\right]$$

In this equation, M is the molecular weight (481.9), C, 177×10^{-6}, is the diamagnetic correction for $Hg[Co(SCN)_4]$, θ, 10°, is the Curie-Weiss temperature, and μ equals 4.44 B.M. Substitution yields the following:

$$\chi = \frac{5.092 \times 10^{-3}}{T + 10} - 0.37 \times 10^{-6}$$

At 24°, the gram-susceptibility of $Hg[Co(SCN)_4]$ is 16.22×10^{-6} c.g.s. units (47).

In most co-ordination compounds, the metal ions, which are the only components of the molecule to give rise to a paramagnetic effect, are kept separated from each other by magnetically inert ligand atoms. Although the diamagnetic susceptibilities of the ligands are small compared to paramagnetic ones, it often happens that the number of ligands in a complex ion so outweigh the single metal atom, to which they are co-ordinated, that their diamagnetism forms an appreciable proportion of the susceptibility of the complex. It is then necessary to correct the observed susceptibility for this contribution. The corrections for the diamagnetism of the ligands and cations were obtained from Pascual's constants (48). The values for the pyridinium and quinolinium ions were obtained from Holm and Cotton (49).

The molar susceptibility of the sample is obtained by multiplying the gram-susceptibility, χ, by the molecular weight. The susceptibility of the metal ion, χ_M', is obtained by correction of the molar susceptibility for diamagnetic species present.

The magnetic moment, μ, can be defined by the following:

$$\mu = \left(\frac{N\beta}{3k}\right)^{-1/2} (\chi_M' T)^{1/2} = 2.84\ (\chi_M' T)^{1/2}\ \text{B.M.}$$

In this equation, N is Avagadro's number, β, the Bohr Magneton, k is Boltzmann's constant, and T is the absolute temperature.

After the sample tube was calibrated, it was filled with a sample of one of the alkoxo compounds and was sealed. The inert atmosphere was necessary because the compounds are sensitive to moisture. The tube was removed from the dry box and the susceptibility was then measured. In all cases, the measured moments of the tetrachlorodialkoxomolybdates corresponded to the spin-only moment of 1.73 B.M., which is characteristic of a d^1 metal ion.

RESULTS AND DISCUSSION

Four compounds, all having the general stoichiometry $BH[Mo(OR)_2Cl_4]$, were prepared and characterized during this investigation. One of these compounds, $C_5H_6N[Mo(OCH_3)_2Cl_4]$, was reported previously but was supposedly prepared by a somewhat different method (23). B^+ was pyridine, quinoline, or tetramethylammonium ion. The alkoxo group was either methoxo or ethoxo.

If the infrared spectra of the tetrachlorodialkoxomolybdates are compared with those of $(C_5H_6N)Cl$, $(C_5H_5N)_2CoCl_2$ (50), $(C_9H_8N)Cl$, $(C_9H_8N)_2CoCl_4$ (51), and $(C_9H_7N)_2CoCl_2$, it can be seen that pyridinium and quinolinium ions are present rather than pyridine or quinoline ligands. In Tables 1, 2, and 3, the infrared frequencies are given for pyridinium and quinolinium ions and ligands as well as those for the tetrachlorodialkoxomolybdates. In each case, the frequency of the alkoxo complex corresponds to that of the pyridinium or quinolinium ion.

The infrared spectra of methoxides and ethoxides have a strong band in the region where the C-O stretching vibration occurs. This band occurs between 1020-1100 cm^{-1} for the methoxides and at 1025-1070 cm^{-1} for the ethoxides. The C-O stretching vibration is present in the infrared spectrum of each of the tetrachlorodialkoxomolybdates in the region between 1040 and 1050 cm^{-1}. Since there is no evidence of the O-H vibrational band, it is assumed that the alkoxide oxygen is coordinated directly to the metal ion. The exact position of the

Table 1. The comparison of the infrared spectra of pyridinium ion and ligand pyridine with that of $C_5H_6N[Mo(OCH_3)_2Cl_4]$.

$C_5H_6N^+$ (51)	ligand C_5H_5N	$C_5H_6N[Mo(OCH_3)_2Cl_4]$
1630 s	1600 s	1630 s
1600 s	1570 w	1600 s
1530 s	1490 s	1530 s
1480 s	1440 s	1480 s
1325	----	1325 s
1240 m	1240 vw	1240 w
1200 m	1215 s	1195 m
1160 m	1150 m	1160 m

vw, very weak; w, weak; m, medium; s, strong

Table 2. The comparison of the infrared spectra of quinolinium ion and ligand quinoline with that of $C_9H_8N[Mo(OCH_3)_2Cl_4]$.

$C_9H_8N^+$	ligand C_9H_7N	$C_9H_8N[Mo(OCH_3)_2Cl_4]$
1630 s	1590 s	1630 s
1590 s	1580 m	1590 s
1550 s	1540 s	1555 s
1400 s	1400 m	1410 s
1300 s	1320 s	1300 s
1220 s	1310 s	1225 s
1160 m	1140 m	1155 m
1140 m	1130 m	1135 m
1080 m	1080 m	1090 m

vw, very weak; w, weak; m, medium; s, strong

Table 3. The comparison of the infrared spectra of pyridinium ion and ligand pyridine with that of $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$.

$C_5H_6N^+$	ligand C_5H_5N	$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$
1630 s	1600 s	1630 s
1600 s	1570 w	1600 s
1530 s	1490 s	1530 s
1480 s	1440 s	1480 s
1325	----	1325 w
1240 m	1240 vw	1235 m
1200 m	1215 s	1190 m
1160 m	1150 m	1160 m

vw, very weak; w, weak; m, medium; s, strong

C-O stretching band for each of the compounds is: $C_5H_6N[Mo(OCH_3)_2Cl_4]$, 1040 cm^{-1}; $C_9H_8N[Mo(OCH_3)_2Cl_4]$, 1050 cm^{-1}; $(CH_3)_4N[Mo(OCH_3)_2Cl_4]$, 1040 cm^{-1}; and $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$, 1040 cm^{-1}. The infrared spectra of these compounds are given in Figures 1-4.

It has been reported that some polymeric ethoxides have two C-O stretching bands (52). The compound, $Nb(OC_2H_5)_5$, which was found to be dimeric, had C-O stretching vibrations at 1029 and 1063 cm^{-1} (53). It was concluded that the two absorptions are due to the presence of both bridging and terminal ethoxide groups. Since only one C-O stretching band was found for $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$, there appears to be no bridging ethoxide groups.

The visible spectra of solutions of the tetrachlorodialkoxomolybdates have been obtained and the absorption maxima are given in Table 4. For $C_9H_8N[Mo(OCH_3)_2Cl_4]$ and $(CH_3)_4N[Mo(OCH_3)_2Cl_4]$, an acetone-methanol mixture was used because of the limited solubility of these complexes in methanol. Sketches of the visible spectra are shown in Figures 5-8.

Table 4. Visible absorption maxima of the tetrachlorodialkoxomolybdates. (in cm^{-1})

Compound	Absorption frequencies ν_1 (cm^{-1})	ν_2	Solvent
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	13,900	23,100	Methanol
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	14,200	23,150	Methanol-Acetone
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	13,900	22,075	Methanol-Acetone
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	14,150	23,525	Ethanol

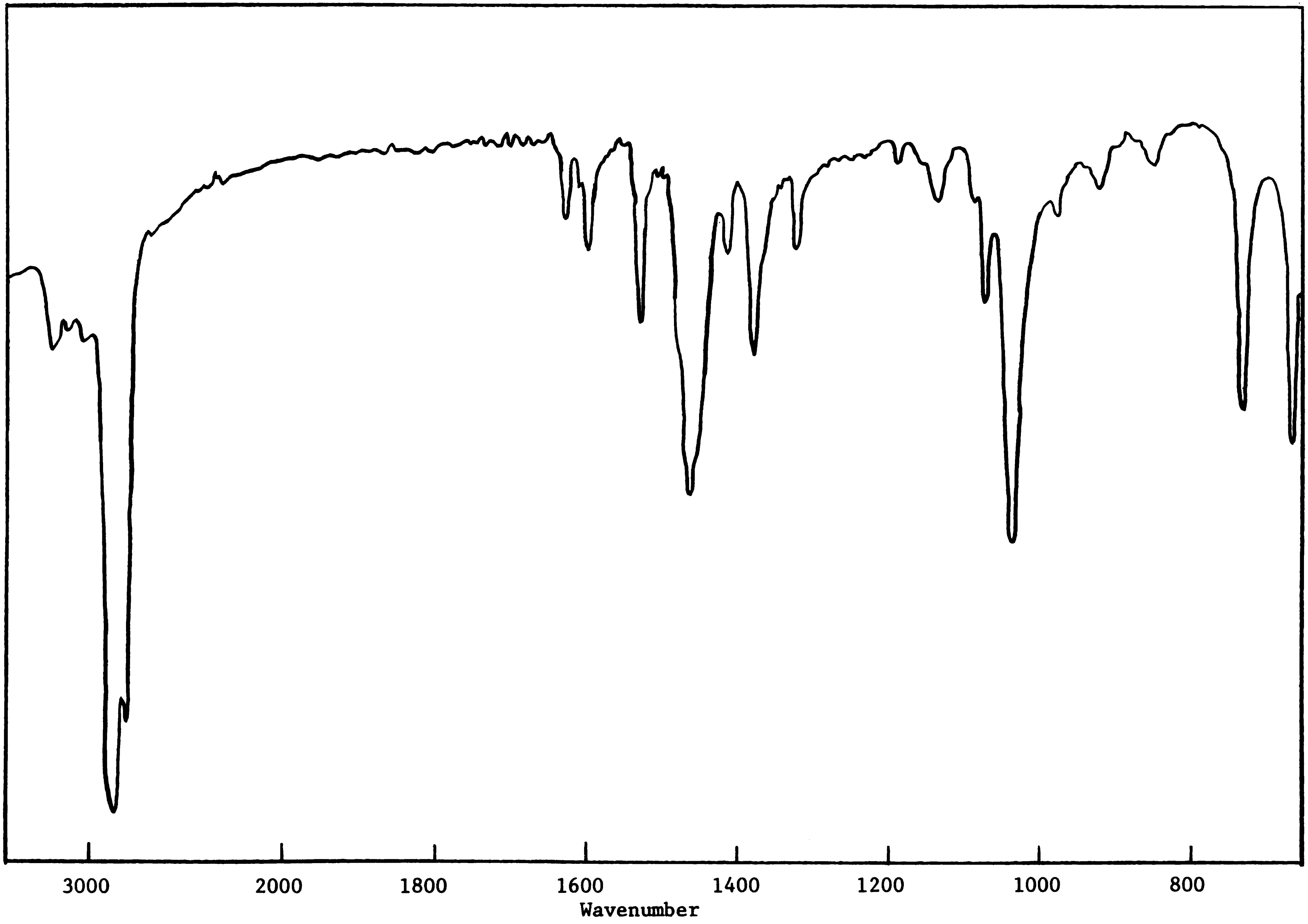


Figure 1. Infrared spectrum of $C_5H_6N[Mo(OCH_3)_2Cl_4]$ (Nujol mull).

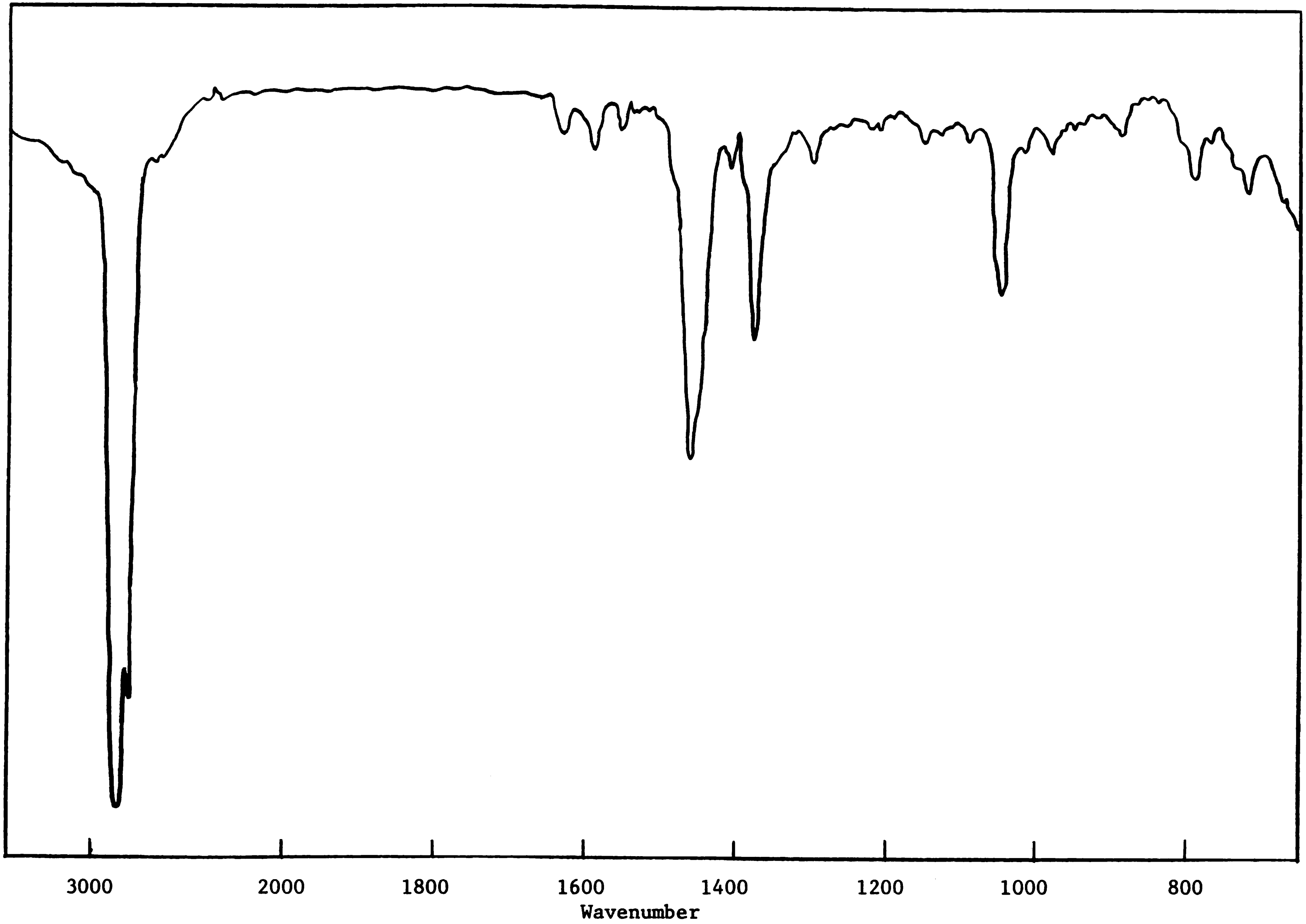


Figure 2. Infrared spectrum of $C_9H_8N[Mo(OCH_3)_2Cl_4]$ (Nujol mull).

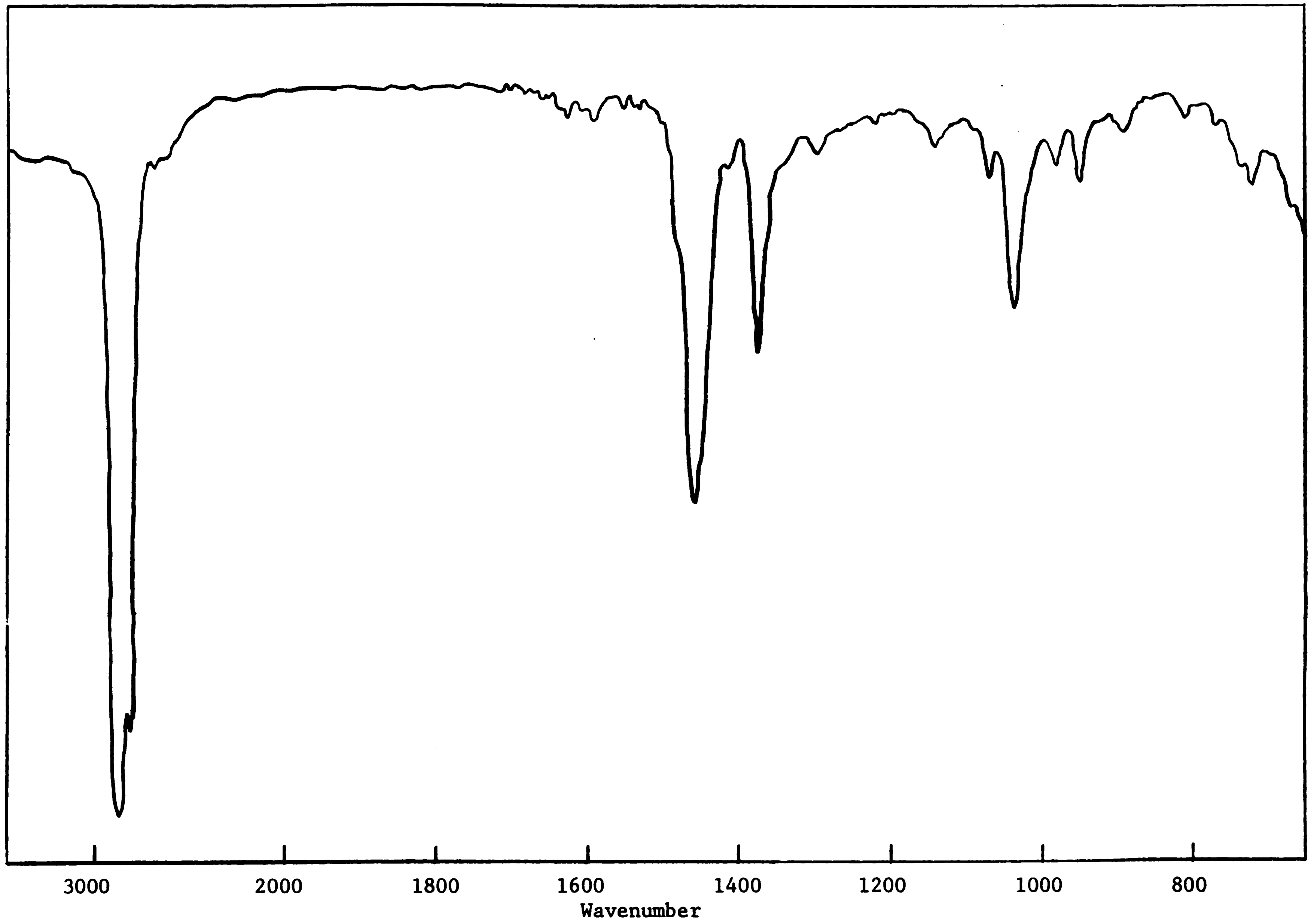


Figure 3. Infrared spectrum of $(CH_3)_4N[Mo(OCH_3)_2Cl_4]$ (Nujol mull).

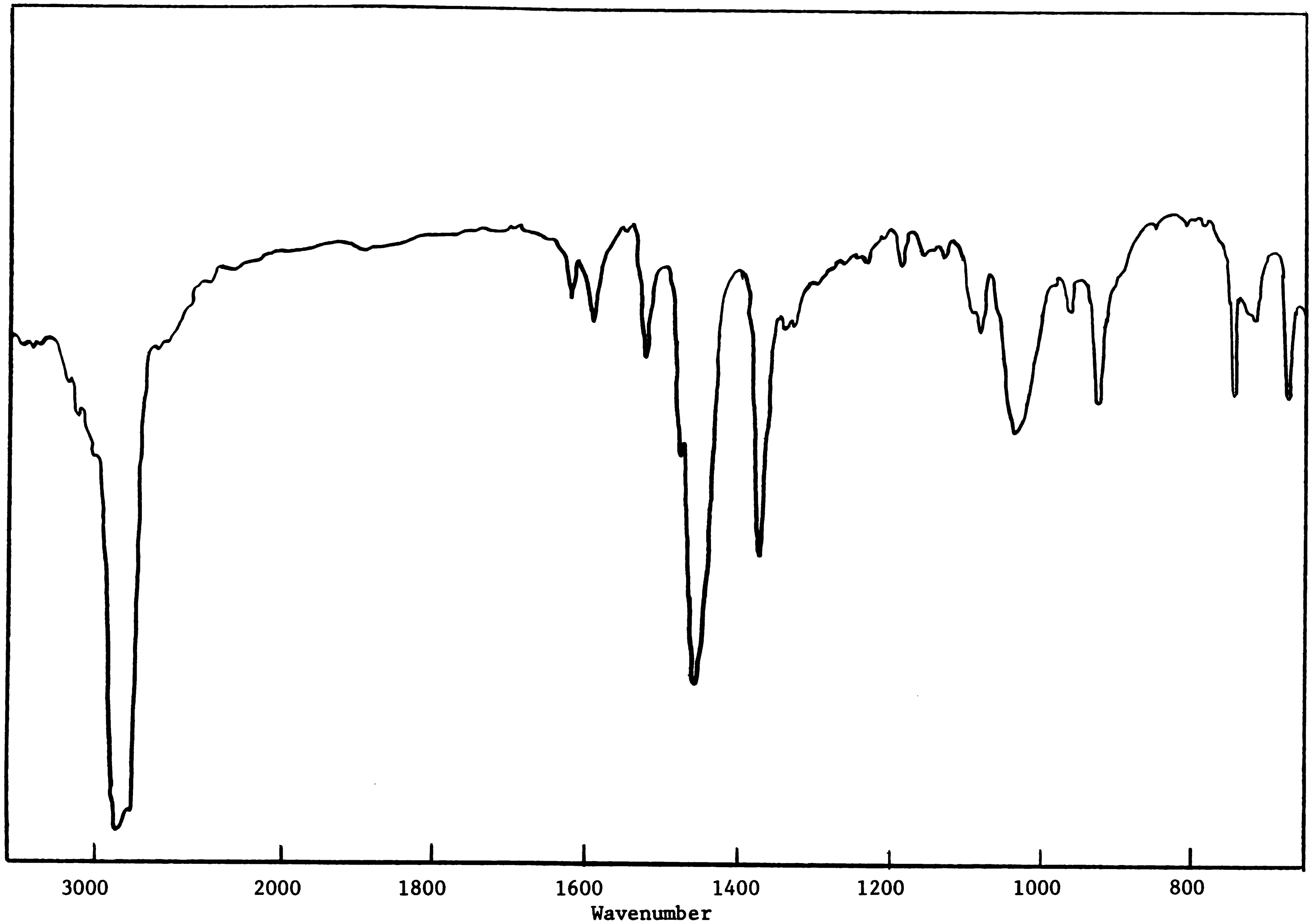


Figure 4. Infrared spectrum of $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$ (Nujol mull).

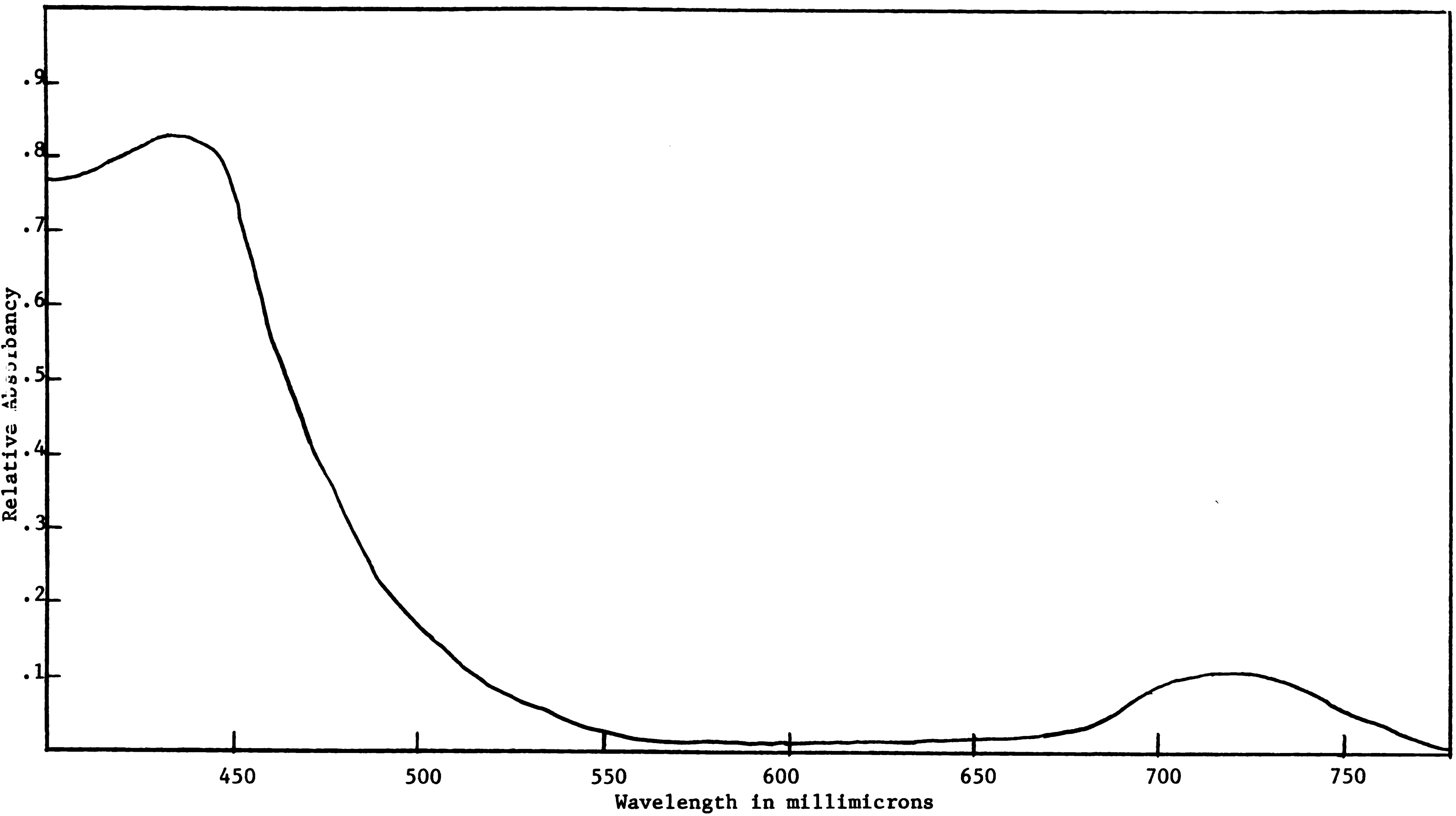


Figure 5. Visible absorption spectrum of $C_5H_6N[Mo(OCH_3)_2Cl_4]$.

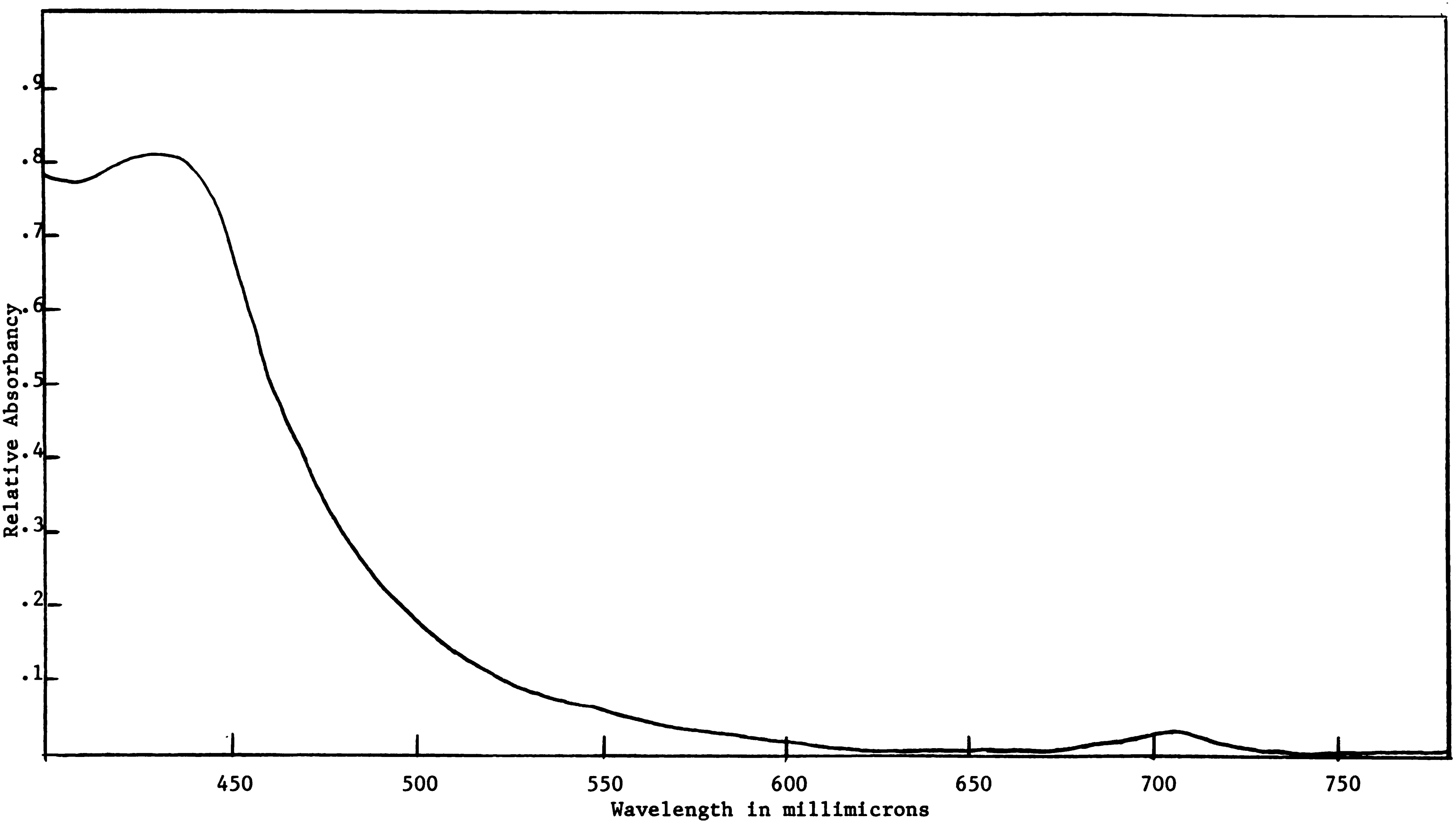


Figure 6. Visible absorption spectrum of $C_9H_8N[Mo(OCH_3)_2Cl_4]$.

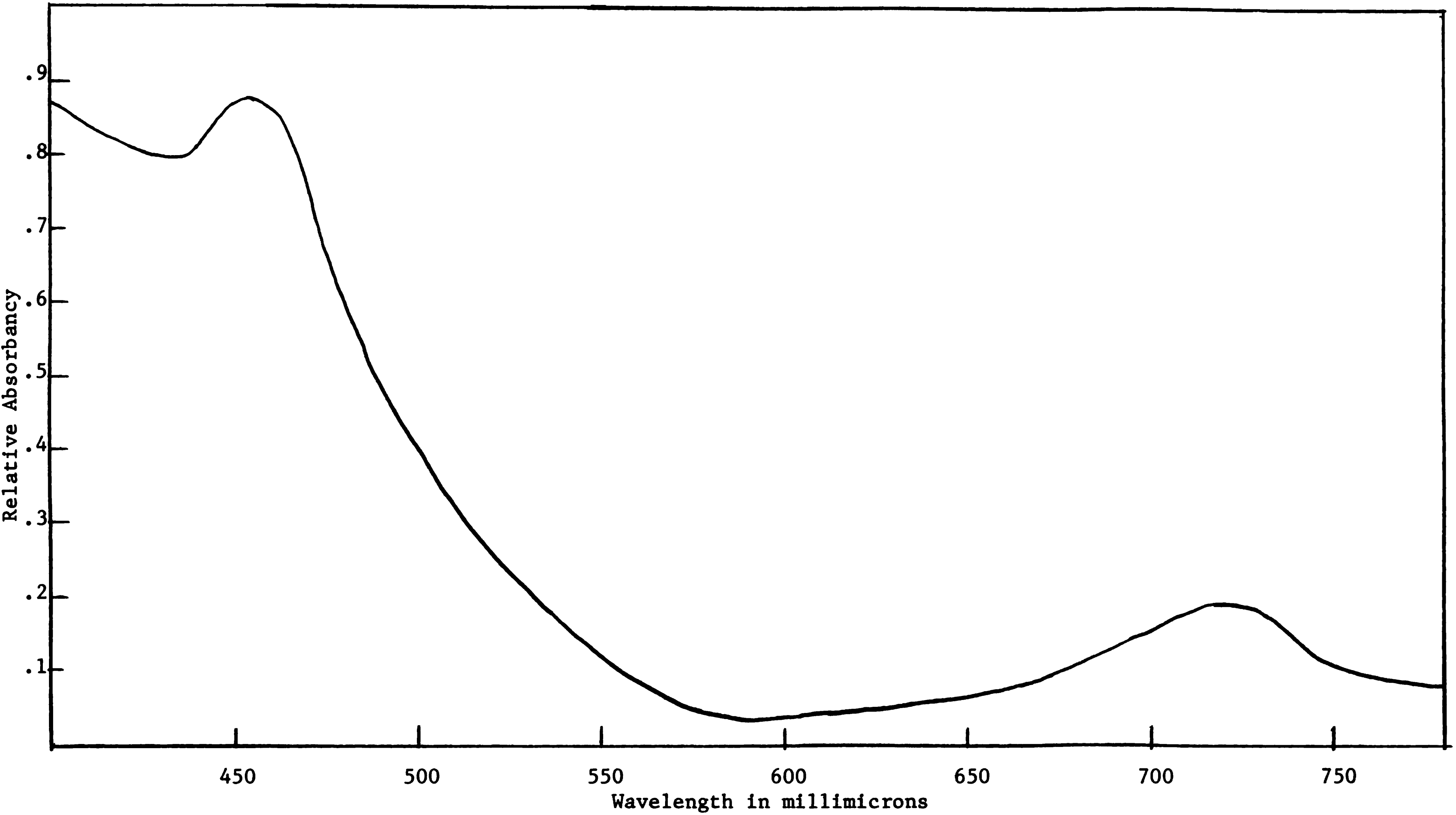


Figure 7. Visible absorption spectrum of $(CH_3)_4N[Mo(OCH_3)_2Cl_4]$.

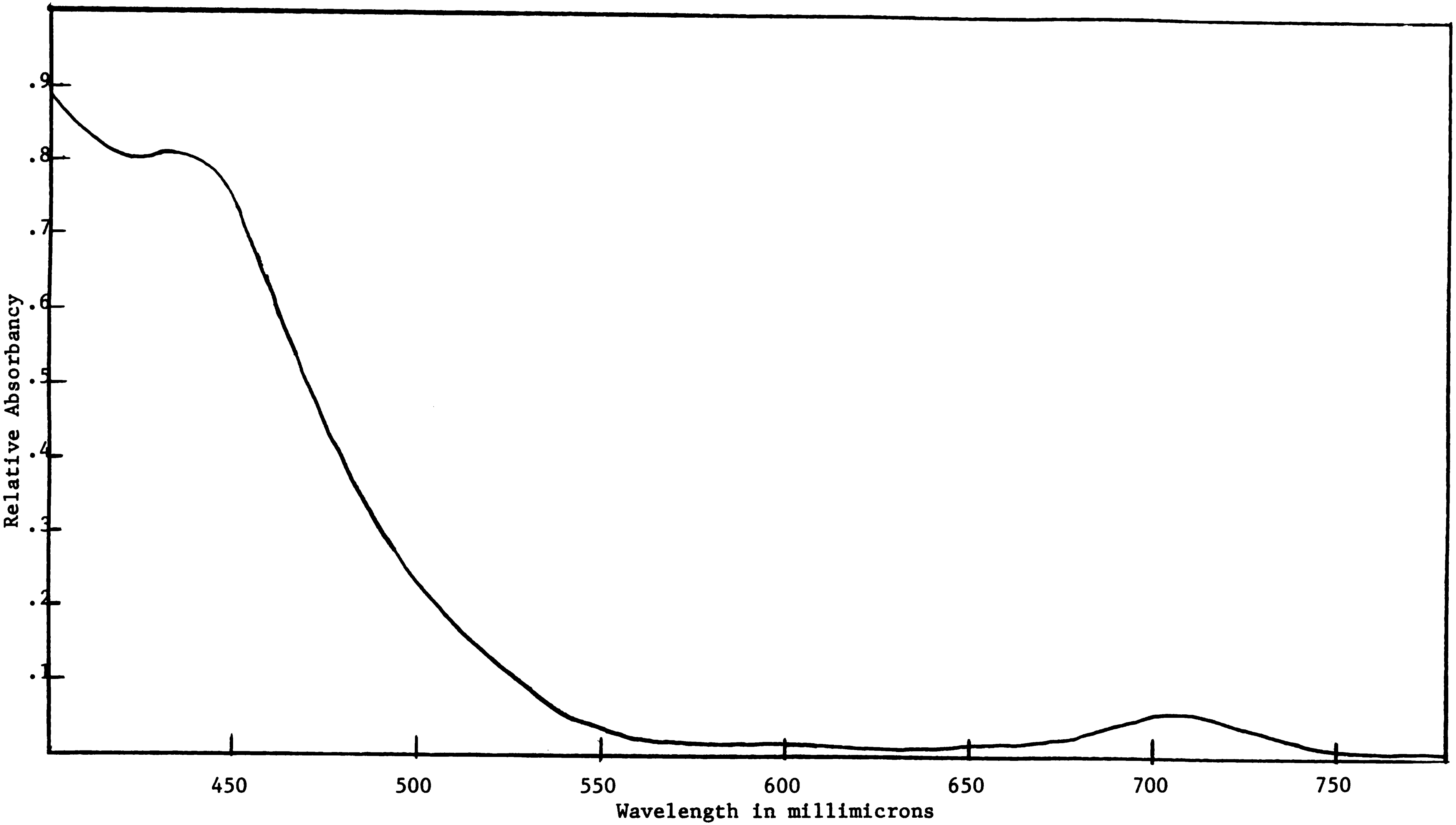
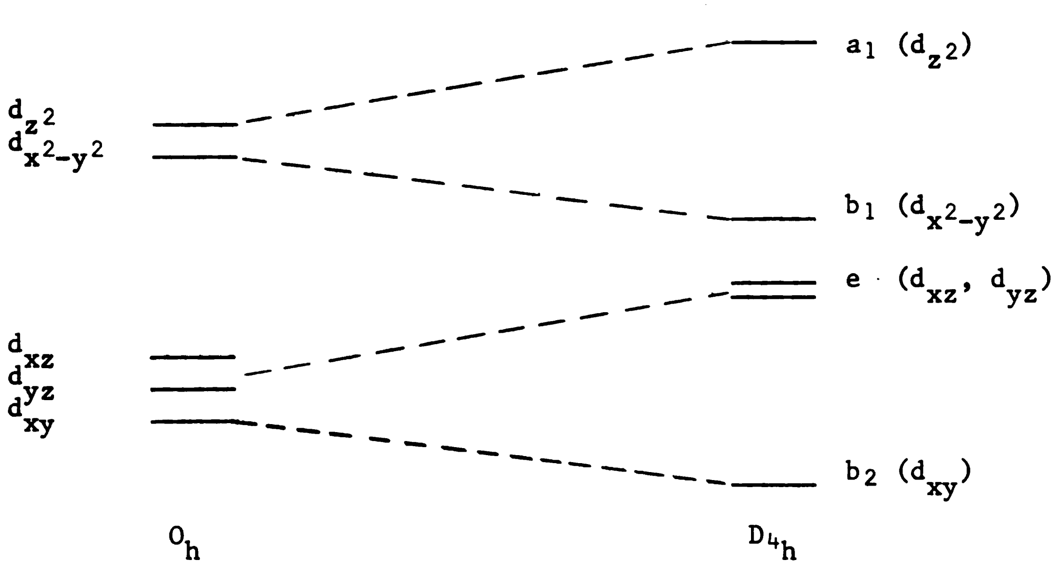


Figure 8: Visible absorption spectrum of $C_5H_6N[Mo(OC_2H_5)_2Cl_4]$.

Just as for the compounds containing the $[MoOCl_5]^{-2}$ ion, the tetrachlorodialkoxo complexes are assumed to be tetragonal with some π-bonding between the alkoxide oxygen and the metal ion. Although there is a difference in the symmetry between the trans-$BH[Mo(OR)_2Cl_4]$ (D_{4h}) and the $R_2[MoOCl_5]$ (C_{4v}) complexes, the energy level diagram of the $[MoOCl_5]^{-2}$ ion should be similar and can be used, at least qualitatively, as a guide in interpreting the spectra of the tetrachlorodialkoxo compounds. The splittings on increased tetragonal distortion are given below:



⟶ Increased Tetragonal Distortion ⟶

There should be three transitions, $b_2 \longrightarrow e$, $b_2 \longrightarrow b_1$, and $b_2 \longrightarrow a_1$. However, only two of these, probably the $b_2 \longrightarrow e$ and $b_2 \longrightarrow b_1$ transitions, are present in the spectra. The $b_2 \longrightarrow a_1$ transition is apparently masked by the charge transfer band at approximately 33,000 cm^{-1}. For the $R_2[MoOCl_5]$ compounds, the first two transitions occur at 14,050 and 22,500 cm^{-1}. Since absorption maxima for the tetrachlorodialkoxo complexes are approximately at the same frequency as those of the $R_2[MoOCl_5]$ compounds, similar assignments have been made.

Molybdenum in the +5 oxidation state has one unpaired 4d electron and should have a magnetic moment close to the spin-only value of 1.73 B.M. It was found that all of the compounds prepared and examined during this research had moments close to this spin-only value. These moments are listed in Table 5. It is assumed that the value of 1.81 B.M. obtained for $C_9H_8N[Mo(OCH_3)_2Cl_4]$ is higher than the other compounds because of difficulty in packing the sample tube. It was much more difficult to get uniform packing for this compound than for the others. The susceptibility of the ethoxo compound was measured at Wayne State University and a small experimental error was produced by not being able to load the sample into the tube under conditions normally required.

Table 5. Magnetic susceptibilities and moments of the alkoxo molybdenum(V) compounds.

Compound	Temp. (°A)	Susceptibility $\chi_M' \times 10^6$ (c.g.s. units/mole)	Moment (B.M.)
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	297	1225	1.71
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	297	1370	1.81
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	298	1235	1.72
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	296	1469	1.88

The data obtained indicate that all of the tetrachlorodialkoxomolybdate(V) compounds are monomeric and contain molybdenum in the +5 oxidation state with a $4d^1$ configuration. The C-O stretch is present in the infrared spectra while the O-H vibrational mode is not, which indicates the presence of the alkoxide ion and not the free alcohol. The alkoxide oxygen should be coordinated directly to the metal ion. The structure of the tetrachlorodialkoxomolybdate(V) ion appears to be that of a tetragonally-distorted octahedron with some π-bonding between the alkoxide oxygen and the metal ion.

It is assumed that only the trans isomer is present for all of the tetrachlorodialkoxomolybdate(V) compounds. For all of the compounds, $g_{\parallel}$ and $g_{\perp}$ have been resolved; if there weren't axial symmetry, $g_{\parallel}$ and $g_{\perp}$ could not be resolved.

In the electron spin resonance study of the tetrachlorodialkoxomolybdate(V) compounds in dimethylsulfoxide, it was observed that the line shape changed corresponding to the replacement of the chloride ligands by dimethylsulfoxide ligands. Upon addition of HCl, the line patterns for the spectra of the chloroalkoxo complexes were obtained again.

When pyridinium tetrachlorodimethoxomolybdate(V) was put into ethanol, it was observed that the line shape of the electron spin resonance spectrum changed with time, indicating possible alkoxo exchange. The spectrum of the pyridinium tetrachlorodimethoxomolybdate(V) compound in ethanol was identical to that of the corresponding ethoxo complex in the same solvent.

APPENDIX

Electron spin resonance is the branch of spectroscopy in which molecules containing electrons with unpaired spins absorb radiation of radio-frequency when placed in a magnetic field. The absorption of a quantum of radiation produces a transition between different electron spin energy states of the unpaired electron.

An electron of spin $s = 1/2$ can have spin angular momentum quantum numbers of $m_s = \pm 1/2$. In the absence of a magnetic field, a doubly degenerate spin energy state exists; if a magnetic field is applied, the degeneracy is removed. The low energy state corresponds to the quantum number, $m_s = -1/2$, and has the spin magnetic moment aligned with the field. The high energy state, $m_s = +1/2$, has its moment opposed to the field. Upon absorption of a quantum of radiation in the radio-frequency or microwave region, the transition between two different electron spin energy states occurs. The energy of the transition is given by:

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

where h is Planck's constant, ν the radiation frequency, β the Bohr magneton, g the spectroscopic splitting factor, and H_o the field strength.

The value of g for a free electron is 2.0023. However, metal ions often have g values much different from that of the free electron. The magnitude of g generally depends on the orientation of the molecule with respect to the magnetic field.

The g value obtained when the z axis of the ion or radical is parallel with the external magnetic field is designated by $g_{\parallel}$, while the g values along the x and y axes are referred to as $g_{\perp}$, and result when the external magnetic field is perpendicular to the z axis.

When an electron comes in the vicinity of a nucleus with a spin I, an interaction takes place which causes the absorption signal to be split into 2I + 1 components. The isotopes ^{95}Mo and ^{97}Mo, both have I = 5/2, and thus six components should result. The isotope ^{96}Mo, with I = 0, would only have one component.

Hare reported a strong central line centered at g = 1.947 for $(NH_4)_2[MoOCl_5]$ in 10-12 M HCl (38). On each side of the central line were three weak satellites. The strong central line was assumed due to the ^{96}Mo (I = 0) isotope, and the weaker satellites due to the ^{95}Mo (I = 5/2) and ^{97}Mo (I = 5/2) isotopes. The $g_{\parallel}$ and $g_{\perp}$ values for this compound were observed to be 1.915 and 1.965 respectively. However, Kon and Sharpless (54) found that $g_{\parallel}$ was greater than $g_{\perp}$ with $g_{\parallel}$ = 1.970 and $g_{\perp}$ = 1.936. The results obtained by Kon for $g_{\parallel}$ and $g_{\perp}$ were in good agreement with those of Garifyanov (55).

A number of other electron spin resonance studies on Mo^{+5} compounds have recently been reported (56, 57, 58).

The electron paramagnetic resonance studies on the tetrachlorodialkoxomolybdate(V) compounds were performed by Larry Dalton. Work is still in progress on the pyridinium tetrachlorodiethoxomolybdate(V) complex. The spectra of both powder and liquid samples were obtained. The data obtained thus far is listed in Tables 6-10.

It is assumed that only the *trans* isomer is present for all of

Table 6. Electron spin resonance data for powder samples of the tetrachlorodialkoxomolybdates(V).

Compound	$g_\parallel$ (±.0002)	$g_\perp$ (±.0002)	<g> (±.0003)
$C_5H_6N[Mo(OCH_3)_2Cl_4]$	1.96897	1.92488	1.93958
$C_9H_8N[Mo(OCH_3)_2Cl_4]$	1.96008	1.92316	1.93546
$(CH_3)_4N[Mo(OCH_3)_2Cl_4]$	1.97056	1.92431	1.93972
$C_5H_6N[Mo(OC_2H_5)_2Cl_4]$	1.96093	1.93285	1.94221

Table 7. Electron spin resonance data for liquid samples of pyridinium tetrachlorodimethoxomolybdate(V).

Solvent	<g>	<a> (gauss)
Methanol	1.94626 ± .0003	52.49 ± 0.3
Acetone	1.94777 ± .0004	51.34 ± 0.3
Pyridine	1.93743 ± .0003	47.35 ± 0.3
Dimethylformamide	1.94529 ± .0003	51.67 ± 0.3
Ethanol	1.94614 ± .0006	52.50 ± 0.6
Dimethylsulfoxide	1.94364 ± .001	54.35 ± 1.0

Table 8. Electron spin resonance data for liquid samples of quinolinium tetrachlorodimethoxomolybdate(V).

Solvent	<g>	<a> (gauss)
Methanol	1.94558 ± .0003	52.67 ± 0.3
Acetone	1.94798 ± .0003	51.40 ± 0.3
Ethanol	1.94556 ± .0003	52.18 ± 0.3
Dimethylformamide	1.94666 ± .0003	51.56 ± 0.3
Chloroform	1.94859 ± .0003	51.01 ± 0.3

Table 9. Electron spin resonance data for liquid samples of tetramethylammonium tetrachlorodimethoxomolybdate(V).

Solvent	<g>	<a> (gauss)
Methanol	1.94587 ± .0005	52.83 ± 0.3
Acetone	1.94856 ± .0003	51.70 ± 0.3
Dimethylformamide	1.94696 ± .0003	51.56 ± 0.3
Ethanol	1.94651 ± .0005	52.51 ± 0.3

Table 10. Electron spin resonance data for liquid samples of pyridinium tetrachlorodiethoxomolybdate(V).

Solvent	<g>	<a> (gauss)
Ethanol	1.94599 ± .0003	52.75 ± 0.3
Methanol-ethanol	1.94600 ± .0003	52.72 ± 0.3

the tetrachlorodialkoxomolybdate(V) compounds. For all of the compounds, $g_{\parallel}$ and $g_{\perp}$ have been resolved; if there weren't axial symmetry, $g_{\parallel}$ and $g_{\perp}$ could not be resolved. Also, according to Dalton, the line shapes would be different if the cis isomer were present.

In the electron spin resonance study of the tetrachlorodialkoxomolybdate(V) compounds in dimethylsulfoxide, it was observed that the line shape changed corresponding to the replacement of the chloride ligands by dimethylsulfoxide ligands. Upon addition of HCl, the line patterns for the spectra of the chloroalkoxo complexes were obtained again.

When pyridinium tetrachlorodimethoxomolybdate(V) was put into ethanol, it was observed that the line shape of the electron spin resonance spectrum changed with time, indicating possible alkoxo exchange. The ultimate spectrum of the pyridinium tetrachlorodimethoxomolybdate(V) compound in ethanol was identical to that of the corresponding ethoxo complex. It was found chemically that there was alkoxo exchange: this was the method used for the preparation of the pyridinium tetrachlorodiethoxomolybdate(V) compound.

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